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研究炉(JRR-3 及び JRR-4)利用における研究成果集 (平成18年度)

Activity Report on the Utilization of Research Reactors (JRR-3 and JRR-4) (Japanese Fiscal Year, 2006)

(編)研究炉利用課

KRVIRV

(Ed.) Research Reactor Utilization Section

東海研究開発センター 原子力科学研究所 研究炉加速器管理部

Department of Research Reactor and Tandem Accelerator Nuclear Science Research Institute Tokai Research and Development Center

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日本原子力研究開発機構

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日本原子力研究開発機構 東海研究開発センター 原子力科学研究所

研究炉加速器管理部

(編)研究炉利用課

(2008年10月10日受理)

平成 18 年度、研究炉 JRR-3 は 7 サイクルの運転(1 サイクル: 26 日連続運転)、JRR-4 については、37 サイクル(デイリー運転: 151 日)の施設共用運転を行なった。

JRR-3は、中性子散乱、即発ガンマ線分析、中性子ラジオグラフィなどの実験利用

及び、放射化分析、原子炉燃料材料、ラジオアイソトープ製造、フィッショントラッ ク年代測定の照射利用等、様々な目的に利用されている。

JRR-4 については、医療照射 (Boron Neutron Capture Therapy: BNCT)、即発ガンマ 線分析、放射線測定器の感度試験、原子炉研修運転実習等の実験利用、及び放射化分析、 ラジオアイソトープ製造、フィッショントラック年代測定のための照射利用等、様々な 目的に利用されている。

本報告書は、研究炉の利用者(原子力機構外を含む)から成果の提出を受け、中性子 散乱 11 分野(構造、磁性、超伝導など)、中性子ラジオグラフィ、即発ガンマ線分析、 放射化分析、その他、の分野別に研究成果を取りまとめたものである。

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(Ed.) Research Reactor Utilization Section

Department of Research Reactor and Tandem Accelerator Nuclear Science Research Institute Tokai Research and Development Center Japan Atomic Energy Agency Tokai-mura, Naka-gun, Ibaraki-ken

(Received October 10, 2008)

In the fiscal year 2006, The research reactor JRR-3 was operated 7 cycles (cycle operation : 26days/cycle) for utilization sharing of the facility. And JRR-4 was operated 37 cycles (daily operation : 151 days).

JRR-3 is used for the purposes below;

- Experimental studies such as neutron scattering, prompt gamma-ray analyses, neutron radiography
- Irradiation for activation analyses, radioisotope (RI) productions, fission tracks
- Irradiation test of reactor materials

etc.

JRR-4 is used for the purposes below;

- Medical irradiation (Boron Neutron Capture Therapy : BNCT)
- Prompt gamma-ray analyses
- Sensitivity measurement of radiation detectors
- Experiment in the nuclear reactor training
- Practice of Reactor operation
- Irradiation for activation analyses, RI productions, fission tracks etc.

The volume contains 294 activity reports, which are categorized into the fields of neutron scattering (11 subcategories), neutron radiography, neutron activation analyses, RI productions, prompt gamma-ray analyses, and others submitted by the users in JAEA and from other organizations.

Keywords: JRR-3, JRR-4, Research Reactor, Neutron Scattering, Neutron Radiography, Neutron Activation Analysis, Neutron Beam, Irradiation 目

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研究炉利用における研究成果集(平成18年度)

はじめに

平成18年度には、JRR-3において7サイクルの共同利用運転、JRR-4において37サイクルの共同利用運転が行なわれ、これに伴いさまざまな利用が行われた。

本報告書は、利用者(原子力機構外利用者を含む)から当該利用の成果の提出を受け、 取りまとめたものである。

提出して頂いた成果の件数は、中性子散乱261件、中性子ラジオグラフィ8件、即発 ガンマ線分析4件、放射化分析14件、その他7件で合計294件であった。なお、本報 告書の一部は、貴重な研究成果を公開する機会を広げるため、下記報告書の中から転載さ せて頂いたものである。

最後に、原稿を提出して頂いた利用者の皆様のご協力に感謝するとともに、今後も研究 炉が有効に利用され、種々の研究がさらに進展されることを期待します。

研究炉利用課長

和田 茂

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| | | RESEARCH issued by ISSP-NSL, University of Tokyo |
| | | (東京大学物性研究所発行) |

レポート番号: Vol.14

- 編 者 :東京大学物性研究所
- 発 行 年 : 2007年
- 2)標 題 : 原子力機構施設利用共同研究成果報告書(平成18年度)
 - 編 者 : 東京大学大学院工学系研究科原子力専攻共同利用管理本部
 - 発 行 年 : 2006年

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1. 中性子散乱 1)構造・励磁

1. Neutron Scattering 1) Structure • Excitation

1-1-1

Low-Energy Phonon Anomaly and Electron-Lattice Interaction in the Pr-Filled Skutterudites

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rare-earth filled skutterudites The RT_4X_{12} (R = rare earth, T = transition metal, X = pnictogen) have been studied in terms of the anomalously anharmonic lattice properties, as well as the various strongly correlated electron phenomena involving 4f electrons. The filled ions are located within the icosahedral X cage, and vibrate with large amplitude detected as the large effect of the Debye-Waller factors. Ultrasonic measurements of PrOs₄Sb₁₂ revealed dispersion of elastic constants indicative of anomalous Pr-ion motion within the Sb cage (T. Goto et al.: PRB 69 (2004) 180511). Recent inelastic x-ray scattering experiment of Sm-based compounds (S. Tsutsui et al.: Physica B 383 (2006) 142, JMMM in press) and inelastic neutron scattering experiment of CeRu₄Sb₁₂ (C. H. Lee et al.: JPSJ 75 (2006) 123602) revealed lower-frequency flat phonon branches corresponding to the motion of filled atoms. We have reported anomalous softening of phonon due to Pr vibration with decrease of temperature in PrOs₄Sb₁₂ (K. Iwasa et al.: Physica B 378-380 (2006) 194). Such vibration has been expected to produce strong electron-phonon coupling that may relate with the electronic phenomena.

We have investigated the low-energy phonon spectra of $PrOs_4Sb_{12}$ and $PrRu_4Sb_{12}$ using the triple-axis spectrometers TOPAN (6G) and HER (C1-1).

The left figure shows phonon spectra of PrRu₄Sb₁₂ measured at the reciprocal lattice point $\mathbf{Q} = (0\ 3\ 3)$. It shows distinct softening of excitation energy by 17% with decreasing temperature from 300 down to 12 K. By the measurements in the Brillouin zone around $\mathbf{Q} = (0\ 3\ 3)$, this mode was confirmed to be less dispersive like an optical mode. We measured phonon spectra also at $\mathbf{Q} = (6\ \zeta\ \zeta)$, as shown in the

right figure. The spectrum measured at $\zeta = -0.4$ is composed of the peak "R" around 4 meV which exhibits softening behavior similar to the less-dispersive optical mode at $\mathbf{Q} = (0 \ 3 \ 3)$ and that around 6 meV ascribed to the transverse acoustic (TA) one which has no softening behavior. The temperature dependence of the integrated intensity of the 4 meV peak is explained by the phonon state dominated by the Pr-ion vibration, so that the low-energy optical mode is given by the large Pr-ion motion "rattling" inside the Sb cage. The spectrum at the zone center $\mathbf{Q} = (6 \ 0 \ 0)$ is unexpectedly quasielastic, whose tail extends beyond 4 meV. Such overdamped response can be attributed to a relaxation phonon due to additional interaction. We will compare the experimental data with the phenomenological phonon susceptibility based on the mode coupling.



Fig. 1. The upper figure shows energy spectra at $Q = (0 \ 3 \ 3)$ of $PrRu_4Sb_{12}$ as a function of temperature, and the lower one shows those at $Q = (6 \ \zeta \ \zeta)$ measured at 300 K.

1-1-2

Split H-site model in synthetic Al-for-Ga substituted germanate-muscovites: FTIR and neutron powder diffraction studies

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FTIR and powder neutron diffraction studies of synthetic deuterated aluminogallogermanate muscovites have been made at ambient temperature. More than three infrared OH/OD-stretching bands were analyzed both OH- and OD-form's micas. A neutron powder diffraction Rietveld analyses for two germanate-micas of the compositions KAl1.5Ga1.5Ge3O10(OD)2 and KGa3Ge3O10(OD)2, up to three hydrogen sites were derived, reflecting a crescent or horseshoe-like H/D distribution sitting on the (1-10) plane with various angles from the (001) plane; their site occupancies and the angles from the (001) plane are 0.36(-3.9), 0.45(29.2), and 0.18(80.8) in the former mica, 0.28(-18.7), 0.45(15.4), and 0.26(62.4) in the latter, respectively. The higher wavenumber infrared OH/ODstretching bands ascribed to the higher angle H/D from the (001) plane. These split H/D-sites are derived mainly by the local negative charges which occur by the short range order of the tetrahedral tetravalent and trivalent cations.

1-1-3

Possible structural transformation in the Eu-Ag-In 2/1 approximant and its relation to the Cd-Yb quasicrystals

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Quasicrystals are characterized by sharp Bragg reflections with a point symmetry that is forbidden in a periodic lattice, such as the five-fold symmetry. For understanding of the formation and stabilization of the quasiperiodic structure, a key fact may be existence of approximant phase near the quasiperiodic compound in phase diagram. An approximant is a periodic crystal which has similar or identical atomic cluster in a finite length scale. For the binary Cd-Yb quasicrystal, there are two approximant phases are known to date; the 1/1 and 2/1 phases. The 2/1 phase has much larger atomic cluster in common to the quasicrystalline phase and thus is intriguing for the elucidation of the stabilization mechanism of the quasicrystalline phase. Recently, a 2/1 approximant phase was observed in the Eu-Ag-In alloy, which is supposed to be isostructural to the 2/1Cd-Yb approximant. In a magnetic susceptibility study an abrupt change of the inverse-susceptibility slope was observed around 70 K, indicating change of electronic state of Eu ions at the temperature. Thus, the anomaly may possibly infer existence of certain structural distortion in the 2/1 approximant. To clarify this point we have performed neutron powder diffraction study using the IMR-HERMES powder diffractometer.

Powder samples of the Eu-Ag-In alloys were prepared by melting constituent elements in a standard manner. Because of the high absorption of the Eu, Ag, and In atoms, we have used an annular sample cell with the sample thickness of t = 0.5 mm. Nevertheless, the diffraction was very weak due to the absorption, and thus unusually long data acquisition time was

necessary to record single diffraction pattern. Shown in Fig. 1 are the observed powder diffraction patterns at the room temperature and the lowest temperature T =4 K. There is an apparent change of the lattice constant, resulting in the change of the Bragg peak positions in consistent way. In addition, some new peaks appear at the lowest temperature; most notable one is marked by a red arrow. This indicates a possibility of magnetic/structural transition between the two temperatures. Detailed analysis of the diffraction patterns is in progress.

Note: the experiment approved by PAC was on the Cd-Yb approximant itself, however, because of the unexpected UK airline confusion due to the terrorism possibility happened just a few days before the assigned HERMES beamtime, the sample delivery was delayed. Thus, we instead performed the most similar experiment with the samples in hand.



Fig. 1. Neutron powder diffraction patterns at T = 4 K (red) and RT (green) obtained at IMR-HERMES.

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Neutron scattering study of phonon dynamics on type-1 clathrate cage compounds (Ba,Sr)8Ga16Ge30

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Large vibration of an atom in an oversized atomic cage, so called rattling, has attracted a great interest since it can be the origin of some exotic physical properties. For example, the rattling can be responsible for an extremely low thermal conductivity. Electronic properties could also be affected via electron-phonon coupling. To clarify the relation between the rattling motion and exotic physical properties in materials having oversize atomic cages, it is very important to understand the nature of the rattling.

(Ba,Sr)8Ga16Ge30 is one of compounds that has large Ga and Ge atomic cages filled with Ba or Sr guest atoms. In the compounds, the guest atoms are considered to behave as rattlers in the oversized atomic cages. To clarify the vibrational motion of filling atoms, we have conducted neutron scattering measurements on (Ba,Sr)8Ga16Ge30 compounds using the 3-axis spectrometers, GPTAS, TOPAN, HQR and AKANE, at JRR-3M reactor of Japan Atomic Energy Agency in Tokai. Sample vomules of Ba8Ga16Ge30 and Sr8Ga16Ge30 single crystals used for the measurements were about 1cc and 2cc, respectively.

Fig. 1 shows the phonon dispersion of Ba8Ga16Ge30 with propagation vector of [100]. The optical phonon mode observed at E = 4.5 meV corresponds to a guest mode, in which Ba atoms vibrate largely. The guest mode shows anti-crossing behavior with acoustic phonon mode around q=(0.5,0,0). The low phonon energy indicates that Ba atoms bound loosely with surrounding atoms consistent with the previous expectation. On the other hand, the anti-crossing behavior indicates that the guest mode mixes strongly with the acoustic mode. Although the energy dependent

dence is weak, the guest mode is still dispersive suggesting the existence of Ba-Ba interaction. In Sr8Ga16Ge30, on the other hand, the energy dependence of the guest mode is weaker and energy gap between the guest and the acoustic mode is smaller than in Ba8Ga16Ge30. It seems that the guest mode in Sr8Ga16Ge30 becomes more Einstein-like mode than in Ba8Ga16Ge30. In Sr8Ga16Ge30, the guest atoms tend to split from the center position of atomic cages, whereas in Ba8Ga16Ge30 they are located on the center. The results show that the guest mode is more Einstein-like in a sample where the atomic splitting is larger.



Fig. 1. Phonon dispersion curves of transverse phonon modes with propagation vector [100] in Ba8Ga16Ge30.

Neutron scattering study of phonon dynamics on La3Pd20Ge6

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Large vibration of an atom in an oversized atomic cage, so called rattling, has attracted a great interest since it can be the origin of some exotic physical properties. For example, the rattling can be responsible for an extremely low thermal conductivity. Electronic properties could also be affected via electron-phonon coupling. In beta-pyrochlore compound KOs2O6, it has been proposed that rattling may assist the appearance of superconductivity [1]. Clarifying the nature of the rattling motion is now a very important issue.

La3Pd20Ge6 is one of compounds that has large Ge and Pd atomic cages filled with La guest atoms. Ultrasonic measurements show that the elastic constant C44 of La3Pd20Ge6 exibits a Debye-type dispersion of around T=20K [2]. It is proposed that the phenomenon is originated from rattling motion of La atoms. However the relationship between the rattling and Debye-type dispersion is still controversial. In the present work, we study phonon dynamics of La3Pd20Ge6 and try to understand the reason of the Debye-type dispersion as well as the nature of the rattling.

Neutron scattering measurements were carried out using the triple-axis spectrometer, TOPAN and GPTAS, at the JRR-3M reactor of JAEA at Tokai. The final neutron energy was fixed at Ef = 14.8 meV using a pyrolytic graphite monochromator and an analyzer. The sequences of the horizontal collimators were 40'-40'-S-40'-40' or 40'-60'-S-60'-60', where S denotes the sample position. Total sample vomule of La3Pd20Ge6 single crystals used for the measurements was about 1.3cc.

Figure 1 shows typical phonon spectra of La3Pd20Ge6 at Q=(8.4,0,0). Peaks at E = 3 and 6 meV correspond to an optical mode where La guest atoms on 4c sites vibrate largely and an acoustic mode. Comparable intensity is due to mixture of both phonon modes. Phonon peaks above E = 8 meV correspond to optical modes where lattice cages vibrate mainly. As other cage compounds, clear anti-crossing behaviour is also observed in La3Pd20Ge6. Analysis in details is now in progress.

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Fig. 1. Energy spectra of longitudinal acoustic and optical phonon peaks with propagation vector [100] in La3Pd20Ge6. The solid lines are the results of Gaussian fits.

Modulated structure of ion-exchanged Ca_{0.4}CoO₂

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We have prepared a single-layered cobalt oxide Ca_xCoO_2 through the solid-state ionexchange method to interrogate the structural difference with the Na-analogue. The ion-exchange was performed by mixing the Na_{0.7}CoO₂ phase and Ca(NO₃)₂·4H₂O and fired the mixture at 310 °C for 48 h.

Neutron powder diffraction patterns were collected at several temperatures from 296 K down to 17 K using HERMES diffractmeter. The crystal structure was determined using the Rietveld refinement program PREMOS [1]. We assumed the superspace group of Cmcm(p10)000 and assigned the [CoO₂] part as subsystem 1 and [Ca] part as subsystem 2. The p parameter is defined as $p = a_{CoO_2}/a_{Ca} = a_1/a_2$. The compound consists of two orthorhombic subsystems of [Ca] and $[CoO_2]$ with b = 4.8798(9) Å c = 10.8946(10) Å and two *a*axes of $a_1 = 2.8208(5)$ Å and $a_2 = 7.2552(5)$ Å at 296 K, yielding an irrational *p* value of p = x = 0.389(1). The final *R*-factor was R_{WP} = 0.082.

On the basis of the adopted superspace group, the modulated structure has been satisfactorily revealed, by considering up to second order modulation amplitudes. The zig-zag arrangement of the Ca ions is realised perpendicular to the *b*-axis and the zig-zag chains stack in an anti-parallel manner along the *c*-axis. A markedly distorted arrangement of the Co ions in the CdI_2 -type CoO_2 layer is also revealed. Fig. 1 shows the temperature evolution of the Co-O bond distances plotted against internal coordinate t'. In the present compound, *t'* is defined as $-px_1 + x_4 \sim -0.389x_2 + x_4$. The coordinates x_1 and x_4 respectively correspond to the *x* coordinate in the subsystems 1 and 2. Although, overall shape does not change very much for all the temperatures, the Co-O distances significantly vary from 1.7 to 2.0 Å which would relate to the highly electrical insulating behaviour, even at room temperature, relative to the Sr-analogue which exhibits metallic behavior down to 10 K. On the basis of the Co-O distances, we evaluated the bond valence sum on the Co ions and we observed a one-dimensionally (1D) charge-separated stripe pattern perpendicular to the zigzag arrangement of Ca ions. The 1D pattern is somewhat similar to that observed in Na_{0.5}CoO₂, but the charge is not fully separated to Co³⁺ and Co⁴⁺. In addition, the nominal valence state of Co is around +3.5 at the positions where the zigzag chains of Ca are not connected.

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Fig. 1. Temperature evolution of the Co-O distances plotted against internal coordinate t'.

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In-situ observation of the tetragonal-cubic phase transition in the CeZrO4 solid solution

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Yashima et al. [1,2] investigated the temperature and compositional dependence of the axial ratio in the CeZrO4 solid solution by ex-situ x-ray, synchrotron xray and neutron diffraction measurements of quenched samples at room temperature. They reported the existence of three metastable tetragonal forms of t, t' and t". The three tetragonal forms belong to the P42/nmc space group. However, as no high-temperature in-situ studies of the crystal structure or cubic?tetragonal phase transition have been conducted for the CeZrO4 solid solution, the temperature dependence of the oxygen displacement and atomic displacement parameters remains an unresolved issue. In this study, we investigated the temperature dependence of the crystal structure of the CeZrO4 solid solution through in-situ neutron diffraction measurements at high temperatures.

A CeZrO4 solid solution was prepared by co-precipitation method. The Ce(NO3)3 and ZrO(NO3)2 aqueous solutions were prepared, which contained 20 mass% CeO2 and 25 mass% ZrO2, respectively. Each solution was mixed with ion-exchanged water so that 1 mass% of CeZrO4 is contained. The mixed solution was put into a 5 mass% ammonia aqueous solution. Hydroxides precipitated at this stage. After sucking filtration and washing of the resultant precipitates, the precipitate was calcined at 800 oC for 3 h. The CeZrO4 powders thus obtained were pressed into pellets, and they were sintered at 1700 oC for 5 h, and then they were annealed at 800 oC for 24 h. The cylindrical product of 19mm in diameter and of 76 mm in height was obtained after the sintering. Neutron

diffraction measurements were performed in air with a 150-detector system, HER-MES, installed at the JRR-3M reactor in Japan Atomic Energy Agency, Tokai, Japan. Neutrons with wavelength 1.8143 were obtained by the (311) reflection of a Ge monochromator. Diffraction data were collected in the 2? range from 5? to 150? in the step interval of 0.1?, from 296 K to 1829 K. A furnace with MoSi2 heaters [3] was placed on the sample table, and used for neutron diffraction measurements at high temperatures. Sample temperatures were kept constant within ?1?C during each data collection. The diffraction data were analyzed by the Rietveld method with a computer program RIETAN-2000 [4].

Rietveld analysis of the CeZrO4 solid solution was carried out by the tetragonal structure with the P42/nmc space group at 296-1543 K. Data at 1829 K were analyzed assuming the cubic fluorite-type structure with space group. The calculated profile is in good agreement with the observed data (Fig. 1).

The unit-cell parameters a t' and ct' of the CeZrO4 solid solution increased with temperature, coinciding between 1523 K and 1829 K due to the t' -c transformation. The axial ratio of the metastable t' -CeZrO4 decreased from 1293 K to 1523 K. The axial ratio became unity between 1523 K and 1829 K, corresponding to the t' -c phase transition. The oxygen displacement d(O) from the regular 8c position of the cubic fluorite-type structure can be estimated by the equation d(O) = c[0.25 ? z(O)]. The d(O) value of CeZrO4 decreased to 0.0 between 1523 K and 1829 K, correspond-

ing to the t'-c phase transition (Fig. 2).

The isotropic atomic displacement parameters of Ce and Zr atoms B(Ce,Zr) and oxygen atoms B(O) increased with temperature (Fig. 3). B(O) was larger than B(Ce,Zr), suggesting the higher diffusivity of oxygen ions (Fig. 3).

In the present study we have confirmed that the CeZrO4 solid solution transforms from the tetragonal t' form to the cubic phase between 1543 K and 1829 K. The c-to-t' phase transition of CeZrO4 is accompanied by oxygen displacement along the c axis and the increase of the c/aF axial ratio from unity.

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Fig. 1. Rietveld pattern (1829 K) (a), temperature dependence of oxygen displacement (b) and thermal parameters (c) of CeZrO4.

Crystal structure and the structural disorder of ceria

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Ceria (cerium dioxide, CeO2)-based compounds are attractive materials for potential use as electrolytes in solid oxide fuel cells (SOFCs) and gas sensors, because the materials have a higher oxideion (O2-) conductivity than that of stabilized zirconia and a lower cost comparing with lanthanum gallate-based phases. Other promising applications of ceriabased materials include the SOFCs anode materials, solid-electrolyte oxygen pumps, and mixed-conducting membranes for oxygen separation and partial oxidation of hydrocarbons. The ceria-based materials are widely used as automotive catalysts. The development of the ceria-based materials requires a better understanding of the conduction mechanism, and crucial to this is the knowledge of the structural disorder of mobile ions at high temperatures where the materials work efficiently. The crystal structure of the CeO2 at high temperatures has been investigated by some researchers. In the present work [1-3], we have reanalyzed the structure with a split-atom model leading to a better fit, because the oxide ions have an anisotropic thermal motion as described below.

Neutron powder diffraction experiments were carried out in air in the temperature range from 40o to 1497oC. Neutron powder diffraction measurements were conducted in air with a 150-detector system, HERMES, installed at the JRR-3M reactor in Japan Atomic Energy Research Institute, Tokai, Japan. Neutrons with wavelength 1.8207 were obtained by the (311) reflection of a Ge monochromator. The experimental data were analyzed by a combination technique of Rietveld analysis, the maximum-entropy method (MEM), and the MEM-based pattern fitting. ing two structural models with the Fm-3m symmetry. One was the ideal fluoritetype structured model where the Ce and O atoms were put at 4a 0,0,0 and at 8c 1/4, 1/4, 1/4, respectively. The other was a split-atom model where the O atoms were distributed at the 8c 1/4,1/4,1/4 and at the 32f x,x,x positions (x=1/4+delta). The isotropic atomic displacement parameters were used for all the atoms. The Rietveld analysis with the split-atom model yielded a better fit than that with the ideal fluorite model. The unit-cell parameter increased with an increase of temperature. The positional parameter x of oxide ion at the 32f site x(O2) varied little with temperature. With increasing of temperature the occupancy of oxide ion at the 32f site g(O2) did not change much between 40o and 703oC, while the g(O2) increased above 703oC. The increase of g(O2) indicates an increase of the disorder of oxide ions at the 8c and 32f sites. Both the isotropic atomic displacement parameters for the Ce atom B(Ce) and for the O atom B(O) also increased with temperature. At higher temperatures the B(O) was larger than the B(Ce), suggesting a larger diffusion coefficient of oxide ions.

MEM analysis was carried out using the structure factors obtained in the Rietveld analysis with the split-atom model. Number of structure factors derived in the analysis was 11. The present results reveal that the oxide ions in the CeO2 have a complicated disorder and spread over a wide area, comparing with Ce ions. The spatial distribution of oxide ions is larger at higher temperatures (Figs. 4 and 5), corresponding to the larger displacement parameters and larger occupancy g(O2). Bulges in the 1/4-delta, 1/4-delta, 1/4+-delta directions (delta >0) are clearly seen in Figs. 4 and 5, indicating anisotropic thermal motions

Rietveld analysis was carried out assum-

around an ideal 8c position. The direction of bulges of oxide ions is opposite side of the Ce ion and the oxide ions shift to the position of the cavity at 1/2,1/2,1/2 position. The bulges are attributable to the repulsion between the Ce and oxide ions. Other small bulges in the 1/4-delta, 1/4delta, 1/4+-delta directions (delta >0) can be seen at the lower density level, which might be due to the experimental error. The bulges in the 11/4-delta, 1/4-delta, 1/4+delta directions indicate a possible diffusion mechanism where the oxide ions move through a face of the surrounding Ce tetrahedron to the octahedral cavity and then re-entering a neighboring anion site).

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Diffusion path of oxide ions in the yttria-doped ceria

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Abstract

Scattering amplitude distribution ceria of yttria-doped an material (Ce0.93Y0.07O1.96, space group: Fm-3m) has been investigated between 23 oC and 1434 oC by the maximum-entropy method (MEM) combined with the Rietveld analysis using neutron powder diffraction data. The refined unit-cell and atomic displacement parameters increased with an increase of temperature. The results of the MEM analysis reveal that the oxide ions have a positional disorder spreading over a wide area. One possible diffusion path of the oxide ions lies on the tie line along the <100> directions. The other pathway of the oxide ions can be seen along the <110> directions. The curved feature in the diffusion path would be common in various ionic conductors.

(1) Introduction

Atomic transport in solids is one of the central themes in contemporary solid state science and technology. Crystalline ionic conductors have extensively been studied by numerous researchers because of their many applications in solid oxide fuel cells (SOFCs), sensors, catalysts, and batteries. The development of better electrolyte materials requires a better understanding of the mechanism of ionic conduction, and crucial to this is a comprehensive knowledge of the crystal structure. Therefore, many researchers have studied the crystal structure and diffusion path of the ionic conductors. It is well known that the ionic conductor has a positional disordering for the mobile ions. To describe the spatial distribution and disorder of the mobile ions, various techniques such

as the split-atom model, the anharmonic thermal motions, the probability density function, the Fourier synthesis have been applied. Recently the maximum-entropy method has been developed for the determination of accurate structural features through the electron and nuclear density distribution in the crystalline materials. In the present work we focus on an oxideion conductor, yttria-doped ceria solid solution, Ce0.93Y0.07O1.96 [1].

(2) Experiments

ceria-yttria solid solution А Ce0.93Y0.07O1.96 sample was prepared from a precursor carbonate including Ce and Y atoms. The precursor carbonate was calcined at 1200 oC and then crushed and ground by a ball-milling technique. The Ce0.93Y0.07O1.96 powders thus obtained were pressed into pellets, and then sintered at 1500 oC for 3 h in air. The sintered product was cylindrical with the size of 19 mm in diameter and 30 mm in height. These pellets were used for the high-temperature neutron diffraction measurements. Neutron powder diffraction experiments were carried out in air in the temperature range from 23 oC to 1434 oC-Neutron powder diffraction measurements were conducted in air with a 150-detector system, HERMES, installed at the JRR-3M reactor in Japan Atomic Energy Agency, Tokai, Japan. Neutrons with wavelength 1.82035 were used. The neutron diffraction data were analyzed by a combination technique of the Rietveld analysis and the maximum-entropy method (MEM).

(3) Results and discussion

All the reflections in the neutron powder

diffraction patterns of Ce0.93Y0.07O1.96 in the whole temperature range of 23 oC to 1434 oC were indexed by a single phase with the cubic fluorite-type structure. Rietveld analysis was carried out assuming the fluorite-type structure with the symmetry where the cation (Ce4+ and Y3+) and anions (O2- and its vacancy) were put at 4a 0,0,0 and at 8c 1/4,1/4,1/4, respectively. The isotropic atomic displacement parameters were used for all the atoms. The calculated profile agreed well with the observed data. The refined crystallographic parameters and the reliability factors in the Rietveld analyses are shown in Table 1. The unit-cell parameter increased with an increase of temperature. Both the isotropic atomic displacement parameters for the cations B(CY) and for the anions B(O) also increased with temperature. The B(O) was larger than the B(CY), suggesting a larger diffusion coefficient of oxide ions. These features are consistent with the previous results in Rietveld analyses for the non-doped and doped ceria materials.

Maximum-entropy method (MEM) analyses were carried out using the structure factors obtained in the Rietveld analysis. Number of structure factors derived in the analysis was 11. In the MEM calculations we used the 111 peak intensity at the lowest 2theta position that is the most important information for the MEM analysis. The MEM map provided much information on the positional disorder of oxide ions, comparing with the structural model obtained in the Rietveld analysis. The conventional simple models consisted of atom spheres are no longer appropriate to describe the positional disorder of oxide ions at high temperatures. The present results reveal that the oxide ions in the Ce0.93Y0.07O1.96 have a complicated disorder and spread over a wide area, comparing with cations. The spatial distribution of oxide ions at 1434 C was larger C, corresponding to than that at 23 the larger atomic displacement parameters. There were two types of bulges in the MEM distribution map. The other exists along the

<110> directions. These directions of oxide ions are opposite side of the Ce and Y cations. The bulges are attributable to the repulsion between the cations and oxide ions. Such anisotropic feature in the neutron scattering amplitude have been observed in the ceria materials.

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Crystal Structure Analysis of (Ga0.93Zn0.07)(N0.90O0.10) Oxynitride Photocatalyst

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Abstract

Gallium oxynitride zinc (Ga0.93Zn0.07)(N0.90O0.10) is a new type of photocatalyst that is capable of overall water splitting under visible light. The crystal structure of (Ga0.93Zn0.07)(N0.90O0.10) the was refined by Rietveld analyses of neutron powder diffraction data. The (Ga0.93Zn0.07)(N0.90O0.10) was confirmed to have a Wurtzite-type structure (space group: P63mc). The present work demonstrates that oxygen substitutes for nitrogen in the crystal structure, and may be responsible for the desirable optical properties of (Ga0.93Zn0.07)(N0.90O0.10) as a photocatalyst for visible light-driven overall water splitting. The neutron scattering amplitude distribution through the maximum-entropy method (MEM) and MEM-based pattern fitting revealed that the crystal structure of the (Ga0.93Zn0.07)(N0.90O0.10) is free of interstitial sites and large disorder.

(1) Introduction

Overall water splitting using a photocatalyst can supply the clean and recyclable hydrogen energy. Maeda et al. reported the gallium zinc oxynitride (Ga1xZnx)(N1-xOx) as a new type of photocatalyst. This is the first example of photocatalyst that is capable of overall water splitting under visible light. The (Ga1-xZnx)(N1xOx) photocatalyst was identified by x-ray powder diffraction to be a single phase with a wurtzite-type structure. The x-ray diffraction peak positions changed with composition x in the (Ga1-xZnx)(N1-xOx), suggesting the formation of solid solution (Ga1-xZnx)(N1-xOx). However, the position and occupancy of nitrogen and oxygen atoms have not yet been known yet, probably due to the difficulty in distinguishing the nitrogen atoms from oxygen atoms through X-ray diffraction method. On the contrary, neutron diffraction can distinguish them from each other, because the neutron scattering length of nitrogen atom (9.36 fm) is different from that of oxygen atom (5.803 fm).

The present work [1] reports a neutron powder diffraction study of the (Ga0.93Zn0.07)(N0.90O0.10), which was determined in the previous study1) to be an active composition for overall water splitting.

(2) Experiments and Data Processing

Powders of (Ga0.93Zn0.07)(N0.90O0.10) were prepared by solid-state reaction under NH3 gas flow. A mixture of Ga2O3 (High Purity Chemicals, 99.9%) and ZnO (Kanto Chemicals, 99%) powders was heated under NH3 flow (250 mL/min) at 1123 K for 5.4×104 s to afford the (Ga0.93Zn0.07)(N0.90O0.10) photocatalyst as a yellow powder.

For neutron diffraction measurement, the (Ga0.93Zn0.07)(N0.90O0.10) powder was placed in a ?10 mm \times 50 mm vanadium cylinder. Neutron diffraction data were collected at 299 K using a multi-detector fixed-wavelength powder diffractometer (HER-MES) of the Institute of Materials Research, Tohoku University, which is installed at the JRR-3M research reactor of the Tokai Research Laboratories, Japan Atomic Energy

Agency. A neutron beam with wavelength of 0.18207 nm was obtained using the (331) plane of a germanium monochromator.

crystal structure The of the (Ga0.93Zn0.07)(N0.90O0.10) powder was refined by Rietveld analysis of the neutron diffraction data using the computer program RIETAN-2000 with neutron scattering lengths of Ga, 7.288; Zn, 5.60; N, 9.36; and O, 5.803 fm. Scattering amplitude distributions were obtained by a maximum-entropy method (MEM) for the structure factors obtained in the Rietveld analysis.

(3) Results and Discussion

The (Ga0.93Zn0.07)(N0.90O0.10) photocatalyst was confirmed to achieve overall water splitting to H2 and O2 under irradiation with visible light. Chemical analysis indicated the average composition of the powder to be Ga0.933(1)Zn0.0670(3)N0.896(1)O0.104(0) where the values in parenthesis are standard errors. Neutron diffraction data for the (Ga0.93Zn0.07)(N0.90O0.10) were successfully analyzed assuming a single hexagonal wurtzite-type phase with space group P63mc. In a preliminary analysis, we refined the occupancy factors of Ga atom g(Ga) and Zn atom g(Zn) with a constraint g(Ga)+g(Zn)=1. The refined g(Ga) and g(Zn) agreed with those obtained in the chemical analysis. In another analysis, we refined the z coordinate of Ga atom z(Ga) and z(Zn) independently. The refined z(Ga) agreed with the refined z(Zn). Therefore, we fixed the occupancy factors: g(Ga)=0.933 and g(Zn)=0.067, and used a constraint: z(Ga)=z(Zn) in the final analysis. The refined unit cell parameters were a = 0.31900(2) and c =0.51835(2) nm, and the refined fractional coordinate z for the (Ga,Zn) cation in (Ga0.93Zn0.07)(N0.90O0.10) (0.3782(2))is in good agreement with that in GaN (0.377(1)). The (Ga,Zn) cation is coordinated with four anions (N,O) to form a (Ga,Zn)(N,O)4 tetrahedron. The interatomic distance between the cation and

anions is in the range of 0.19473?0.1960 nm. The estimated quadratic elongation and angle variance6) are 1.000 and 0.35 (deg2), respectively, indicating that the (Ga,Zn)(N,O)4 tetrahedron is regular.

The refined occupancies of N and O atoms determined by Rietveld analysis are g(N)= 0.89(2) and g(O) = 0.11(2), where the constraint g(N) + g(O) = 1.000 was assumed. The corresponding chemical formula Ga0.93Zn0.07N0.89(2)O0.11(2) agrees well with that determined by chemical analysis (Ga0.93Zn0.07)(N0.90O0.10), indicating that oxygen substitutes for nitrogen in this material. In the previous study, the variation of the x-ray powder diffraction profile and diffuse reflectance spectra with x in (Ga1-xZnx)(N1-xOx) suggested this substitution. The present results thus provide direct evidence of the substitution of oxygen for nitrogen in this structure.

The validity of the refined crystal structure and the possible disorder in (Ga0.93Zn0.07)(N0.90O0.10) were investigated by calculating the scattering amplitude distribution using a maximumentropy method (MEM) and MEM-based pattern fitting (MPF). The MEM equicontour map reproduces the atomic positions determined by the Rietveld analysis, but does not indicate any interstitial sites. This result confirms the validity of the refined crystal structure. The MEM density map also indicates that the structure is free of large positional disorder. Since all the atoms are localized near the stable position and do not exhibit large positional disorder, the reliability factors in the MPF analysis are nearly equaled to those in the Rietveld analysis.

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Phonons in NaNbO3

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Sodium niobate NaNbO3 has a simple cubic perovskite structure above 913 K. NaNbO3 shows a complicated sequence of phase transitions as a function of temperature.[1] First, the cubic to a tetragonal phase transition takes place at 913K. Next, three distinct orthorhombic phases are found in the intermediate range between 643 and 848K. Then an antiferroelectric monoclinic phase exists in the range between 193 and 643 K. Below 193 K, NaNbO3 has a ferroelectric orthorhombic structure. First-principles calculations have predicted the coexistence of zone-center and zone-boundary instabilities in cubic NaNbO3.[2]

Diffuse X-ray and neutron scattering experiments for NaNbO3 strongly suggest the zone-boundary phonon instability.[3-4] In addition, infrared reflectivity measurements show that the frequency of zonecenter TO phonon in the cubic phase decreases gradually on cooling.[5] Unfortunately, there is no data for the phonon dispersion relations. Here we report preliminary results for cubic NaNbO3.

Inelastic neutron scattering measurements were performed using the triple-axis spectrometer T-11 (HQR) at JRR-3M. Figure 1 shows the TA phonon dispersion relation along the [111] direction determined at 933 K. The essential feature is the R-point softening in the cubic phase. The measurements up to 1223 K indicate that the frequency of the R-point TA phonons in cubic NaNbO3 increases gradually with increasing temperature. In addition, we found out the M-point softening of the TA phonons along the [110] direction with the polarization parallel to the [1 -1 0] direction. The softening at the R and the M points suggests that the rotation of the oxygen octahedra becomes unstable. The zone-boundary phonon softening roughly explains results for diffuse X-ray scattering in the cubic phase.[3-4] Further experiments are necessary to investigate the lattice dynamics of cubic NaNbO3.

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Fig. 1. Phonon dispersion relations for cubic NaNbO3 along the [111] direction.

Phonon dipsersion relations in PbTiO3

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Lead titanate PbTiO3 undergoes only a single first-order transition at Tc=490 C from a cubic paraelectric to a tetragonal ferroelectric phase. PbTiO3 is also the end member of relaxor ferroelectrics (1-x)Pb(Zn1/3Nb2/3)O3-xPbTiO3 (PZN-PT) and (1-x)Pb(Mg1/3Nb2/3)-xPbTiO3 (PMN-PT). In the 1970s, Shirane et al. [1] have reported the phonon dispersion relation along the [100] direction in cubic PbTiO3. They revealed the existence of the well-defined soft mode. Recently, phonon dispersion relations have been studied extensively for relaxor ferroelectrics. [2-3] We have studied the lattice dynamics of tetragonal PbTiO3. [4] Here we report on the phonons in the cubic phase.

The inelastic neutron scattering measurements were performed on the triple-axis spectrometer T-11 (HQR) at JRR-3M. Figure 1 plots typical constant-E scans across the TO branches along the [1 1 0] direction. The zone-center TO phonon energy is found to be approximately 4meV at 520 C. The present data is roughly consistent with the value reported by Shirane. [1] The TO phonon curve along the [100] direction up to q=0.1 is almost the same as the TO phonon curve along the [110] direction. This suggests the isotropic nature of TO phonon dispersion relations around the zone center. Results for TA phonons along the [100] and the [110] directions also suggest the isotropic nature. Further experiments are necessary to determine the lattice dynamics of cubic PbTiO3.

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Fig. 1. Constant-E scans for cubic PbTiO3 measured at 520 C.

Low temperature neutron diffraction studu of (La0.8Sr0.2)ScO3- δ perovskite

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Recently, strontium doped LaScO3-based perovskites, (La1-xSrx)ScO3- δ have been investigated as the electrolyte materials of hydrogen sensors, etc., because of the relatively high proton conductivity and high chemical stability against CO2. Of these, x = 0.2 compound, (La0.8Sr0.2)ScO3- δ (LSS82) shows the highest proton conductivity of 6 \times 10-3 S/cm at 873K [1]. However, the detailed crystal structure and the proton conduction mechanism of this compound are not clear. In this study, we measured the low-temperature neutron diffraction data of LSS82 between 3 and 297K, and investigated the crystal structure and the site occupation of proton.

High purity LSS82 powder was prepared by a solid-state reaction method. Obtained LSS82 powder was hold in an electric furnace at 923K for 30 hrs under wet 21%O2-79%Ar gas flow condition. The absorbed H2O content was evaluated by using a TG-MASS analyzer, and the final chemical composition was determined as (La0.8Sr0.2)ScO2.9885H0.177 (LSS82-H2O). The LSS82-H2O powder packed in a vanadium cell was set in a He gas circulating refrigerator (4K-cryo). Neutron diffraction measurements were performed with HERMES installed at JRR-3M in JAEA (Tokai) [2]. Neutron wavelength was 1.81963(4)A. Diffraction data were collected in the 2 θ range from 20 to 153 deg in the step interval of 0.1 deg, between 3 and 297K. The diffraction data obtained were analyzed by using a computer program RIETAN-2000 [3] and a maximumentropy method (MEM)-based pattern fitting. MEM calculation was carried out using a computer program PRIMA [4].

All the reflections of LSS82-H2O between 3 and 297K were indexed by an orthorhombic symmetry (Pnma). Figure 1 shows the crystal structure of LSS82 at 3K and the speculated six hydrogen positions. Of these, the most plausible sites were H3 and H6 positions.

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Fig. 1. The crystal structure of LSS82 at 3K and the speculated hydrogen sites. The most plausible positions: H3 and H6.

Low temperature neutron diffraction study of Ba(Zr0.8Y0.2)O3- δ perovskite

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Since the discovery of proton conduction in acceptor-doped BaZrO3 by Iwahara et al. [1], BaZrO3-based perovskites, such as Ba(Zr1-xYx)O3- δ (0<=x<=0.3), have been attracting attention, because they have high proton conductivity and chemical stability. However, the detailed crystal structures of these compounds are not yet clear. In this study, we measured the lowtemperature neutron diffraction data of Ba(Zr0.8Y0.2)O3- δ (BZY82) between 3 and 299K, and investigated the crystal structure.

High purity BZY82 powder was prepared by a solid-state reaction method. The BZY82 powder obtained was hold in an electric furnace at 773K for 20 hrs under wet 21%O2-79%Ar gas flow condition. The BZY82 powder packed in a vanadium cell was set in a He gas circulating refrigerator (4K-cryo). Neutron diffraction measurements were performed with HERMES installed at JRR-3M in JAEA (Tokai) [2]. Neutron wavelength was 1.81638(2)A. Diffraction data were collected in the 2 θ range from 20 to 153 deg in the step interval of 0.1 deg, between 3 and 299K. The diffraction data obtained were analyzed by using a computer program RIETAN-2000 [3].

Figure 1 shows the diffraction patterns of BZY82 at 3, 76, and 299K. Super lattice peaks appeared at around 2 θ = 42, 56, 79, and 111 deg, which cannot be indexed as a cubic perovskite phase (Pm-3m, NO.221). These peaks were not observed by X-ray diffraction measurement at 298K. All the peaks of BZY82 could be indexed hypothesizing a trigonal perovskite phase (R-3c, The intensity of super lattice NO.167). peaks decreased with increasing temperature, and the peaks almost disappeared at 299K. In a previous study, the similar super lattice peaks were observed for LaGaO3based perovskite-type oxide-ion conductor, (La0.8Sr0.2)(Ga0.8Mg0.15Co0.05)O3- δ at high temperatures above 1273K [4].

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Fig. 1. Neutron diffraction patterns of BZY82 at 3, 76, and 299K. The arrows show the position of super lattice peak.

Martensitic transformation of Heusler-type Ni₂MnGa shape memory alloy

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Process of a thermally induced martensitic transformation of a Heusler-type offstoichiometric Ni₂MnGa single crystal was investigated. A triple-axis neutron spectrometer, AKANE, was used. The composition of the alloy was Ni_{2.16}Mn_{0.78}Ga_{1.06}, having a martensitic transformation temperature around room temperature (293 K) coincident with a Curie temperature. It is ferromagnetic in the martensitic phase and paramagnetic in the mother phase and is expected as a magnetic field-induced shape memory alloy. Change of a cubic (020) peak on (hk0) reciprocal-plane (h=-0.36 -0.36, k=1.76 - 2.36), where the cubic structure is in the mother phase, was observed with decreasing temperature from 293 K to 100 K. The result was compared with magnetic field dependence of the pattern measured by TAS-2, where the field was changed up to 10 T at 293 K. The diffraction patterns projected on (hk0)-plane at typical temperatures, 279 K and 100 K, under no magnetic field and the pattern under 10 T at 293 K are shown in Fig. 1. At 279 K peaks belonging to orthorhombic structure in the martensitic phase¹, are seen. Two peaks near k=2.1 due to orthorhombic (002), a peak at k=2.0 due to orthorhombic (020) and two peaks near k=1.9 due to orthorhombic (200) are observed. Other four peaks on the corner of the (hk0)-plane, the intensity of which are very weak, indicate that there are some long period in the orthorhombic structure. The origin of this long period is not yet analyzed. Peaks near (0 2.3 0) and (0 1.72 0) were found to be the foot of (0 2.3 \pm 0.3) and (0 1.72 \pm 0.26). At 100K the structure changed to a tetragonal structure in the martensitic phase¹⁾. Peaks near k=2.12 belong to tetragonal (200) and the peaks near k=1.78 belong to tetragonal (002). Under the magnetic field of 10 T at 293 K, the observed orthorhombic structure was guite similar to that at 279 K under no field. It is suggested that temperature decrease of 14 K in this alloy causes the same effect of magnetic field of 10 T. The magnetic field as high as 10 T is not enough to cause the tetragonal structure, which is the equilibrium martensitic structure at low temperature. However, these experimental results show that magnetic field-induced shape memory effect becomes promising, because we already know that the addition of small amount of boron to the alloy or making a foil of the alloy improve the brittleness of the material and make the transformation easier.

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Fig. 1. Temperature dependence and magnetic field dependence of cubic (020) peak on (hk0) reciprocal plane.



Measurement of Thickness of Thin Lubricant Film at Solid-Solid Interface by Neutron Reflectometry

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Tribological phenomena usually occur at a solid-solid interface, where the presence of a lubricant greatly contributes to low friction. A lack of lubricant causes substantial wear and even seizure of two bodies under severe conditions. However, an in-situ observation is difficult to perform if some lubricant is present at a solid-solid interface because any common rays, such as X-rays and visible rays, cannot penetrate into metals. A neutron beam, on the other hand, is well known to be able to penetrate into almost all metals. Thus, we propose to apply a neutron scattering method to judge whether or not a lubricant is present at a metal interface. Reflectometry is generally recognized as a useful method to analyze vertical structures precisely on a target surface. In this study, we try to measure a thickness of thin lubricant film formed between two silicone blocks by neutron reflectometry. The instrument we used was 'MINE', which is a neutron reflectometer, in JAEA. First, some basic samples with periodic surface roughness were prepared; a grating thin film made of nickel was formed on one of the silicone blocks by photo-lithographic technology as part of a simple roughness model. In addition, the other plane silicone block was covered on the grating surface, resulting in our being able to obtain an 'interface model' with a well-defined clearance between the two silicone blocks. The clearance was set at about 100, 50, and 10 nm and was filled by air or two kinds of lubricants: water or base oil. As a result, we obtained different reflectivity profiles depending on each medium at the interface. In addition, the thickness of the lubricant film could be estimated by intervals of the interference fringes of the reflectivity profiles. We conclude that neutron reflectometry is a useful method to estimate lubricants quantitatively, even at a metal interface.



Fig. 1. Reflectivity profile of lubricant film at interface of two silicone blocks

Phase Transition and Debye-Waller Factor of KDP

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The mechanism of the phase transition in KDP (KH_2PO_4) has been interested widely. The isotope effect could be explained by the famous proton tunneling model[1] for long years. But the replacing proton by deuteron changes atomic distance, which could also present the characteristic isotope effect.[2]

With using neutron diffractometry, detailed structural studies were performed in a quarter century ago, and the orderdisorder picture of proton distribution was revealed.[3] However, the analysis was limited above 127K, so the temperature range should be expanded to discuss the proton motion definitely.

A single crystal of KDP was set in a cryostat mounted on a diffractometer (FONDER) installed at JRR3M reactor in JARERI, Tokai.

First sample was used in the paraelectric phase P (tetragonal I-42d). In the ferroelectric phase F (orthorhombic Fdd2), dc bias field was applied to make the second sample single. Diffraction data up to 2theta <156 (neutron wave length 1.2452A) were collected at two and four temperatures in phase P and F, respectively. Absorption and extinction correction was performed by using RADIEL. Atomic parameters were refined by least-squared calculations. Nuclear density was estimated by PRIMA and visualized by VEND.[4]

Figure shows the nuclear density images at 150K. The elongated ellipsoids indicate the disordered protons. In the phase F below 122K, the proton distribution is ordered and atoms move along the z-axis with a deformation of PO.4 tetrahedrons. The temperature dependence of the Debye-Waller factor U's is plotted in Figure. The split atom method is applied for protons in the tetragonal phase, where the factor becomes smaller than the phase F. Our results are consistent with the previous one.[3] However, since the samples were different, the direct comparison between the phase P and F should be reserved currently.

The values of U at T=0 indicate that nucleus have a finite width corresponding to their wave functions. The detailed analysis will predict the local potential in which each atom is constrained.

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Fig. 1. Nuclear density at 150K in the tetragonal phase (top) and the temperature dependence of the thermal parameters (bottom). In the bottom, the previous results after ref. 3 are shown by broken lines.

A coupling between an acoustic phonon and the diffuse scattering in the relaxor ferroelectric $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3-xPbTiO_3$ near morphorobic phase boundary

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Relaxor ferroelectrics are a class of disordered crystals showing extremely high, broad and frequency dependent peak in dielectric susceptibility. It is widely believed that the polar nanoregions (PNR) play an important role in relaxor behavior occurring at temperatures much above T_c , the so-called Burns temperature T_d [1]. Neutron scattering measurements by Naberezhnov et al. on the typical relaxor Pb(Mg_{1/3}Nb_{2/3})O₃ (PMN) revealed the onset of strong diffuse scattering at or very near T_d [2], indicating a close connection between the PNR and the diffuse scattering. A solid solution of PMN and ferroelectric PbTiO₃ (PT) exhibits a maximum dielectric susceptibility near PMN-30%PT, the boundary between the rhombohedral phase and the tetragonal one, which is the so-called morphorobic phase boundary (MPB). Last year, we investigated PMN-34%PT which locates on the tetragonal side of the MPB and reported that the Q-pattern of the diffuse scattering changes from ellipsoid elongating along $\langle 110 \rangle$ direction in the cubic phase to cross elongating along $\langle 100 \rangle$ direction in the tetragonal phase. This year, we report an overdamped acoustic phonon coupled with the diffuse scattering.

Figures 1 show constant *Q* scan spectra at (0.944 1.056 0) and (0.92 1 0) taken at T = 440 and 410 K. At T = 440 K (cubic), the diffuse scattering extends along the [110] direction; the diffuse scattering is strong at (0.944 1.056 0) but weak at (1.021 1 0). We found the acoustic phonon at (0.944 1.056 0) is overdamped while that at (1.021 1 0) is underdamped, as shown in Fig.1(a) and (b). At T = 410 K (tetragonal), the overdamped phonon becomes underdamped concomitantly with the disappearance of the diffuse scattering at (0.944 1.056 0). On the other hand, at (1.021 1 0), the well-

defined phonon peak observed in the cubic phase disappears presumably due to overdamping. These results indicate a coupling between the acoustic phonon and the diffuse scattering. Similar damped acoustic modes were observed in PMN by Stock et al. [3] and the authors successfully simulated the phonon spectra by Michel-Naudts model which takes into account a coupling between a phonon mode and a relaxation mode [4]. From their model, an acoustic mode is overdamped and peak at E = 0appears when a characteristic relaxational frequency is less than or nearly equal to phonon frequency. The current results indicate slow relaxation mode may exist along the particular direction at which the diffuse scattering is strong.

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Fig. 1. Constant Q scans at (a),(c) (0.944 1.056 0) and (b),(d) (0.92 1 0) taken at T = 440 and 410 K. Solid lines show fits to the sum of a sharp Gaussian peak at E = 0 for the central peak and a Lorentzian peak for the acoustic phonon.

Investigation of the local crystal distortion in the relaxor ferroelectric $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3-xPbTiO_3$ ($0.0 \le x \le 0.40$) using extinction effect

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Relaxor ferroelectrics of the form PbBB'O₃ are receiving a great deal of scientific attention as a result of the extremely high piezoelectric response over a wide temperature range. The key concept to understand the relaxor behavior is believed to be the so-called polar nanoregions (PNR) at temperatures much above However, these clusters cannot be T_c . detected from the profiles of the X-ray and neutron diffraction Bragg peaks due to their extremely small size. In a nearly perfect crystal, the scattering intensity of a strong Bragg peak becomes smaller than the calculated value due to scattering by various crystallites, which is called secondary extinction. To elucidate the evolution of the PNR in the relaxor system, we investigated the thermal variations of Bragg peaks in the relaxor ferroelectric $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3-xPbTiO_3$ (PMNxPT; x = 0.0, 0.10, 0.20, and 0.40) which could be associated with the thermal variation of the local crystal distortion by the secondary extinction effect. Neutron scattering experiments were performed on the triple-axis spectrometers PONTA installed at the JRR-3 Reactor of the JAEA.

Figure 1 (a) shows the temperature dependence of the integrated intensity at the (200) Bragg peak for PMN-10%PT. The peak intensity increases sharply at T = 615and 280 K, which could be explained by a release of the secondary extinction effect due to the tilt of the crystal mosaics. Figure 1 (b) shows zero field phase diagram of PMN-*x*PT. Open circles denote the value of the local T_C at which a structural phase transition was observed by x-ray diffraction, but not by neutron diffraction. A bulk structural phase transition, however, was observed for $x \ge 0.27$, shown by closed The higher temperature of the circles.

rapid increase in the (200) Bragg (T_d extinction: open rectangles) corresponds to the onset of the diffuse scattering, which can be associated with an appearance of PNR. The lower one (T_c extinction: open triangles) matches the structural phase transition temperature, which could be associated with an ordering of PNR. Both temperatures increases with PT substitution. In addition, the difference between these temperatures becomes small with x, which is expected to be zero at PbTiO₃.



Fig. 1. (a) The temperature dependence of the (200) Bragg peak. (b) Zero field phase diagram of PMNxPT.

Damped acoustic phonon in the relaxor ferroelectric $Pb(Mg_{1/3}Nb_{2/3})O_3$

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Relaxor ferroelectrics have gained great interest recently due to their promising application as piezoelectric devices. $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) is a typical relaxor which shows a broad and frequency dependent peak in dielectric susceptibility. It is widely believed that the polar nanoregions (PNR) occurring at temperatures much above T_c , the so-called Burns temperature T_d , play an important role in such relaxor behavior. Neutron scattering measurements by Naberezhnov et al. on PMN revealed the onset of strong diffuse scattering at or very near $T_d \sim 600$ K [1], indicating a close connection between the PNR and the diffuse scattering. The lattice dynamics in PMN are characterized by a soft, zone center, transverse optic (TO) mode observed below T_d . Thus, it is expected that the local crystal distortion in PNR is driven by the soft TO. However, recently, the soft TO mode was observed in the normal ferroelectric PMN-40%PT [2], which casts doubt on the soft mode concept of the PNR. To elucidate the lattice dynamics in PNR, we investigated the acoustic phonon and low energy excitations in PMN. Neutron scattering experiments were performed on the triple-axis spectrometers HER installed at the JRR-3 Reactor of the JAEA.

Figures 1 show the constant *Q* spectra at (1.1 1.1 0) and (1.1 0.9 0) taken at T = 650, 500, and 400 K. At T = 650 K ($\geq T_d$), a well-underdamped transverse acoustic (TA) phonon and longitudinal one (LA) shown by dotted lines were observed at 2.67 \pm 0.03 and 3.57 \pm 0.15 meV, respectively. At T = 500 K, the TA mode becomes overdamped and a resolution-limited peak at E = 0 (central peak: dotted line) develops at (1.1 0.9 0), while the LA mode remains underdamped and no enhancement of the central peak was observed at

(1.1 1.1 0). The central peak corresponds to the (110) diffuse scattering which elongates along the transverse directions. In addition, a quasielasctic scattering (dotted and broken line) appears below T = 500 K. The central peak and quasielastic scattering develops especially at (1.1 0.9 0) with decreasing temperature. The overdamped TA mode coupled with the strong diffuse scattering and quasielastic scattering indicates a coupling between TA mode and PNR, which is consitent with the uniform phase shift concept proposed by Hirota et al. [3] On further cooling, the underdamped TA mode recovers and the quasielastic scattering disappears below $T_c \sim 213$ K at which PMN becomes ferroelectric on electrical field-cooling.

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Fig. 1. Constant *Q* scan at (1.1 1.1 0) and (1.1 0.9 0). Solid lines showfits to the sum of a sharp Gaussian peak at E = 0 (dotted line), a broad Lorentzian peak at E = 0 (dotted and broken line), and a damped-harmonic-oscillator peak (broken line).

The diffuse scattering in the relaxor ferroelectric compound

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Relaxor ferroelectrics have attracted considerable attention since the discovery of giant piezoelectricity in relaxor-based single crystals. (Na_{0.5}Bi_{0.5})TiO₃ (NBT) forms perovskite structure with two different ions Na^+ and Bi^{3+} at the A site of ABO₃. Temparature anomalies in dielectric properties of and two structural phase transitions have been investigated since 60's: the structural symmetry is lowered from cubic to tetragonal phase at T = 813 K and from tetragonal to rhombohedral phase at approximately 533 K [1]. Recently, NBT regains attention as promising applications to piezoelectric devices containing no toxic lead. NBT exhibits extremely high and broad peak in the dielectric susceptibility which is very similar to that in typical relaxors. It is widely believed that the polar nanoregions (PNR) play an important role in relaxor behavior occurring at temperatures much above T_c . the so-called Burns temperature T_d [2]. The purpose of the present work is to study the Qstructure and thermal variations of the diffuse scattering to clarify nature of PNR in NBT. Neutron scattering experiments were performed on the triple-axis spectrometers PONTA installed at the JRR-3 Reactor of the JAEA.

Figure 1 shows intensity contours of the diffuse scattering near (110) and (100) measured at T = 440 K. The diffuse scattering was observed in the rhombohedral phase, which is elongated along the [100] and [010] directions transverse to the wave vector. Such $\langle 100 \rangle$ -type diffuse scattering indicates a short-ranged atomic shift with tetragonal symmetry in the matrix with rhomboheral one. In addition, the diffuse scattering has more intensity along transverse direction than that along longitudinal

direction, suggesting a close connection between the diffuse scattering and soft transverse optical mode.

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Fig. 1. Intensity contours of the diffuse scattering near (a) (110) and (b) (100) measure at T = 400 K.

Crystal structural change of Ba-doped-tricalcium phosphate

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Abstract

Crystal structural change of bariumdoped-tricalcium phosphate (TCP) has been investigated using high-temperature neutron powder diffraction and Rietveld method. The alpha-alpha' phase transition temperature decreased with an increase of Ba composition x in Ca3(1-x)Ba3x(PO4)2. Structural refinement of Ba-doped-TCP was successfully performed by P21/a. Temperature dependence of unit cell parameters was determined around the alpha-alpha' phase transition point. Unitcell parameter a discontinuously changed at the alpha-alpha' transition temperature, indicating that the transition is of first order.

(1) Introduction

Tricalcium phosphate [TCP: Ca3(PO4)2] has increasingly been used as a biocompatible material for bone replacement or for the coating of bone prostheses. There are many studies to investigate doped TCPs. Although many researches for crystal structure of doped-TCP have been reported for ?-phase, crystal structure of alpha-type doped-TCP has been insufficiently understood and studied, probably due to their complicated crystal structures. In this study, we investigated the crystal structural change of Ba-doped-TCP using high-temperature powder neutron diffraction analysis.

(2) Experiments and Data Processing

High-purity alpha TCP was prepared by solid-state reactions from beta Ca3(PO4)2 and Ba3(PO4)2. Stoichiometric amounts of high-purity CaHPO4 (99.6% purity, Kyowa Chemical Industry, Takamatsu, Japan) and CaCO3 (99.99% purity, Kojundo Chemical Lab. Co., Ltd., Sakado, Japan) powders were mixed for about 3.0 h in an agate mortar. The mixture was pressed into pellets under a uniaxial pressure of 150 MPa. The pellets were sintered for 12 h at 1000?C to obtain single phase beta TCP. Ba3(PO4)2 was obtained after sintering BaCO3 and NH 4 H2PO4 mixture at 1000 C deg. for 12 hours. The sintered pellets of beta Ca3(PO4)2 and Ba3(PO4)2 were ground and mixed (Ca/Ba atomic ratio= 95/5). And the mixtures were sintered at 1400 C deg. for 6 h. The resultant products were used for neutron powder diffraction study.

To investigate the temperature dependence of the crystal structure of Ba-doped-TCP, neutron powder diffraction experiments were carried out at high temperatures in air with a 150-detector system, HERMES, installed in the JRR-3M reactor at the Japan Atomic Energy Agency, Tokai, Japan. Neutrons with a wavelength of 0.182 nm were obtained by the (311) reflection of a Ge monochromator. The diffraction data were collected in the 2 theta range from 3 deg. to 153.9 deg. in a step interval of 0.1 deg. in the temperature range from 24 to 1533 C deg. A furnace with MoSi2 heaters was placed on the sample table, and used for the neutron diffraction measurements at the high temperature. The unit-cell and structural parameters of the Ba-doped-TCP were refined by Rietveld analysis using the RIETAN-2000 computer program. The diffraction patterns were fitted with a Pearson VII type function.

(3) Results and Discussion Figure 1 shows the temperature dependence of the neutron diffraction pattern for 5 mol% Ba doped TCP. Closed and open circles in Fig. 1 denote neutron diffraction peaks of high-temperature alpha 'and low-temperature alpha-phases, respectively. At 1449.9 C deg., the pattern exhibited both peaks of the alpha (closed circles in Fig. 1) and alpha' (open circles in Fig. 1) phases, indicating the alpha and alpha ' phases co-existed at this temperature. The characteristic peaks of the alpha phase (closed circles in Fig. 1) disappeared between 1425.9 and 1474.8 C deg. Therefore, the alpha-TCP transforms into alpha'phase between 1425.9 and 1474.8 C deg.

Structural refinement was successfully performed by a monoclinic structure, space group P21/a. The reliability factors were Rwp = 5.32%, S = 2.05, RI = 0.40%, RF = 0.19%. The unit-cell parameters obtained from the Rietveld analysis were a = 1.2936(3), b = 2.7540(3), c = 1.5252(4)nm, alpha = beta = 90 deg., gamma = 126.66(1) deg.

We successfully determined the temperature dependence of the unit-cell parameters a for TCP around the alpha? alpha ' phase transition point. Thus we were able to clearly indicate that the alpha? alpha ' phase transition is of first order.



Fig. 1. Neutron powder diffraction patterns of 5mol% Ba-doped-TCP at different temperatures. Closed and open circles denote neutron diffraction peaks of high-temperature alpha'- and low-temperature alpha-phases, respectively.

Magnetic fluctuation in ternary alloy CuFePt₆

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The ternary alloy CuFePt₆ is one of a series of the newly found ternary alloys CuMPt6 (M is 3d metal). It has a single phase at this stoichiometric composition and forms a Cu₃Au type ordered structure below the order-disorder transition temperature 1313 K [1]. In the magnetization measurements, a transformation to ferromagnetic order is observed at $T_{\rm C}$ = 210 K in the alloy with the Cu₃Au type order. Magnetic moment per one CuFePt₆ molecule estimated from the value of magnetization at 5T is 4.1 μ B for 5 K [2]. In the weak magnetic filed of 0.01 T, on the other hand, magnetic susceptibility of ZFC process shows further phase transition with anti-ferromagnetic-like cusp at $T_{\rm N} = 100$ K, though no anomaly has been found for that of FC process. In the pulsed-neutron diffraction measurements, magnetic reflection appears at Γ point below T_{C} , and at Mpoint below T_N with keeping the intensity of Γ point reflection unchanged. These results indicate an existence of strong fluctuation in the magnetic structure of CuFePt₆. In order to understand the origin of the magnetic fluctuation in the alloy, inelastic scattering measurements were performed at 5G (PONTA). Figure 1 shows inelastic scattering line profiles along [011] axis passing through 0 1/2 1/2 (M point) and 0 11 (Γ point) RLP at 7 K. The inelastic intensities spread along this axis with a strong peak at 0.1/2.1/2 over an energy of 5 meV. It has been found from the measurements along [100] axis that the inelastic intensities also spread along this axis. In Fig. 2, line profiles for 2 meV inelastic scattering are shown for 7 K and 145 K (above T_N). The 0 1/2 1/2 inelastic peak persists above $T_{\rm N}$ with higher intensity, indicating that the magnetic fluctuation arises from a temperature far above $T_{\rm N}$. Further investigation is

necessary to understand the magnetic behavior in the alloy.

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Fig. 1. (a)Inelastic scattering line profiles of 2, 3, 5 meV obtained at 7 K . (b)Inelastic scattering line profiles of E = 2meV obtained at 7 K and 145 K.

Structure and phase transition in a lead-based inorganic-organic perovskites

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The structure and phase transition in the one-dimensional semiconductor C₅H₁₀NH₂PbI₃ has been investigated by using neutron and x-ray single crystal diffraction methods. C₅H₁₀NH₂PbI₃ has a lead-based inorganic-organic perovskites structure consisting of semiconducting parts which are composed of one-dimensional chains of face-sharing lead-iodide octahedra and barrier parts composed of $C_5H_{10}NH_2^+$ molecules. It has been shown by Raman scattering that the structure undergoes successive phase transitions below the room temperature which involves rotational/orientational ordering of the organic $C_5H_{10}NH_2^+$ parts However, its precise structure has [1]. not been determined even for the room temperature. The aim of the present study is to clarify the structural change and its effects on the electronic state in the phase transitions of C₅H₁₀NH₂PbI₃ by combining the data obtained by neutron and x-ray single crystal diffraction.

The neutron data were obtained at T2-2, FONDER at room temperature (R.T.), and analyzed by using program SHELXL with 199 unique reflections. In the refinement, positional parameters for Pb and I are fixed to the values previously obtained by x-ray structural analysis [2]. Positional information for nitrogen and hydrogen atoms which were not taken into account in the x-ray data analysis is obtained with R =0.09. The nitrogen atom in the $C_5H_{10}NH_2^+$ molecule tends to occupy C1 and C2 carbon sites, which are closer to the lead-iodide chain than the C3 site. The occupancies of nitrogen atoms at C1 and C2 sites are found to be 0.42 and 0.58, respectively. The hydrogen atoms are found as CH₂ groups with the distances of the hydrogen bonds being 0.8769 Å from C1, 1.0687Å from C2 and 1.1403Å from C3. Figure 1 shows the structure of the organic $C_5H_{10}NH_2^+$ part at R.T. obtained from the neutron data. In the figure, C3 site obtained from the x-ray data is shown together as C3' for a comparison. The structure of the molecule obtained by the neutron data clearly shows a chair form which has grater strain than that obtained by the x-ray data. It is expected that the twisting motion between the two identical chair conformers is present in the molecule and plays an important role in the phase transitions.

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Fig. 1. Structure of the organic $C_5H_{10}NH_2^+$ part obtained from neutron data. C3' site is positional data obtained from x-ray data.

Diffusion Path of Oxide Ions in a Fast-ion Conductor La0.64(Ti0.92Nb0.08)O3 with a Double Perovskite-type Structure

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Materials with high oxide-ion conductivities have received special attention in recent years owing to the potential applications of such materials in batteries and solid-oxide fuel cells. Information on the diffusion path and positional disorder of mobile oxide ions at high temperatures, where the materials work most efficiently, is indispensable for developing better oxide-ion conductors.

The lanthanum titanate solid solution La(2+-x)/3(Ti1-xMx)O3 (M = Al or Nb, 0.05<x<0.20) has an A-site deficient double perovskite-type structure and exhibits high oxide-ion conductivity at high temperature. Yoshioka [1] studied the electrical properties of La(2+-x)/3(Ti1-xNbx)O3 (x = 0.05-0.15) and reported that a sample with x = 0.10 displayed the highest ionic conductivity (10-2 S cm-1 at 700 C deg.) of the samples examined. In this study, we have examined the crystal structure and pathway of oxide-ion diffusion in A-site deficient layered double perovskite-type oxide, La0.64(Ti0.92Nb0.08)O3, at high temperature.

Neutron powder diffraction data for La0.64(Ti0.92Nb0.08)O3 were collected at 496 C deg., 1008 C deg. and 1358 C deg. using powder diffractometer HERMES with a furnace [2] to heat the sample. The sample temperature was maintained within +-1.5 C deg. during each measurement. Incident neutron wavelength was 0.18143 nm. The diffraction data were analyzed by the Rietveld method followed by application of MPF [3] using the computer programs RIETAN-2000 [4]. The MEM calculations were performed with the unit cell divided into 64 X 64 X 128 pixels. To reduce the bias imposed on the nuclear density by the simple structural model adopted in the Rietveld analyses, an iterative procedure called the REMEDY cycle was employed following MEM analyses.

All reflections in the neutron powder diffraction patterns for La0.64(Ti0.92Nb0.08)O3 at 496 C deg., 1008 C deg., and 1358 C deg. were indexed on the basis of a tetragonal P4/mmm cell. Refinements of anisotropic atomic displacement parameters (Uij) for cations resulted in no significant improvement in the reliability (R) factors. Therefore, Uij were refined only for oxygen sites in subsequent Rietveld refinements. The oxygen atoms located at 4i site displayed large anisotropy in the atomic displacement parameters, suggesting a directionality in the movements of oxide ions around the stable positions.

At 496 C deg., the O3 atoms are localized near the stable 4i site (1/2, 0.0,0.234). The O3 atoms display small bulges in the [101] direction which become larger at 1008 C deg. and 1358 C deg. The probability density of an O3 atom is connected with that of nearest-neighbor O3 atoms, indicating diffusion along a pathway following the [100] and [010] directions. The O3 atoms migrate to the nearest-neighbor 4i site through a triangle formed by adjacent La1, La2, and (Ti,Nb) atoms. At the intermediate points, the densities of the coherent-scattering lengths of oxide ions (4i site) are 0.13 fm ?^(-3) at 1358 C deg., 0.10 ?^(-3) at 1008 C deg., and 0.03 fm ?^(fm 3) at 496 C deg. Such an increase in the density of oxide ions with increasing temperature is consistent with the higher conduc-

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tivity at higher temperatures.

The O3 atom migrates following a curved route so as maintain a relatively constant distance from (Ti,Nb) atoms rather than a direct linear path. Yashima et al. [5] in their study of the nuclear density distribution of an ideal cubic perovskite-type compound (La0.8Sr0.2)(Ga0.8Mg0.15Co0.05)O2.8 found similar curved migration pathways.

The oxide-ion conductor with an ideal perovskite-type structure exhibits diffusion paths along the [100], [010] and [001] directions to form a three-dimensional network of equivalent diffusion pathways, as shown by Yashima et al. [5]. On the contrary, in the present double perovskitetype La0.64(Ti0.92Nb0.08)O3, a twodimensional diffusion pathways is present, by which O3 atoms migrate along the [100] and [010] directionsThis two-dimensional feature is attributable to the layered structure of the La0.64(Ti0.92Nb0.08)O3, which consists of La-occupied La1-O1, (Ti,Nb)-O, and La-deficient La2-O2 layers.

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Crystal Structure of Apatite-type La9.7(Si5.7Mg0.3)O26.3

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Solid materials with high oxide-ion diffusivity are of vital interest in materials science due to their potential applications of such materials in batteries and solid-oxide fuel cells. It is important to understand the ionic transport behavior of the solids and to relate their crystal structure to ionic conductivity in order to design and develop new oxide ion conductors. Lanthanum silicates La10-xSi6O26+d having apatite-type structure are one of the promising groups exhibiting significant oxide ion conductivity. Two kinds of conduction pathways, a direct linear path through the hexagonal [0,0,z] channel and a non-linear sinusoidallike path through interstitial oxide ion site have been proposed for the apatite-type structure [1]. But the understanding of the conduction mechanism in this structure remains subject to uncertainties. Here, we have investigated the crystal structure and diffusion pathway of oxide ions in apatitetype compound La9.70Si5.7Mg0.3O26.25 at 1558 C deg.

The neutron powder diffraction data were collected at 1558 C deg. on HER-MES installed at the JRR-3M reactor. Incident neutron beams with a fixed wavelength of 1.8265 were obtained by a vertically focusing (331) Ge monochromator. A furnace [2] with an MoSi2 heater was used to heat the sample and the sample temperature was maintained within +-1.5 C deg. during the measurement. The resulting diffraction data were analyzed by the Rietveld method with RIETAN-FP [3] and whole-pattern fitting approach based on the maximum-entropy method (MPF) [4]. The MEM calculation was done with the unit cell divided into 100 X 100 X 80 pixels and whole-pattern fitting using RIETAN-FP.

The Rietveld refinement was performed with neutron powder diffraction data of La9.7(Si5.7Mg0.3)O26.3 measured at 1558 C deg. on the basis of hexagonal P63/m. The calculated pattern agreed will with that of observed pattern. The refinement was carried out with anisotropic thermal displacement parameters for all the cations and anions. The thermal displacement parameters of oxygen O3 atoms showed strong anisotropic along the a-axis with large U11 value (0.00135(5) nm²) while that of O4 showed stronger anisotropic along the c-axis with larger U33 value (0.0044(3) nm²). The reliability values obtained from the refinement were Rwp = 2.96 %, Rp = 2.23 %, RI = 1.29 % RF = 0.73 % and S = 3.30. The Rietveld refinement suggested an interstitial oxygen atom site (O5) at the periphery of the c axis accompanied by a slight improved profile fitting results.

Crystal structure and the structural disorder of yttrium tantalate

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Yttria-tantalum oxide system has various phases such as defect-fluorite, webertite phase and cubic phase. Defect-fluorite type structure has high diffusion coefficient of oxide ions. On the other hand, the weberite-type structure exhibits lower diffusion coefficient. In this study, we prepare defect-fluorite-phase Y0.79Ta0.21O1.7 and investigate the crystal structure and positional disorder of oxide ions through MEM (Maximum Entropy Method) analysis of neutron powder diffraction data measured at RT and at high temperatures

Neutron powder diffraction experiments were carried out in air in the temperature range from 298 K to 1824(3) K. Neutron powder diffraction measurements were conducted in air with a 150-detector system, HERMES, installed at the JRR-3M reactor in Japan Atomic Energy Agency, Tokai, Japan. Neutrons with wavelength 0.18207 nm were obtained by the (311) reflection of a Ge monochromator. The experimental data were analyzed by a combination technique of Rietveld analysis, the maximum-entropy method (MEM), and the MEM-based pattern fitting.

Rietveld analysis was carried out assuming the ideal fluorite-type structure where the (Y,Ta) and O atoms were put at 4a 0,0,0 and at 8c 1/4,1/4,1/4 sites of Fm-3m symmetry, respectively. The isotropic atomic displacement parameters were used for all the atoms. At higher temperatures the B(O) was larger than the B(Y,Ta), suggesting a larger diffusion coefficient of oxide ions. MEM analysis was carried out using the structure factors obtained in the Rietveld analysis. Number of structure factors derived in the analysis was 11. The spatial distribution of oxide ions is larger at higher temperatures and it seems to have disordering along <100> directions, indicating the diffusion path. (Figures (a), (b) and (c)).



Fig. 1.

Dependence of thermodynamic stability and crystal structure on substisution and Li content of Lix(Mn,Ni,Co,M)O2 as a cathode active materila for Li secondary battery

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Many lithium-intercalated transition metal oxides have been studied as positive electrode materials in high energy density rechargeable batteries. In recent years, the layered-structured LiNixCo1-2xMnxO2 has been extensively studied as a candidate to replace the LiCoO2 cathode materials. But, it is not clear that relationship between thermodynamic stability, structure stability and cycle performance. We had been reported that the relationship between thermodynamic stability, structure stability and cathode performance of LiMn2-yMyO4 (M=Cr, Al, Mg, Co, Ni, Zn), LixMn1-yMyO2 (M=Mn, Al, Cu). In this study, LiNi1/3Co1/3Mn1/3O2, LiMn0.3Co0.3Ni0.3M0.1O2 (M=Al,Ti,Fe) LiMn1/3Co1/3-0.1Ni1/3Al0.1O2 and were prepared by the solid-state and solution reaction. We investigated the relationship between the thermodynamic stability, crystal structure, properties, and electrode performance depend on synthesis method, substitution and Li content.

The samples were prepared by two methods. The samples synthesized by solid-state reaction using each simple oxide as starting materials. Another samples synthesized by solution reaction using each metal acetate dissolved in distilled water and mixed with aqueous solution of citric acid. Li+ extraction from LiMni1/3Co1/3Ni1/3O2 were carried out 0.5mol ??dm-3 (NH4)2S2O8 solution by a batch method. Li content was controlled by immersing time. The heat of dissolution was measured by a twin-type multi-calorimeter. The enthalpy change per mole of atoms for the formation reaction, ??HR, were calculated from the heat of dissolution by applying Hess ??law. We considered a similar experiment about Li+ extraction samples. The crystal structure was determined by powder neutron diffraction using HERMES of IMR at the JRR-3M. The data were refined using the Rietan-2000. The nuclear densities determined by powder neutron diffraction and the electron densities determined by powder XRD were calculated by MEM using the PRIMA.

All samples were determined to single phase with a well-defined layer structure (R-3m, 166) by XRD. The intensity ratio of (003) and (104) peaks in the XRD patterns is greater than 1.2 and there is a clear splitting of the (006) and (102), (108) and (110) doublet peaks in the all compounds, which confirms there is little cation mixing in the layered structure. The lattice parameter, a, decrease and c increase with the decreasing Li content. LiMn1/3Co1/3Ni1/3O2, which obtained by solution reaction, was more high discharge capacity and good cycle ?? performance than that obtained by solidstate reaction. ??One of these factors controlled cycle performance, we investigated the thermodynamic and structure stability. From the crystal structure analysis, the cation mixing was little change with decreasing Li content. The bond lengths of Li-O increased and M-O {M=(Mn, Co, Ni)} decreased with decreasing Li content. From the results of electronic and crystal structure, the change of covalent bond and cation mixing were small by substitution. The chemical diffusion coefficient of Li+ was little change by each

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synthetic method. The enthalpy change per mole of atoms for formation reaction,

??HR, of LixMn1/3Co1/3Ni1/3O2 obtained by each synthetic method is linearly changed with Li content. It is thought that there is not structure changes (0.4 < x < 1.0), and it corresponds to the crystal structure analysis. From the results, the host structure is structurally and thermodynamically stable of the all amounts of Li con-??HR of the sample by tent. Moreover, solution reaction decreased compared to that of the sample by solid-state reac-??HR increased with decreasing Li tion. content and LixMn1/3Co1/3Ni1/3O2 and LixMn1/3Co1/3-0.1Ni1/3Al0.1O2, which obtained by solution reaction, was more thermodynamically stable than that obtained by solid-state reaction. It was suggested that these factors should provide an effective cycle performance.

Magnetic Structure of $Pr_xY_{1-x}Mn_6Sn_6$ Alloys

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Ternary YMn₆Sn₆ alloys have the hp13 type (MgFe₆Ge₆ type) layer structure. It should be noticed that Mn atom layers on 6i $(1/2, 0, z_2)$ and $(1/2, 0, -z_2)$ sites are well separated by Sn atom layers on 2c (1/3, 2/3, 0), 2d (1/3, 2/3, 1/2) and 2e $(0, 0, z_1)$ sites and Y atom layer on 1a (0, 0, 1/2) site. This alloy shows an inhomogeneous helical antiferromagnetism with the Néel temperature $T_N = 333$ K and the paramagnetic Curie temperature $\theta_P = 394$ K.

Recently, we have made magnetization measurements on YMn₆Sn₆ alloy, and obtained interesting results; the magnetization approaches saturation around 11 T at 77 K; the saturated magnetization corresponds to the magnetic moment of $2.0\mu_B$ /Mn atom.[1]

We have found that $Pr_x Y_{1-x} Mn_6 Sn_6$ ($0 \le x \le 0.4$) alloys have the hp13 type structure, and carried out neutron diffraction experiments using HERMES.

Figure 1 shows neutron diffraction pattern for $Pr_{0.1}Y_{0.9}Mn_6Sn_6$ alloy at 10 K. There are several magnetic reflections in addition to the nuclear Bragg reflections. These magnetic reflections are the satellite reflections of the nuclear ones with propagation vector $\boldsymbol{q} = (0, 0, \frac{1}{9})$ as indexed in Fig. 1. It is remarkable that there are only first order satellite reflections and there is no higher order satellite reflection.

We supposed the helical structure propagating along *c*-axis. The magnetic moments on Mn atom layers in *c*-planes at $z = z_2$ and $z = 1 - z_2$, $\mu_{Mn} (= 2.3 \ \mu_B)$, and on Nd atom layer in a *c*-plane at z = 1/2, $\mu_{Pr} (= 3.2 \ \mu_B)$, are ferromagnetic arrangement each other, where *z* is parallel to the *c*-axis in unit of the lattice constant *c*. In other words, a ferromagnetic slab is composed by in a set of these three magnetic layers, and lay in the *c*-plane. The direction of the magnetic moments change their orientation by an angle, θ , of 80° between the adjacent ferromagnetic slabs along the *c*-axis.

The Pr_{0.2}Y_{0.8}Mn₆Sn₆ alloy also show the helical structure with propagation vector $q = (0, 0, \frac{1}{6})$ and the angle $\theta = 60^{\circ}$.

The $Pr_{0.4}Y_{0.6}Mn_6Sn_6$ alloy shows a simple ferromagnetic arrangement. The direction of magnetic moment is perpendicular to *c*-axis.

It is likely that the magnetic moments μ_{Mn} and μ_{Pr} keep constant values of 2.3 μ_B / Mn atom and 3.2 μ_B / Pr atom respectively, and lay in the *c*-plane in whole composition (0 < *x* ≤ 0.4).

We have also carried out the magnetization measurements with an extraction method using a 18T-SM super conducting magnet up to 18 T at the High Field Laboratory of Tohoku University. The magnetic moments obtained from the saturated magnetizations, μ_S , linearly increase with increasing *x* in the whole composition $(0 < x \le 0.4)$ as expressed by a formula $\mu_S = 12.82 + 2.91 x$ (μ_B /f.u.); suggesting the magnetic moments of Mn and Pr atoms, μ_{Mn} and μ_{Pr} , are $\mu_{Mn} = 2.14 \mu_B$ /Mn atom and $\mu_{Pr} = 2.91 \mu_B$ /Pr atom. This result is consistent with the neutron data.

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Fig. 1. Neutron diffraction pattern for $Pr_{0.1}Y_{0.9}Mn_6Sn_6$ alloy obtained by using HERMES at 10 K.

Magnetic excitation spectrum in the frustrated magnet CuFe1-xAlx02

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CuFeO2 with delafossite crystal structure has been extensively studied as one of model materials of geometrically frustrated triangular lattice antiferromagnets (TLA). The magnetic properties in CuFe1-xAlxO2 are highly sensitive to nonmagnetic Al3+ impurity; quite small amount of nonmagnetic Al3+ impurity successively induces ferroelectric incommensurate (FEIC) state (0.014 < x < 0.030) and the oblique partially disordered (OPD) state (x > 0.030) from the 4-sublattice (4sub) ground state of CuFeO2 [1]. Such dramatic changes due to nonmagnetic Al3+ impurity can be found also in the significant difference between the magnetic excitation spectrums of 4sub and FEIC magnetic orderings; while higher energy (HE) branch is insensitive, lower energy (LE) branch is quite sensitive.[2,3]

The magnetic orderings in OPD phase is also very curious in the viewpoint of thermodynamics, because, even in the lowest temperature, the length of the magnetic moment is modulated owing to the thermal fluctuation. In present study, in order to investigate the magnetic excitation spectrum for OPD state, we have performed inelastic neutron scattering on the sample with x=0.05(344mg) using GPTAS (Kf=2.67[A-1], 40-80-PG-40-40) for high-energy region and HER (Ki=1.25[A-1], Open-Open-Be-80-80) for low-energy region at JRR-3M. Note that we have also measured TA phonons for both x=0.015 and x=0.05 samples so as to quantitatively compare the magnetic excitation spectrums for OPD with these obtained previously for FEIC states.

As shown in the inset of Fig.1, in the typical constant-Q scan for HE branch, spin wave spectrum of the x=0.05 sample can be seen as is for the x=0.015 sample, suggesting that the HE branch still remains for OPD state. On the other hand, as is clearly seen in the typical constant-delta E scan for the x=0.05 sample shown in Fig.1(b), welldefined four spin wave peaks seen in the x=0.015 sample disappears and only diffusive magnetic response can be seen in the low energy region where LE branch for the x=0.015 sample exists.

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Fig. 1. (a)Spin wave dispersion relation for FEIC state, inset :Typical constant-Q scan profiles for higher branch, (b) Typical constant-dE scan profiles for lower branch

Crystal Structure and Origin of Polarization of Hydrogen-Bonded Organic Ferroelectrics Composed of pi-Condugated Supramolecules

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Ferroelectrics have been motivated not only by basic science but also by application because of those various utilizations for electronics. Recently we have developed new ferroelectrics by using a molecular solid with supramolecular structure, the cocrystal of phenazine (Phz, C12H8N2) with chloranilic acid (H2ca, C6H2O4Cl2) or bromanilic acid (H2ba, C6H2O4Cl2), in which nonpolar pi-conjugated molecules are connected by the intermolecular O-H...N hydrogen bonds. Here, we report the low-temperature crystal structure of Phz-H2ca and Phz-H2ba [1] obtained by the neutron diffraction in order to make clear for the origin of polarization.

Figure 1a shows the crystal structure of ferroelectric phase of Phz-H2ba at 110 K obtained by a neutron crystal structure analysis. Lattice parameters, space group (P21), and atomic coordinates except for hydrogen atoms, agree with those obtained by the X-ray diffraction experiments. The O-H bond in the hydrogen-bonded site is clearly observed, suggesting that both molecules (Phz and H2ca or H2ba) are neutral even in the ferroelectric phase, which is consistent with the infrared spectra. The molecular structure of H2ba at paraelectric phase (300 K) and ferroelectric phase (110K) are shown in Figs. 1b and 1c. One can find a highly elongated thermal ellipsoid of one hydrogen atom in the low-temperature structure, which implies disordering of the hydrogen atom position. A similar situation is observed in the ferroelectric phase of Phz-H2ca.

Figure 1d is summarized interatomic distances between O-H (a, b) and N...H (c, d) and N...O (e, f) related with the hydrogen bonding in the paraeletric and ferroelectric phases of the Phz-H2ca and Phz-H2ba crystals obtained by the present neutron study. As can be seen from the asymmetric OH bond, the two hydrogen-bonded sites are not equivalent in the ferroelectric phase. This asymmetry in the hydrogenbond chain is the origin of the polarization in the Phz-H2xa (x=Cl, Br) system.

Appendix

Phz-H2ca 300K: C18H10Cl2N2O4, Z = 2, Monoclinic P21/n, a = 12.422(6) A, b =3.849(6) A, c = 16.981(12) A, beta= 107.83(4) deg., V = 772.9(14) A3, R = 0.0531 for 725 independent reflections (|Fo| > 4 sigma). Phz-H2ca 160K: C18H10Cl2N2O4, Z = 2, Monoclinic P21, a = 12.423(4) A, b = 3.788(8) A, c = 16.914(6) A, beta = 107.89(3) deg., V = 757.5(17) A3, R = 0.0488 for 919 independent reflections (|Fo| > 4 sigma). Phz-H2ba 300K: C18H10Br2N2O4, Z = 2, Monoclinic P21/n, a = 12.386(5) A, b = 3.908(5) A, c = 17.433(7) A, beta = 107.86(3) deg., V = 803.1(12) A3, R = 0.0460 for 685 independent reflections (|Fo| > 4 sigma). Phz-H2ba 110K: C18H10Br2N2O4, Z = 2, Monoclinic P21, a = 12.371(4) A, b = 3.845(3) A, c = 17.342(5) A, beta = 107.74(2), V = 785.8(7) A3, R = 0.0387 for 1314 independent reflections (|Fo| > 4 sigma).



Fig. 1. a-c) Crystal structure of Phen-H2ba at ferroelectric (a,c) and paraelectric (b) phase. d) Schematic structure of hydrogen-bond chain in Phz-H2xa and related bond lengths.

Investigation of drag reduction phenomena in a surfactant solution by a surfactant solution by neutron refrectometer

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It is known that turbulent frictional pressure drop of a liquid flow in a tube is reduced much by solving long-chain polymer or surfactant in the liquid after Thom's discovery in 1949. The effect is called drag reducing (DR) effect or Thom's effect. Recently it is used in intermediate heat exchanger systems for saving pump power. However, no standard physical model has not been established on this effect. Some models have been reported that the long chain polymers or rod-like micelles of the surfactant suppress the turbulence of the flow over the tube or near the wall of the tube.

This study is based on the model that the rod-like micelles suppress the turbulence of the flow near the wall. The neutron reflection rate measurement was conducted to investigate the micelle behavior near the inner surface of the wall made of monocrystal Silicon. The solution flew in a rectangular tube, 1 mm x 30 mm in cross section. Water solution of surfactant, Esogard, 4000 ppm in concentration with counter ions, salicylic acid, 50 in mole rate was tested.

Preliminary experiments were carried out on the reflection rate measurement on the test section without liquid, with water, with the stagnant solution and with the flowing solution where the DR effect was observed. The results were compared with theoretical values by one-dimensional Schrodinger Equation. The measured reflection rate without liquid, i.e., with air, agreed well with the theoretical ones within the standard derivation. It was shown that the measurement was accurately conducted. The measured values with water were slightly smaller than the theoretical ones and were well predicted by the theoretical ones with surface roughness of about 3 nm. It was expected that the wettability of the solution and the Silicon wall caused the decrease of the reflection rate at their interface. Those with the stagnant solution were also smaller than the theoretical ones and were predicted well with the surface roughness of about 1.9 nm. The measured values with the flowing solution were apparently smaller than those with the stagnant solution. The difference of them was more than two times of the standard deviation. Assuming the surface roughness of 1.9 nm for the flowing solution, it was estimated that the concentration of the surfactant at the wall was about 5200 ppm, higher than the averaged concentration of 4000 ppm by 1200 ppm. It was expected that the molecular structures near the wall were different for the stagnant and the flowing solution and the difference might cause the DR effects. It can be shown that the reflection measurement was available for the investigation of the DR effect. More experiments were required to discuss physical models of the DR effect.

Successive Magnetic Transitions and H-T Phase Diagram of Kagome Staircase Compound Co3V2O8

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Co3V2O8 is an insulating system with Co2+ spins (fictitious spin S=1/2) arranged in a kagome staircase structure or in a buckled kagome plane. It is interesting to investigate the magnetic behavior of this twodimensional spin system at low temperature T, because it has the geometrical frustration inherent in its crystal structure. Another interesting view point of this system is their dielectric properties, because for the iso-structural system Ni3V2O8, the multiferroic behavior has been reported, that is, magnetic and ferroelectric transitions take simultaneously at a critical temperature.[1] Theoretically, the mechanisms of the multiferroic behavior are proposed to be expected in system with the transverse spiral order.[2] The magnetic structure of Co3V2O8 has also been investigated by neutron diffraction study. The detailed results and discussions are reported in ref. 3.

We have carried out the magnetization, specific-heat and dielectric measurements on single crystal samples Co3V2O8 in various magnetic fields along three crystallographic axes up to 5 T. Neutron measurements on a powder sample as well as a single crystal with magnetic field along c have been carried out down to 2 K. Neutron measurements on a single crystal were carried out at T1-1 (HQR), where the double axis condition was adopted. In zero magnetic field, the system exhibits three transitions at temperatures Tc1~11.2 K, Tc2~8.8 K and Tc3~ (6.0-7.0) K, where the last transition has the co-existence region of T due to its first order nature. No evidence for ferroelectric transitions has been observed in the measurements of the dielectric constant with the electric fields along three crystallographic axes, a, b and c.

On the basis of the results of the neu-

tron scattering study, detailed magnetic structures are proposed in zero magnetic field. The ordered moments have the sinusoidal nature with the modulation vector (0,delta,0) in the antiferromagnetic phases (Tc3<T<Tc1), and the single crystal data present clear evidence for the noncollinear nature of the magnetic structures in all magnetically ordered phases. The transverse spiral state does not exist in Co3V2O8, which is in a clear contrast with the case of the multiferroic Ni3V2O8. It is consistent with the fact that no evidence for the occurrence of the ferroelectric transition has been found in the dielectric data, that is, the difference between Co3V2O8 and Ni3V3O8 can be understood by the existing theories. Only small dielectric anomalies closely connected with the magnetic phase transitions have been found. We have constructed detailed field (H)temperature (T) phase diagrams for the fields parallel to the three crystallographic directions a, b and c as shown in the figure. The abbreviations P, ICAF, CAF and CF represent paramagnetic, incommensurateantiferromagnetic, commensurate- antiferromagnetic and commensurate- ferromagnetic phases, respectively. The delta value is estimated from the position of the 02delta 0 magnetic reflections. Solid symbols are the transition temperatures determined by the magnetization and specificheat data. The phase boundaries plotted by the open symbols are determined by the neutron scattering studies in the magnetic field H(//c). The dotted lines are drawn to connect the crosses defined as the inflexion points of the M-T curves, and may not correspond to the phase boundaries. In the Tregion below these inflexion points, the relatively large ferromagnetic component is induced by the applied magnetic field. The phases stabilized by the external field are very sensitive to the strength of the field. In the magnetic field H along c, the magnetically ordered phases with delta =1 and delta =2/3 have been found in the H-region of H > 1 T. The existence of various phases can be considered to be due to the geometrical frustration.

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Fig. 1. The H-T phase diagrams of Co3V2O8 for the magnetic fields H along (a)H//a, (b)H//b and (c)H//c.

Phonon Dispersion of Martensitic Material showing 2nd-order-like Transformation

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Martensitic Transformation is known to be typical first-order transformation. TiNi(Fe) alloy system, some of Ni atoms were replaced by Fe, has been studied for long time from fundamental point of view and application point of view. Alloy composition close to Ti50Ni47Fe3 was used for the studies of the martensitic transformation mechanism because of small hysteresis. Recently, high Fe composition alloy was reported that the alloy shows second-order-like transformation in resistivity measurements and calorimetric mea-The alloy Ti50Ni44Fe6 was surements. studied previously and reported that diffuse scattering appeared around 1/3 of (110) (incommensurate) at 200 K and approached to commensurate position with lowering temperature (180 K). Electrical resistivity showed minimum value at 209 K. Inelastic neutron scattering measurements were performed on this composition alloy and showed minimum phonon energy at 200 K. On the other hand, the alloy Ti50Ni42Fe8 studied in this experiment showed incommensurate transformation and does not show commensurate transformation on further cooling. This behavior may relate to the martensitic transformation and immediate study was required.

Ti50Ni42Fe8 alloy was grown by floating zone method. The single crystal sample was obtained by heat treatment at 1283K for 24 h and quenched. Electrical resistivity of this alloy shows minimum temperature at 179 K. Inelastic scattering experiments were performed at the triple-axis spectrometer 5G-PONTA. Initial energy of neutron was 14.7meV and collimators used were 40 '-40 '-sample-40 '-40 '. Measured phonon mode was [zz0]TA2 at various temperatures. Figure shows E-const measurements at q=(0.25, -0.25, 0) around (120) reflection at various temperatures. The phonon energy decreases with lowering temperature. Approaching to z=1/3 and above, phonon peaks became broader, that is, over-damping was occurred. It is not clear the reason of the over-damping. The precise analyses have been undertaken for obtaining relationship between the phonon and transformation behavior.



Fig. 1. Phonon Energy at q=(0.25, -0.25, 0) at various temperatures.
Dependence of ferroelectric performance and crystal structure on composition and heat treatment of (Bi,M)4(Ti,Si)3O12(M=La,Nd) ferroelectric oxide

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1. Bi rich (Bi,La)-Ti-Si-O Ferroelectric Material

The La-substituted (Bi4-xLax)Ti3O12 is an attractive lead-free material for ferroelectric random access memory (FeRAM) applications because of its relatively large remanent polarization and fatigue-free characteristics. The bulk materials of Bi3.25+xLa0.75Ti3O12(x=0, 0.15. 0.25)[BLT] and Bi4Si3O12 (BSO) at specific compositional ratio were prepared for ferroelectric materials and some of samples annealed under the vacuum or high oxygen partial pressure(Po2). We investigated the relationship between the physical properties, crystal structure and ferroelectric performance of the sample before and after various heat treatments and changing composition.

From the results, Pr increases with increasing BSO content, but Pr decreased with increasing Bi content. Moreover, Pr decreased and Ec increased by heat treatment in the most of samples. On the other hand, the dielectric constant (ε s) at Tc of BLT remarkably increased by adding BSO. From the crystal structure analysis, the bond length and the bond angles of Ti-O are changed. Consequently, the change of distortion in Ti-O6 octahedra will effect of the change of ferroelectric performance, such as Pr.

2. (Bi,Nd)-Ti-Si-O Ferroelectric Material

We synthesized the new ferroelectric bulk materials of Bi4Si3O12 (BSO) added Bi4xNdxTi3O12(x=0.75,0.85,1.0,1.2). We investigated the dependence of ferroelectric performance and crystal structure on content and heat treatment for Bi4Si3O12 added Bi4-xNdxTi3O12.

From the results, the remanent polarization (Pr) of Bi4-xNdxTi3O12 (x=0.75, 0.85, 1.2) samples increased by adding BSO. On the other hand, Pr of Bi4xNdxTi3O12(x=1.0) sample shows a maximum, but Pr decreased by adding BSO. Moreover, Pr decreased by heat treatment in the most of samples. The dielectric constant (ε s) at room temperature and Tc of BSO added Bi4-xNdxTi3O12 remarkably increased by adding BSO. Tc and ε s at Tc decreased and the dielectric loss (tan δ) at Tc remarkably decreased by heat treatment. From the results of neutron diffraction analysis, the bond length of Bi1(Nd)-O6 shows the maximum of BSO added Bi2.8Nd1.2Ti3O12, and it shows the minimum for BSO added Bi3NdTi3O12. The bond length of Bi1(Nd)-O6 increased with decreasing of Nd content, x, of BSO added Bi4-xNdxTi3O12(x<1.0). The total calculated spontaneous ferroelectric polarization(Ps) along a-axis shows a maximum at BSO added Bi3NdTi3O12. The similar tendency was obtained of no BSO addition sample. It was found that the Ps is related to the Pr. Moreover, the bond length of Bi1(Nd)-O6 changes by heat-treatment and it affects to Pr.

Magnetic excitations in La2-xCaxCoO4

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Layered transition metal oxides have attracted much attention due to their wide variety of magnetic, electrical and structural properties. In some of the doped transition metal compounds, there is a real space ordering due to the charge carriers in a certain carrier concentration, resulting in an orbital ordering (OO) and sometimes a charge ordering (CO). In a recent neutron scattering study, Zaliznyak et al. observed a checkerboard charge order of Co2+/Co3+ and Co2+ magnetic order in the half-doped cobaltate La1.5Sr0.5CoO4 [1]. From the analysis of the magnetic and charge order scattering, they concluded a checkerboard arrangement of Co2+ and non-magnetic Co3+ ions in the CoO2 plane. On the other hand, Y. Moritomo et al. reported the drastic change of effective moment μ eff in La2-xSrxCoO4(0.4<x<1.0), suggesting a spin-state transition of Co3+ ions from the high-spin to intermediate spin state[2]. Our purpose of this study is to clarify the exchange interaction between Co spins, spin and charge configurations of CoO2 plane and to observe the intermediate spin state.

Single crystal of La2-xCaxCoO4 ($0.3 \le x \le 0.8$) was grown by the TSFZ method. The sample volume was about 1.0 cc each and it was mounted in a cryostat with the b-axis vertical, allowing the wave vector transfers in the (h0l) reciprocal lattice plane. The crystal structure remains in the tetragonal phase (space group I4/mmm) even at the lowest temperature. However, to index the superlattice peaks it is convenient to choose a unit cell as twice as the primitive unit cell, corresponding to a space group F4/mmm. The neutron scattering experiments were carried out on the 3-axis spectrometer TOPAN (6G).

In order to clarify the exchange interac-

tion, we have performed the inelastic neutron experiments. Spin wave dispersion at Q=(h, 0, 3) are shown in Fig.1-(a). This spinwave is seen up to 16meV, in contrast to 50meV in La1.5Sr0.5NiO4. This indicates a much weaker exchange interaction in the cobaltates than that in nickelates. We have obtained the magnetic dispersion curves for the different Ca concentrations and its spin excitations are basically same. These results suggest that magnetic interaction is not changed by Ca substitutions. To solve this strange phenomena, we examined the hole-doping dependence of magnetic correlation in a wide carrier-doping range of 0.3 < x < 0.8.

Fig.1-(b) shows Ca dependence of magnetic correlation lengths. From the holedoping dependence, the in-plane correlation lengths of spin order are found to give a maximum at x=0.5 and spin ordered peaks exist in the entire x range. From the results, unchanged magnon dispersion can be understood as existing the long ranged magnetic order in a wide holedoping range.

Moreover, we discovered the Ca dependence of two types of magnetic peaks for a different Ca concentration. In the lower doping samples (x<0.5), we only observed the l=half-integer (type 1 stacking) patterns, while we observed the l=integer (type 2 stacking) patterns in higher doping samples(x>0.5). This result is consistent with the Larochelle 's result of perovskite manganites[3]. From this point of view, La2-xCaxCoO4 can be explained by the two-type of stackings and CE-type spin and charge configuration was clearly observed in this system.

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Fig. 1. (a) Ca dependence of magnon dispersion at Q=(h, 0, 3) and (b) Ca dependence of magnetic correlation lengths in La2-xCaxCoO4.

Preliminary experiments of D2O scattering for MIEZE spectrometer with AGNES

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Mieze spectrometer is a modified version of NSE spectrometer, in which echo condition (cancellation of Larmor precession phase) is realized when the distance between the detector and the last p/2-flipper is adjusted and hence, contrast of NSE signal depends on the distance. Since the sensitivity on the distance is proportional to the energy resolution of the Mieze spectrometer, the thickness of the detector and the size of the sample should be small (less than a few millimeter) for high resolution. Since besides the other NSE spectrometer, no spin analyzer is required between the sample and the detector in Mieze spectrometer, new types of experiments such as inelastic or quasi-elastic scattering with neutron spin flip is measurable with Mieze.

We intend to construct Mieze spectrometer as one of the three NSE spectrometers. In order to reduce the sensitivity on the detector position, the energy resolution of the Mieze spectrometer is confined to that of the conventional inelastic scattering spectrometers. The advantage of the Mieze comparing to the inelastic scattering spectrometer is the compactness of its size and the beam intensity at the sample position.

In order to check the properties of Mieze, it is important to measure standard samples and compare the measured data to that of some conventional spectrometer. For this purpose, we measured the inelastic scattering of D2O (as the standard sample) using the inelastic scattering spectrometr AGNES (as reference spectrometr).

D2O is contained in a Al-cell and the measurements were performed at various temperatures under normal pressure. An example of the results for the temperature of 4 degree is shown in Fig.1. Coherent scattering in the low Q region is obviously observed. Scattering intensity in high Q region (over 1.5 Å⁻¹) is much reduced when

the sample temperature rises. Due to the improvement of AGNES spectromter, S/N-ratio is much improved especially when the count rate is low. These data will be used for calibration of Mieze spectrometer.



Fig. 1. The result of neutron inelastic scatterin from D2O at 4 degree.

The Ordering Structure of Water Molecules in The Superconductor NaxCoO2.yD2O and The Magnetic Excitation in Na0.5CoO2

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Na0.3CoO2.1.3H2O exhibits the superconducting transition at 4.5 K[1]. Because strong magnetic fluctuation expected for correlated electrons on the 2-dimensional triangular lattice may play an important role in realizing superconductivity, the hydrated Co oxide, which may have such electrons have attracted much interest. We are also intersted in roles of the water intercalation in realizing the superconductivity of this system.

In the present work, two kind of neutron scattering studies have been carried out on aligned single crystals of Na0.5CoO2 and NaxCoO2.yD2O. First, we have investigated the intensity of magnetic excitation in Na0.5CoO2 which exhibits the magnetic transition at 87 K to compare to that in superconductor. Second, we have investigated the D2O ordering pattern in NaxCoO2.yD2O. This crystal contains superconducting phase (bilayer system, y~1.3) and non-superconducting phase (non-deuterated system). The volume fractions of these systems were estimated to be 80% and 20%..

Neutron measurements were carried out using the spectrometer 5G with the tripleaxis condition installed at JRR-3 in Tokai. The aligned crystals of Na0.5CoO2 were used with the [100] and [001] axes in the scattering plane. The crystal of Nax-CoO2.yD2O was used with the [100] and [001] axes and [110] and [001] axes in the scattering plane.

In Na0.5CoO2, we carried out inelastic scattering along (h, 0, 3) and (1/2, 0, 1) at 90 K for some transfer energies (E) between 2.5 and 15 meV. As the result, we observed peaks at Q = (1/2, 0, 3) which is the magnetic Bragg position. The E-dependence of spectral weight kai" (Q, E) shows that these peaks are due to the magnetic fluc-

tuation. In the neutron inelastic scattering on aligned crystals of NaxCoO2.yD2O with half of the molar number of Na0.5CoO2, no evidence has been found in the search for the ferromagnetic fluctuations in the superconducting phase [2]. These results indicate that magnetic fluctuations in Nax-CoO2.yD2O are rather weak, if they exist. It can be said especially for ferromagnetic fluctuations and is consistent with the results of the NMR Knight shift reported by the present authors ' group[3, 4]. In NaxCoO2.yD2O, in the elastic scans along (1/2, 0, 1), (3/2, 0, 1) and (1/2, 1/2, 1) at room temperature, we have observed a significant diffuse scattering contribution, which has an intensity modulation with a periodicity of c* of the bilayer system. The ordering is short-ranged along the c direction, while the in-plane correlation of D2O or the correlation length within a layer is almost infinite (at least more than 300 A), judging from the widths of the 1/21/20reflection in the scan along (h, h, 0). Analyzing these data, we can find that scatterings originate from the intercalated D2O molecules. The ordering pattern is basically similar to the model proposed by Argyriou et al.[5]. Recently, it is shown that the transition temperature (Tc) changes with time for about 1000 hours after sample preparation by Barnes et al.[6]. We think that it is important to study the relationship between details of the D2O ordering pattern and Tc to clarify possible roles of the water intercalation in realizing the superconductivity of this system.

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Phonon Measurements on Protonic Conductor $K_3H(SeO_4)_2$

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K₃H(SeO₄)₂ undergoes first-order phase transition at 390 K (T_C). The crystal shows remarkable high protonic conductivity in the high-temperature phase (phase I), and ferroelastic in the room-temperature phase (phase II). The crystal belongs to the rhombohedral system with the space group $R\bar{3}m$ in the phase I, and monoclinic system with the space group C2/c in the phase II. Super lattice reflections expressed as (h k/2 l) are observed in the phase II, that is, the crystal structure in the phase II is super structure of phase I. It suggest that the phase transition may be caused by a zone boundary mode with $\mathbf{k} = \frac{1}{2}\mathbf{g}_2$, and the phase transition is improper ferroelastic type.[1]

Inelastic neutron scattering (INS) measurement was carried out using a high energy resolution triple-axis spectrometer (C1-1 HER) installed at JRR-3M reactor, Japan Atomic Energy Agency, Tokai, Japan. Incident energy E_i was fixed at 5 meV. The measurement was performed from (0 2 0) to (0.5 2 0) zone with the energy transfer range form -10.0 meV to -0.4 meV.

Figure 1(a) shows INS spectra at vicinity of Γ -point, (0.1 2 0), obtained at 413 K and 388 K. A large peaks correspond to transversal acoustic (TA) mode were observed at -1.6 meV. As sown in the figure, no abnormally accompanied by the phase transition was found on the TA-mode. The result is consistent with the nature that the phase transition is improper ferroelastic type. Figure 1(b) exhibits INS spectra at L-point, (0.5 2 0), obtained at 413 K, 388 K and 363 K. Diffuse scatterings are observed around 0 meV in the phse I and near the phase transition temperature $T_{\rm C}$. It is considered that the spectra are caused by a over-dumped phonon or structural fluctuations of local structure. In order to make clear the phase transition mechanism and proton conduction mechanism, further detailed measurements of the zone-boundary mode are needed.

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Fig. 1. Inelastic neutron scattering spectra of $K_3H(SeO_4)_2$ obtained at: (a) vicinity of Γ -point (0.1 2 0), (b) L-point, (0.5 2 0).

Activity Report on Neutron Scattering Research: Experimental Reports **14** (2007) Report Number: 170

Powder Neutron Diffraction of Ta- and Al-doped Zn2TiO4

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When the tantalum ions are partly substituted in stead of titanium ions in Zn2TiO4 accompanied by the deficiency of zinc, Zn2-x/2Ti1-xTaxO4, oxide ion conduction appears at elevated temperatures [1,2]. From the powder density measurements and TOF neutron diffraction, this type of substitution was found to form the cation vacancies at the octahedral site of the inverse-spinel structure, contributing to the oxide ion conduction [3].

Recently, it was found that in addition to tantalum, aluminum substitution which reduces the cation deficiency also forms the solid solution, and any obvious enhancement of oxide ion conduction was not observed when equimolar tantalum and aluminum ions are substituted [4]. However, structural investigation of both Ta- and Aldoped Zn2TiO4 was not made and even the position of aluminum was uncertain. In the present study, neutron diffraction experiments were carried out on x = 0.15 of Zn2-x/2Ti1-xTaxO4 (ZTT) and Zn2Ti1-2xTaxAlxO4 (ZTTA) up to 500 K to clarify the conduction mechanism.

Samples of ZTT and ZTTA were prepared by conventional solid-state reaction method started from ZnO, TiO2, Ta2O5 and Al2O3. The calcining and sintering temperatures were selected as 1000 and 1200 °C, respectively. About each 10 g of the crushed samples were charged in vanadium cells, which were mounted in the high-temperature CTI. Neutron diffraction experiments were carried out 300, 400 and 500 K on the multi-counter type diffractometer HERMES installed in the JRR-3M reactor of JAEA [5]. The wavelength of the neutron beam was 1.8265 A. Structure refinement was performed using Rietveld refinement program RIETAN-2000 [6].

The refined structure of ZTT at room temperature essentially agrees with that of previous one obtained by TOF neutron diffraction; the tantalum substitution and vacancy formation were made at octahedral site of the inverse-spinel type structure. On heating, any apparent structural change, e.g. symmetry or occupancy of each site, was not detected. The diffraction data of ZTTA can be also refined with relatively worse Rwp values, although additional diffraction peaks caused by ZnO were detected. Multi-phase analysis suggested the amount of ZnO was estimated as about 5 % in weight. While the tetrahedral site was occupied only by zinc ions, octahedral one was by zinc, tantalum and aluminum ions. When the Rietveld fitting was carried out assuming all the cations were stuffed and allowing the occupation factor of oxide ion to vary, the deduced occupancy of oxide ion was g(O) = 1.015(12). This indicated that, although small amount of vacancy might be introduced in the cation site, any significant deficiency was not supposed to be occurred.

The lattice parameters, interatomic distances between cation-oxide ions, and isotropic temperature factors of oxide ions were plotted versus temperature in Fig. 1, all of which essentially grew larger with temperature. While the tetrahedral cation-oxide ion lengths show similar values (Fig. 1(b)), octahedral ones represent some discrepancy (Fig. 1(c)). This is consistent with the result of the cation distribution that tetrahedral site was occupied by Zn without deficiency in both systems whereas the octahedral position contains different species between these two systems. While isotropic temperature factors become larger with temperature in both systems, ZTTA shows apparent enhancement at 500 K comparing with ZTTA. This

Activity Report on Neutron Scattering Research: Experimental Reports **14** (2007) Report Number: 175 also consistent with the fact that cation deficient ZTT shows oxide ion conduction at elevated temperatures while stuffed ZTTA was not. High temperature experiment was expected to show more apparent behavior. In addition, further precise investigation would reveal the oxide ion motion and oxide ion conduction mechanism of ZTT.

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Fig. 1. Temperature dependence of (a) lattice parameters, (b) tetrahedral cation-oxide ions and (c) octahedral cation-oxide ion interatomic distances and (d) isotropic temperature factors of oxide ions. \bigcirc : ZTT and \bigcirc : ZTTA.

Phonon Dispersions in Hexagonal BaTiO3

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Hexagonal BaTiO3 is one of the two polymorphic forms of BaTiO3: the other is the well known perovskite type (cubic BaTiO3). Hexagonal-BaTiO3 undergoes a structural phase transition from the hexagonal phase (space group P63/mmc) to the orthorhombic phase (C2221) at T0 = 222 K . This phase transition is believed to be caused by freezing of a soft E2u silent mode at the zone center. Below T0, the E2u mode becomes two Raman-active soft optical mode, Omega1 and Omega2. With further decreasing temperature, it undergoes a ferroelectric phase transition related to a c66 soft acoustic mode at TC = 74 K.

We have studied in order to clarify the mechanism of the phase transitions in hexagonal BaTiO3 and difference in physical property between hexagonaland cubic-BaTiO3. As the first step, we performed inelastic neutron scattering experiments on the hexagonal BaTiO3 by using the triple-axis spectrometers (4G and T1-1) at JRR-3M in JAERI (Tokai). Single crystals were grown from the molten Ba-TiO3. A crystal with the dimensions of 5 \times 5 \times 6 mm was used for the neutron experiment. The data collections were carried out in the h0l and hhl scattering planes. The measurements of phonon dispersion were performed along the lines 006-106, 006-116, where the indices are referred to the unit cell of the hexagonal phase, and so on.

Figure 1 shows the phonon dispersion curves at 300 K in the major symmetry directions M-K-Gamma-A. The E2u soft mode was clearly confirmed at about 3 meV around Gamma point and shows a weak softening as the temperature approaches T0 from above. It was difficult to observe the whole branches, because some parts of branches were so broad and weak. On the other hand, the presence of E2u soft mode has not been clearly confirmed in the major symmetry directions M-Gamma-A. The Bragg reflections at the position hhl: l=odd appeared at T0 and increased in intensity with decreasing temperature. Data analysis is now in progress.



Fig. 1. Phonon dispersion curves at 300 K in the major symmetry directions M-K-Gamma-A. Peak positions of the clearly observed peaks are plotted.

Structural change of a zirconia-scandia solid solution

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Zirconia-scandia solid solutions are some of the highest oxygen ion conductors in the zirconia-based materials. Here, we report the crystal structure and the nuclear density distribution of a zirconia-scandia solid solution using the high-temperature neutron powder diffraction data.

Neutron-diffraction measurements of a zirconia solid solution (Zr0.81Sc0.19O1.905) were performed in air with a 150-detector system, HER-MES, installed at the JRR-3M reactor in Japan Atomic Energy Association, Tokai, Japan. Neutrons with wavelength 0.18142 nm were obtained by the (311) reflection of a Ge monochromator. Diffraction data were collected in the 2 theta range from 5 deg to 150 deg in the step interval of 0.1 deg. A furnace with MoSi2 heaters [1] was placed on the sample table, and used for neutron-diffraction measurements from 267 to 495.3+-0.6 C deg. The diffraction data were analyzed by Rietveld method with a computer program RIETAN-2000.

neutron All the diffraction peaks of the zirconia solid solution (Zr0.81Sc0.19O1.905) sample measured from 267 to 495.3 C deg were indexed with a trigonal cell. Rietveld analysis was performed with the trigonal structure. Calculated profile agreed well with the observed data. Figure 1 shows the temperature dependence of (a) unit-cell parameter a, (b) cell parameter c and (d) unit-cell volume. The a increased with temperature. The c parameter did not change largely. The unit-cell volume of the trigonal phase increased with temperature.



Fig. 1.

Neutron Diffraction Analysis of Hydrogen-Bonding Networks of the Inosine 5'-Monophosphate Hydrate Stable in Medium Humidity Range II

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Disodium inosine 5'-monophosphate (Na₂IMP) hydrates undergo phase transitions depending on temperature and relative humidity conditions. We have carried out a series of neutron diffraction analyses [1], and clarified reconstruction of hydrogen-bonding networks accompanied by the phase transitions. Besides, nuclear distributions of oxygen and hydrogen atoms indicated fluctuating figures of crystal water molecules which are hydrated to biomolecules. In the case of the heptahydrate, which is stable in the relative humidity range 40 - 60 %, there were uncertain sites of a part of sodium ions and water molecules [2]. Under such circumstances, we reinvestigated neutron diffraction analysis of the heptahydrate.

A crystal with approximate dimensions $11.4 \times 7.7 \times 1.4 \text{ mm}^3$ was sealed in a quartz tube. The crystal volume was about 2.5 times larger than that of the previous experiment. Data collection was carried out using a four-circle diffractometer, FONDER, at T2-2 of JRR-3 in JAERI (Tokai). With the neutron wavelength of 1.24 Å, 1563 unique reflections up to 0.76 Å resolution ($2\theta = 110^{\circ}$) were measured at room temperature. Two crystal settings were used due to the limitation of the diffractometer. There remained inconsistency in intensities of a few reflections after the absorption correction.

Initial difference Fourier maps were calculated based on non-hydrogen atoms of IMP molecule determined by X-ray analysis. In a series of full-matrix least squares refinement cycles fixing non-hydrogen atoms of IMP molecule followed by difference Fourier syntheses, sodium ions, O and H atom sites of water molecules were assigned and refined. Then the sites of IMP molecule and those of sodium ions and water molecules were refined alternatively. All hydrogen atoms of the IMP molecule and 13 hydrogen sites of seven crystal water were determined (Fig. 1). The R factor is 0.075 for 1385 observed reflections ($|F_o| > 4\sigma(F_o)$) at the present stage. The crystal structure is essentially the same to that of the previous study except the atomic displacement parameters of the uncertain sites of sodium ion (Na3) and water molecule (W7).

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Fig. 1. Crystal structure of $Na_2IMP.7H_2O$ viewed along the *a* axis.

Pr-site filling fraction in the filled skutterudite PrFe4Sb12 synthesized under high pressure

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The filled skutterudite compounds RT4X12 (R: rare earth or actinide, T: transition metal, X: pnictogen) crystallize in the bodycentered cubic space group Im-3, in which R ion is surrounded by a cage of 12 X ions. These compounds show a wide variety of thermal, magnetic and transport properties due to strong c-f mixing effects and a rattling motion of R ion resulting from the unique crystal structure. Among them, PrFe4Sb12 has been much interest because of the drastic effect of Pr-site filling fraction on the magnetic properties. On the physical properties of PrFe4Sb12 prepared under ambient pressure, three independent groups have reported different magnetic ground states below 5 K; ferromagnetic [1], antiferromagnetic [2], and ferrimagnetic ordering [3]. Moreover, different crystal-field (CF) level schemes are proposed; the triplet ground state with the singlet first excited state in ref. [2] and the triplet ground state with the non-Kramers doublet first excited state in ref. [3]. Such a disagreement may be partly ascribed to the filling fraction of Pr ions. In fact, the filling fractions of Pr ions were reported to be 73% and 87% in refs. [2] and [3], respectively. Recently we have succeeded in synthesizing the filled skutterudite PrFe4Sb12 under high pressure [4]. In this crystal, no magnetic transition has been confirmed down to 0.15 K. From the temperature dependence of magnetic susceptibility and specific heat, furthermore, the CF ground state is estimated as a singlet with first excited state of a triplet above 20 K. This singlet ground state differs completely from the triplet ground state proposed in refs. [2,3], but is the same as that in other Pr-based filled skutterudite compounds.

In order to clarify the origin of the big difference of magnetic properties between the crystals prepared under ambient pressure and high pressure, it is necessary to estimate the Pr-site filling fraction of the crystal synthesized under high pressure exactly. Therefore, we have performed the powder neutron diffraction experiments by using the multicounter diffractometer HERMES. Figure 1 shows the diffraction pattern at room temperature. From the Rietveld analysis using the software RIETAN-2000, the Pr-site filling fraction of the PrFe4Sb12 synthesized under high pressure has been estimated as 97% +- 2%.

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Fig. 1. Neutron powder diffraction pattern of PrFe4Sb12 at room temperature.

Crystal Structure Refinement of visible-light driven photocatalyst

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In recent years, photocatalytic materials that function under visible light have been studied extensively in an attempt to improve solar energy conversion and reduce the environmental impact of energy production. Overall water splitting using a heterogeneous photocatalyst is an attractive solution for the production of H2 as a clean and recyclable energy source. The overall water splitting reaction has already been well established in many wide gap oxide semiconductors in the early 1980s. These oxides absorb only the UV region photons. The response to visible light is, however, desired for photocatalytic water splitting from the view point of efficient solar energy conversion. In this study, we reported the crystal structure of yellow (Hf,Zr)V2O7 with V 3d electron.

The samples were prepared by a conventional solid state reaction. Starting materials were stoichiometric mixtures of HfO2, V2O5 and ZrO2 powders. The mixture was pressed into a pellet and heated in a platinum boat at 973 K for 4 h in air. The completion of the reaction and the phase purity of the samples were confirmed by powder X-ray diffraction methods. We performed neutron powder diffraction experiments on the Kinken powder diffractometer for high efficiency and high resolution measurements, HERMES with 0.18196 nm wavelength, of Institute for Materials Research(IMR), Tohoku University, installed at the JRR-3M reactor in Japan Atomic Energy Research Institute (JAERI), Tokai. The fine powder sample was sealed in a vanadium cylinder. Rietveld structure refinement was carried out with the program RI-ETAN2000.

Crystal structures of HfV2O7 were first reported by Turquat et al. They refined HfV2O7 on the basis of a cubic system with space group Pa-3 (a = 0.87530 nm) However, since these structures were deduced only from the electron and powder X-ray diffractions, the information on light elements, especially for oxygen atom, was quite poor. To investigate the substance Zr for Hf, the powder neutron diffraction data were collected from the single phase samples with x = 0.5.

The crystal structure of (Hf,Zr)V2O7 can be considered as related to the NaCl structure, with the (Hf,Zr)ZrO6 octahedron centered at the ideal Na site and the bridging oxygen of the V2O7 group at the ideal Na site and the bridging oxygen of the V2O7 group (O3V-O-VO3) at the Cl site. All of the diffraction peaks were well indexed on cubic system Pa-3(0.8742(1)nm). A good fitting profile were obtained with Rwp = 8.33 %.

Structure Determination of Ordered Perovskite-type Oxides, Ca2MTeO6 (M = Mn, Co) by Neutron Diffraction

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The B site of the perovskites can accommodate two kinds of metal ions. The general formula of such a system is given as A2B ' B "O6, while the B' and B" ions are either in an ordered or a disordered arrangement. Many researches including two kinds of magnetism ions, such as Sr2FeMoO6, have been carried out. However, there were few researches on high-oxidation cation of Te6+ in the B site. Ordered perovskitetype oxides, Ca2MTeO6 (M = Mn, Co), belonged to space group P21/n and were insulators at room temperature. However, their electronic conductivities tended large gradually with a rise of temperature. Ca2MnTeO6 and Ca2CoTeO6 showed antiferromagnetism, and their Neel temperatures were 10 K and 7 K, respectively. The effective magnetic moment of manganese ion was 5.8 _B while its valence was bivalence in Ca2MnTeO6.

Neutron diffraction measurements were performed above (50 K) and below (3 K) TN to determine the changes in the crystal and magnetic structures of Ca2MTeO6 (M = Mn, Co). Powder neutron diffraction patterns were recorded using the high efficiency and resolution powder diffractometer, HERMES, of Institute for Materials Research, Tohoku University, installed at the JRR-3M Reactor in JAEA (Tokai). The wavelength of a neutron incident is . The crystal and magnetic 1.82646(6) structures were analyzed using the Rietveld analysis program, RIETN2000. The neutron diffraction patterns of two samples at 50 K were well fitted with a space group P21/n (No. 14) by Rietveld analysis. The lattice parameter of Ca2MnTeO6 and Ca2CoTeO6 were determined to be a = 5.4917(3), b = 5.6678(3), c = 7.8371(5) , β =90.251(4), and a = 5.4448(2) , b = 5.5899(2) , c = 7.7196(3)

, β = 90.269(3), respectively. The lattice parameters became smaller with decrease of an ion radius in order of M = Mn, Co. At 3 K, some additional Bragg peaks were observed indicating the magnetic ordering for two samples. Fig. 1 shows the case of Ca2CoTeO6. These magnetic peaks could be indexed on the same crystallographic unit cell, the neutron diffraction patterns of Ca2CoTeO6 at 3 K were refined with a space group P-1 (No. 2). As a result, a direction of magnetic moment seems to turn to the direction deviated from c-axis. However, the refinement for Ca2MnTeO6 did not succeed.

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Fig. 1. Powder neutron diffraction patterns of Ca2CoTeO6 at (a) 3 K and (b) 50 K. Indices for magnetic reflections are based on crystallographic unit cell.

In situ experiment of magnetic scattering, dielectric constant and electric polarization of $ErMn_2O_5$ and $TmMn_2O_5$

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We have performed in situ experiment of neutron magnetic scattering, dielectric measurement and *D-E* hysteresis measurement of ErMn₂O₅ and TmMn₂O₅ at FONDER.

The system shows complicated magnetic and dielectric phase transitions due to a large magneto-electric coupling, and called as multiferroic system. Preveous works we have performed reveled that all of transition temperature of magnetic and electric properties are coincide each other. However, the experiments were performed at off-line, that is, dielectric measurements were performed at laboratory system so that the transition temperature are not so precisely consistent.

New measurement system was constructed on this work, and in situ measurements of magnetic scattering, dielectric constant and electric polarization are now available. We have performed such in situ measurements of ErMn₂O₅ and TmMn₂O₅. In addition, new cryostat introduced at FONDER gives 2.7K, far below we could achieve. Then new measurements at very low temperature were also performed. The results were somehow slightly controversial, and the interpretation of the 2D-ICM to 1D-ICM transition and 1D-ICM to CM transition temperature against the dielectric transition of ErMn₂O₅ must be changed. Further, we have newly found that the lowest phase, LT-1DICM phase, is long-range stable phase. This phase was considered that rapid quench treatment down to 8K could create as a shortrage ordering state. However, the experiment down to 2.7K revealed that long rage 1D-ICM with the propagation vector (1/2, $(0, q_z)$ is stable. Not only that this phase shows drastic decrease of electric dipole moment without anomaly of dielectric constant. The results of in situ experiment of ErMn_2O_5 are summarized in Figure. Magnetic propagation vector q_x and q_z , intensity of magnetic peak, electric polarization and dielectric constant are shown as a function of temperature near the transition temperature around 2D-ICM to 1D-ICM to CM phase, and around CM to LT-1DICM phase. These new evidence will give slightly different scenario we had, and the detail analyses is required.



Fig. 1. The results of in situ experiment of ErMn_2O_5 . Magnetic propagation vector q_x and q_z , intensity of magnetic peak, electric polarization and dielectric constant as a function of temperature.

Structure Analysis of P-type Icosahedral Zn-Mg-Ho Quasicrystal

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Since the first discovery of icosahedral quasicrystals (i-QCs) in 1984 [1], structure determination of these exotic materials remains a challenging problem. The p-Zn₇₅Mg₁₆Ho₉ belongs to a series of i-QCs known as p-Zn-Mg-R (R = rare earth elements) that was found in 2002 [2]. It is known that three large occupation domains (ODs, or atomic surfaces) in a unit cell characterize its six-dimensional (6D) structure by an x-ray diffraction study [3]. In addition, a triacontahedral cluster that is considered as an extended icosahedral cluster of Bergman type has been identified as one of the fundamental building units for the structure description [3]. Although, the 3D structure can be understood as an aperiodic arrangement of such triacontahedral clusters, its detailed atomic structure is still undetermined, since p-Zn₇₅Mg₁₆Ho₉ is a ternary alloy and the location of the lightest element, Mg, is not easy to determine by x-ray diffraction. In order to obtain complementary structural information to x-ray diffraction technique for determining a structure model of the p-Zn₇₅Mg₁₆Ho₉, we have performed a neutron scattering experiment on this i-QC.

The neutron four-circled diffractometer FONDER installed by Tohoku University at the beam line T2-2, JRR-3M in JAERI was used for the experiment. The neutron wave length of 1.24 Å(Ge 311 monochromator) was used. The volume of single crystal sample used was 66 mm³. The intensity data of selected strong 544 Bragg reflections ($2\theta < 150^{\circ}$) were measured and 324 reflections were observed at room temperature.

Using the present neutron diffraction data, together with the structural phases from a model by x-ray diffraction, nuclear densities in the 6D space have been reconstructed (figure 1). The reconstructed nuclear densities exhibit ODs in which contribution from Mg atoms is enhanced compared with the electron densities that were obtained by x-ray diffraction data [3]. In particular, an extra small OD, which was not recognized in the previous study, was found as indicated by the ellipse in Fig.1. Structure refinment based on a detaield structure model of p-Zn₇₅Mg₁₆Ho₉ is now under way.

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Fig. 1. 2D cut of the 6D nuclear densities containg a threefold axis in both external and internal directions.

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Phonon modes of beta-Na0.33V2O5

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Introduction

Vanadium bronze, beta-Na0.33V2O5, was recently found to undergo superconducting phase transition at 8K under 8Gpa by Yamaguchi, Ueda and Mori1). Since then, doped vanadium bronze, beta-AxV2O5 with A=Na, Ka, Sr, Cu, Ag etc. and x=0.2-0.6, have been identified as a group of n-type ceramic superconductors in a low temperature range under high pressure. These materials exhibit relatively high negative Seebeck coefficient, e.g., about 100microV/K at 380K for A=Cu and x=0.602). The unit cell of beta-AxV2O53) consists of three different 1D VOn (n=5 or 6) sublattices extended parallel to b-axis, namely, two leg ladders, two rows of corner shared VO6 octahedra and zigzag VO5 square pyramids, respectively. Doped cations sit at roomy interstitial sites situated adjacent to the zigzag VO5 square pyramids. Present neutron inelastic scattering measurment was aimed to elucidate phonon spectra, i.e., DOS and low energy modes related with the spin/charge ordering and structural instabilities which could have connections with 2kf-CDW, superconductivity as well as high Seebeck effect being observed for the doped vanadium bronzes , beta-AxV2O5.

Experimental Procedures

Beta-Na0.33V2O5 powder sample was prepared by the solid sate reaction method. Mixture of appropriate molar ratio of Na2V2O7, V2O3 and V2O5 powders was mixed in an agate mortar, then pelletized and fired at 650 celsius deg. for 12hrs in vacuum. Same pellets were pulverized , mixed and sintered at 650 celsius deg. for a couple of times. Neutron scattering experiment was carried out by the use of a cold neutron spectrometer JRR3M-AGNES at room temperature, 100K, and 10K. For comparison, room temperature run was carried out for the V2O5 reference powder sample. Neutron inelastic intensities observed by 328 He3 gas counters were added in an appropriate way then DOS curves were calculated. Pulsed cold neutron radiation with lambda=4.22 was utilized through out the experiment. Results

Figure 1 shows phonon-DOS spectra of V2O5, Ca0.26V2O5, and Na0.33V2O5 samples obtained from the anti-Stokes side, i.e., the neutron energy gain side of the inelastic scattering intensities. Phonon-DOS curves of V2O5 and Ca0.26V2O5 were obtained previously. Observed inelastic scattering intensities are mostly due to the vibration of vanadium atoms because of their very large incoherent scattering cross section, σ i=5.08 barn, relative to oxygen and calcium atoms. Discontinuity of DOS curves from 24meV to 36meV is due to the contamination of lambda/2 incident neutron beam. There are obvious differences in the three DOS curves in the range from 7 to 20meV. V2O5 sample shows a peak intensity at 9meV but the DOS curves of Ca0.26V2O5 and Na0.33V2O5 shows rather flat features. In Na0.33V2O5, some softening feature is seen at around 10meV relative to the calcium system.

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Fig. 1. Observed phonon density of states curves of V2O5, Ca0.26V2O5, and Na0.33V2O5.

Phonon Dispersions in the Thermo-electric Material of Bi0.88Sb0.12

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Bi0.88Sb0.12 is known as a thermoelectric material with a high cooling power under magnetic fields due to high mobility of electrons and holes [1] and from that it is also inferred that the heat conduction by phonons may be affected by the application of strong magnetic fields [2]. So in the present experiments we try to investigate this problem by measuring phonon dispersions without magnetic fields first.

Single crystals of Bi0.88Sb0.12 were obtained with the brigeman method and the mosaic width of the crystal used in the present experiments was good enough (about 0.1 deg.) for phonon measure- ments and the crystal was confirmed to be consisted mostly with a single grain. A triple axis neutron spectrometer of 4G was used with collimators of 40'-40'-40' and the single crystal sample was cooled to 77K by using a refrigerator. Bi0.88Sb0.12 is a disordered alloy with the trigonal symmetry (R m) containing two atoms in a unit cell which usually indexed as a hexagonal cell. Figure 1(a) shows acoustic branch of phonon dispersions measured along the trigonal axis (the c-direction in the hex. cell). Along with our data Smith's data of pure Bi measured at 75K were inserted to compare to our Sb added Bi data. Acoustic branches of Bi0.88Sb0.12 almost agree with that of Bi for longitudinal and transversal modes, however, for longitudinal scans a branch which appears below TA mode was observed, which is not identified at present. The branches along the c-direction suggest that the force constants along the c-planes are not much altered by the addition of Sb atoms .

Figure 1(b) shows acoustic branches measured along the a-axis, which appear above that of pure Bi. This suggests that the addition of Sb makes the bonding between atoms fasted in the c-plane. This is consistent with the improvements of the thermoelectric properties for directions in the cplane by the addition of Sb in Bi.

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Fig. 1. 1 (a) Phonon dispersions of Bi0.88Sb0.12 along the c-direction as a function of the wave vector q. The data of pure Bi [1] are shown. (b) Phonon dispersions of Bi0.88Sb0.12 along the a-axis.

In situ neutron diffraction study of formation and decomposition process in clathrate hydrate

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The neutron diffraction measurements were carried out on HERMES installed at JRR-3. A single-crystal sapphire cell was used as a high-pressure sample cell. The Bragg peaks of the sapphire cell were excluded by Cd Blade of HERMES.

Figure 1 (a) shows time resolved diffraction patterns of methane hydrate (MH). Each measurement was done for 14 min. Analysis was based on the previous crystal structure data [1, 2]. The temperature and pressure dependence of mass fraction was obtained as shown in Figure 1 (b).

The CH4 gas was gradually applied D2O ice until 6 MPa at 216 K as isothermal process. The diffraction peaks of MH were observed in this condition and the mass fraction of MH was 0.05. The pressure was kept at ca. 6 MPa for 18.5 hours. However, the mass fraction of MH did not change. We changed temperature from 216 K to 240 K and then the pressure increased to 6.7 MPa. The CH4 gas was applied until 7 MPa at 240 K. And the pressure was kept at ca. 7 Pa for 18.5 hours. The mass fraction of MH slightly increased to 0.07. Following, temperature increased to 260 K and the pressure changed to 7.5 MPa. The mass fraction of MH increased until 0.13.

Next, we released the pressure and decrease temperature. The mass fraction of MH decreased to 0.07. We repeated to change temperature in the same way although the pressure was only applied up to 6 MPa at a maximum. In this case, the mass fraction of MH increased until 0.1 at 240 K. Here, 0.13/7.5*6=0.104. Accordingly, it is clarified that the mass fraction of MH was proportional to the CH4 gas pressure. Finally, temperature was increased at 6 MPa as isobaric process. The D2O ice did not melt at 277 K. When temperature in-

creased to 282 K, the D2O ice melted and the Bragg peak of MH grew rapidly. There was no Bragg peak of D2O ice (Ih) at 282 K. However, when temperature decreased to 240 K, the Bragg peak of D2O ice appeared and the mass fraction of MH was 0.6. Accordingly, methane hydrate covered D2O ice and D2O water did not flow out. In addition, it is proposed that unreacted water remained because we used coarse-grained powder of D2O ice (<400 micrometer). As a result, it is clarified that the growth rate depends on the pressure of CH4 gas, although we considered that the growth rate didn't depend on the pressure under the sufficient pressure for the growth.

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Fig. 1.

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Structural analysis and Observation of Spin-Gap in Vanadium Oxide V₄O₉

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Among various binary systems, a number of binary vanadium oxides are reported. They have been searched for and extensively studied for a long time. However there remains one binary vanadium oxide whose crystal structue is not known yet. Obviously, its physical properties are not reported. That compound is V_4O_9 . Here, we present the crystal structure and physical properties of V_4O_9 .

 V_4O_9 is unstable at high temperature. Hence, it is impossible to obtaion single crystals. Using V₄O₉ powder samples we started structural analysis by means of transmission electron microscopy(TEM) and powder X-ray diffraction(XRD). And then, we determined lattice constants and positions of vanadium atoms. But it was difficult to identify the positions of oxygen atoms, since the diffraction intensity of oxygen atom is too weak in XRD. To get the information about oxygen positions, powder neutron diffraction measurements(ND) were carried out on the Kinken powder diffractometer for high effciency and high resolution measurements, HERMES (T1-3) at JRR-3M of JAERI in Tokai with wave length 1.82646(6) Å. In the result of the experiment, oxygen atomic position was improved. Furthermore, it was clarified that previous our estimation of the space group and the unit cell is wrong. Combined with TEM and ND, we reassingned the space group to Cmcm with a doubled unit cell. The precise structural analysis of V_4O_9 is now in progress.

Temperature dependence of magnetic susceptibility of V_4O_9 indicates spin-gap behavior. To elucidate details of spin-

gap nature, inelastic neutron scattering mesasuremets were carried out on the ISSP-PONTA triple axis spectrometer (5G) at JRR-3M of JAERI in Tokai. The obtained spin-gap energy is 8.3 meV (see Fig. 1) which is consistent with the χ measurement. Constant-Q scan at 2.3 K with a peak at Q=1.2 Å⁻¹ can be fitted by dimer model. From structural point of view , our V₄O₉ model can be regarded as an isolated dimer system. The result is reasonable with our V₄O₉ model.



Fig. 1. Neutron scattering profiles at Q=1.2 Å⁻¹ at several tempertures.

Phase transition mechanism of KTaO3 doped with Li by neutron quasi-elastic scatterings

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Quantum paraelectrics KTaO3 becomes a relaxor when Li ions are doped in K+ site. KTaO3:Li (KLT) is a new class of relaxor in which A-sites are occupied with two kinds of isovalent ions (K+ and Li+). Therefore, the structure is much simpler than that of widely investigated relaxors of Pb(B1,B2)O3 compounds, and could give a new approach to the general understanding of relaxor nature and its origin.

In this investigation, we performed neutron diffuse scattering experiments to confirm the appearance of polar nano-regions (PNR) in the temperature range which we have recently found using second harmonic generation microscopic observations and high-presision X-ray diffraction studies.

The results are still preliminary, nevertheless interesting for further investigations.

The neutron diffuse scattering distribution (DSD) of KLT-7% at 85K around the reciprocal point (110) is shown in Fig.1.

When we subtract the DSD at room temperature, we obtain the rod-like distribution stretching along [100] and [010] directions.

We also measured the temperature dependence of DS and found that it exhibits a sharp increase at Tc. This phenomenon indicates that DS of KLT-7% consists of the critical diffuse scattering (critical opalescence) and that originating from PNRs.



Fig. 1. Neutron diffuse scattering of KLT-7% around (110) reciprocal lattice point at 85K.

Colloidal Complexes obtained from Charged Diblock Copolymer and Oppositely Charged Surfactant

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During the past decade, there has been a widespread interest for the design and synthesis of polymer-based colloidal particles of high stability in aqueous solutions. Among these particles, colloidal complexes have emerged as a new type of microstructure with potential applications in drug delivery. The block copolymer is the key feature of the electrostatic self-assembly. The overall size and the stability of the colloid depend on the nature of the electrostatic charges, on the molecular weight, and on the flexibility of the chains.

We report on the formation colloidal complexes resulting from the electrostatic selfassembly of polyelectrolyte-neutral diblock copolymers and oppositely charged surfactant. In the diblock/surfactant system, the polyelectrolyte block is negatively charged poly(sodium acrylate) and the neutral block is poly(N-isopropylacrylamide). The copolymer is studied in aqueous solution in the presence of cationic surfactant dodecyltrimethylammonium bromide (DTAB). Using light and neutron scattering experiments, and fluorescence spectroscopy, the diblock copolymer associate with oppositely charged surfactant into colloidal complex that have core-shell microstracture. For surfactant/polymer charge ratio Z lower than a threshold (Zc ~ 0.4), the complexes are single DTAB micelle attached by few copolymers. Above the threshold, the formation of hierarchical core-shell structure takes place. The core of typical radius 15-17 nm is composed of densely packed surfactant micelles connected to polyelectrolyte blocks. The corona of the colloidal complex is constituted from poly(N-isopropylacrylamide). Typical hydrodynamic radius of the complex is around 30 nm. Due to the LCSTtype thermosensitive property of poly(N-

isopropylacrylamide) corona, the complexes form larger aggregates with the hydrodynamic sizes ~ 300 nm. We have also investigated the colloidal stability under the different degree of neutralization and the presence of salt.



Fig. 1. SANS profiles for 0.4wt% PNIPAM-b-PANa/DTAB in D2O at various temperature and schematic illustrations of complexes.

New-Type Phase Transition of Honeycomb Lattice System Li₂RuO₃

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Li₂RuO₃ has layers of the honeycomb lattice of edge-sharing RuO₆ octahedra with a LiO₆ octahedron at the corner of each hexagon of RuO₆. The Ru valence is +4 and the four electrons exist in the 4*d* t_{2g} orbits. Li atom layers are between the honeycomb layers. For this system, we have found a phase transition at temperature $T = T_c \sim$ 540 K.¹) With decreasing *T*, the electrical resistivity exhibits an anomalous increase at T_c , suggesting the "metal-to-insulator"-like transition, and the magnetic susceptibility also shows a sharp decrease.

To clarify the mechanism of the transition, powder neutron diffraction measurements were carried out at room temperature (RT) and 600 K using a high resolution powder diffractometer (HRPD) installed at JRR-3 of JAEA in Tokai, and Rietveld analyses were carried out using RIETAN-2000. Although the space group at RT was previously reported to be $C2/c^{2,3}$, several superlattice peaks which cannot be explained by C_2/c were observed. To reproduce these reflections, we adopt the space group $P2_1/m$. The result of the Rietveld fitting with $P2_1/m$ is rather well. As the possible space group at 600 K, we have adopted C2/m, the minimal non-isomorphic supergroup of $P2_1/m$, because this space group allows the secondorder transition at $T_{\rm c}$. (From the experimental data, it is not easy to definitely distinguish if it is the second-order one or the first-order one.)

At 600 K, Ru atoms form an almost ideal honeycomb structure. At RT, a significant reduction (by ~ 13 %) of the bond lengths was found between two of the six Ru-Ru pairs of the hexagon (figure (right panel)). To answer why such drastic changes take place, we consider the coupling of the lattice distortion with the formation of the molecular orbits of



Figure 1: The distortion pattern of Ru-honeycomb skeleton at RT (left) and the energy levels of the molecular orbits of Ru^{4+} - Ru^{4+} pairs (right) below T_c . The electrons in these levels are shown by the arrows presenting the spin directions.

the t_{2g} electrons of Ru⁴⁺-Ru⁴⁺ of edge sharing RuO₆ octahedra. The energy levels of the bonding and corresponding antibonding orbits are shown in the Figure 1(right), where we can see that the nonmagnetic electron configuration is realized below T_c .

Although transitions accompanied with the significant anomalies of the electrical resistivity and the magnetic susceptibility similar to those of the present system have been reported for La₄Ru₂O₁₀ with corner-sharing RuO₆ octahedra and for Tl₂Ru₂O₇ with a pyrochlore structure, their microscopic mechanisms are different from that presently proposed. Li₂RuO₃ with edge-sharing RuO₆ octahedra is considered to present, as far as we know, a new type of phase transitions associated with the structural distortion induced by the molecular-orbit formation of the *d* electron states.

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Magnetic Microstructure of $LaMnO_{3+\delta}$ Nanocrystals in Mesoporous Silica

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We have synthesized a perovskite-type manganite LaMnO_{3+ δ} (LMO) with an average size of 20 nm to study the characteristic electronic states in nanocrystals^{1,2}). The magnetization, susceptibility and neutron diffraction measurements have revealed that the ferromagnetism (FM) with $T_C =$ 260 K coexists with the antiferromagnetism (AFM) with $T_N = 90$ K. It is reasonable for us to assume that LMO nanocrystals of large AFM core with a short correlation length of \sim 5 nm were coated with a thin FM shell. We performed small-angle neutron scattering (SANS) measurements at SANS-J at JRR-3 so as to confirm the core-shell magnetic microstructure of the LMO nanocrystals.

We used an average wavelength ($\lambda = 0.4$ nm) with a relative wavelength spread $\Delta \lambda / \lambda \sim 10\%$ at sample to detector distances of 2.5 and 10 meter, respectively, to cover a magnitude of the wavevector transfer range 0.02 nm⁻¹ < q < 2 nm⁻¹. The measured intensities were normalized by the intensities of a standard aluminum sample. The magnetic SANS intensity I(q) was obtained by subtracting the nuclear scattering obtained at 300 K from the total SANS intensity obtained at 9 K with applied field of 1 T (Fig. 1).

We have found a definite ferromagnetic contribution in the magnetic SANS spectrum. A characteristic change in the slope of the scattering curve around $q = 0.1 \text{ nm}^{-1}$ is associated with the size of LMO nanocrystals, and the q^{-2} dependence in the q range $q < 0.1 \text{ nm}^{-1}$ is attributed to the effect of interparticle scattering. In the high q region, I(q)is generally expected to decrease according to a function of q^{-4} , which is well known as Porod's law, however, the magnetic SANS spectrum exhibits a $q^{-3.5}$ dependence in the

q range 0.1 nm⁻¹ < q < 1 nm⁻¹. Thus it is considered that the observed magnetic SANS spectrum in this q range originates from the intra-particle contributions and the q dependence of the magnetic SANS spectrum changes into q^{-4} in q > 1 nm⁻¹. Then the thickness of the FM shell is estimated to be less than 1 nm, which is consistent with our core-shell model. It is considered that the FM state occurs through the double exchange mechanism owing to the hole doping near the surface with the excessive oxygen. The hole-doped bulk LMO with a rhombohedral structure shows only ferromagnetism but no antiferromagnetism. Thus the rhombohedral AFM phase newly appeared is ascribed to the size effect.



Figure 1: Ferromagnetic SANS spectrum of LMO nanocrystals in mesoporous silica.

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原子炉:JRR-3 装置:SANS-J(C3-2) 分野:中性子散乱(構造)

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Crystal Structure Analysis of $LiGa_5O_8$ by Neutron Powder Diffraction

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Recently, many researchers have developed a type of glass-ceramic composites in which nanosize crystalline phase including Ni ions were frozen in the glass matrices. Transition metal-doped glasses are generally not applicable to gain media for laser and optical amplifiers, since nonradiative decay processes dominate the relaxation of the excited state in transition metals and the quantum efficiency is very low in glasses. However, transition metals can have sufficiently large quantum efficiency in single crystals, though it is very difficult to fabricate single crystal fibers. Glassceramics have the advantage of both crystalline and glass materials.

Nickel stably takes the divalent state in almost all the hosts and shows the broadband near-infrared emission from Ni^{2+} ions. It is expected that the Ni^{2+} ions occupy the octahedral site of spinel oxides in crystalline phases from the absorption and emission spectrum. Transparent Li₂O-Ga₂O₃-SiO₂ glassceramics embedding Ni-doped nanocrystals are very attractive as a host matrix for Nidoping¹⁾. If Ni²⁺ ions are incorporated into the LiGa₅O₈ nanocrystals in glasses, high potential glass-ceramics can be synthesized. In this study we performed neutron powder diffraction experiments in order to clarify the crystal structure of $LiGa_5O_8$.

The neutron diffraction experiments were carried out on the high resolution powder diffractometer HRPD ($\lambda = 0.18229 \text{ nm}$), using a powder sample synthesized by the conventional solid state reaction. The horizontal collimation was 12' - (monochromator) - 40' - (sample) - 6' - (detector). The crystal structure was determined by the Rietveld analysis using the program RIETAN-2000²).

Figure 1 shows the observed diffraction pattern (plus marks) and calculated intensity after Rietveld refinement (solid line) of LiGa₅O₈. The diffraction pattern was satisfactorily explained by the cubic type structure with a space group $P4_332$. This symmetry type structure has an octahedral 12*d* site like the octahedral 16*d* site in spinel oxides. Based on this result, next diffraction experiments for Ni: LiGa₅O₈ are under contemplation.

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Figure 1: The high resolution neutron powder diffraction pattern of $LiGa_5O_8$ at room temperature.



Neutron Diffraction Study on Successive Structural Phase Transitions of $TlCoCl_3$

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Successive structural phase transitions of TlCoCl₃ are studied through single-crystal neutron diffraction measurements. The measurements were performed with the tripleaxis spectrometer TAS-2. $TlCoCl_3$ is one of the KNiCl₃ family compounds.¹⁻³⁾ The KNiCl₃ family compounds are distorted from the CsNiCl₃-type structure (space group $P6_3/mmc$) through successive structural phase transitions. Each structural phase is labeled as I, II, III, IV or V, from the high temperatures. The CsNiCl₃-structure has a -NiCl₃- chain along the *c*-axis, and the chains form a triangular lattice on the c-plane. The lattice deformation of the KNiCl₃ family compounds is characterized by upward or downward shifts of the chains along the c-axis. The crystal symmetries of phase II, III and V structures of TlCoCl₃ were reported to be $P6_3/mmc$, $P6_3cm$ and Pbca, respectively⁴⁾. The chain shift along the *c*-axis of the $P6_3cm$ and Pbca structures was arranged in an upup-down and up-up-down-down manner in a unit cell, respectively. However, the phase IV structure was not determined.

Here we closely investigated q-scan profiles on the $(h \ h \ 2)$ line of TlCoCl₃ and found a small but definite peak at $(\frac{1}{6} \ \frac{1}{6} \ 2)$, which appeared only in phase IV (68 K< T <75 K). The representative profiles of $(h \ h \ 2)$ from h = 0.1 to h = 0.4 at 86.4 K (phase III), 71.7 K (phase IV) and 60.0 K (phase V) are shown in Fig.1(a). The temperature dependence of the height of $(\frac{1}{6} \ \frac{1}{6} \ 2)$ peak is shown in Fig. 1(b). The temperature dependence of $(\frac{1}{3} \ \frac{1}{3} \ 2)$ and $(\frac{1}{4} \ \frac{1}{4} \ 2)$ peaks that characterize phases III (75 K< T <165 K) and V (T <68 K), respectively, were also measured. As a result, we confirmed that the phase IV structure was characterized by the $(\frac{1}{6}, \frac{1}{6}, 2)$ peak. We proposed possible crystal structures of phase IV with $2\sqrt{3}a \times 2\sqrt{3}a \times c$ unit cells.



Figure 1: (a) Neutron diffraction intensities of TlCoCl₃ scanned parallel to $(h \ h \ 2)$ directions at T = 86.4 K (phase III), 71.7 K (phase IV) and 60.0 K (phase V) with deliberately shifted base lines. (b) Temperature dependence of $(\frac{1}{6} \ \frac{1}{6} \ 2)$ peak height.

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原子炉:JRR-3 装置:TAS-2(T2-4) 分野:中性子散乱(構造)

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Location of Deuterium Atoms in $BaSn_{0.5}In_{0.5}O_{2.75}$ by Neutron Powder Diffraction at 77-473 K

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Aliovalently-doped perovskite oxides often show significant proton conductivity in a humid atmosphere at high temperatures¹). While several computational approaches² have yielded consistent results with respect to the hydrogen site in these materials, none of the neutron diffraction studies³ had verified the results until our latest study⁴ revealed that the deuterium atoms in D₂O dissolved BaSn_{0.5}In_{0.5}O_{2.75} at 10 K are located at or very close to the 12*h* site of the perovskite structure (space group $Pm\bar{3}m$) with an O-D distance of 1.0 Å.

In the present study, we measure neutron diffraction patterns of $BaSn_{0.5}In_{0.5}O_{2.75}$ with and without dissolved D₂O at higher temperatures. The diffraction data, especially when analyzed by the maximum entropy method (MEM), might be able to visualize the diffusion paths of hydrogen atoms and/or dynamic disorder (momentary displacement) of other atoms associated with hydrogen diffusion.

The BaSn_{0.5}In_{0.5}O_{2.75} samples with and without dissolved D₂O were prepared by the same procedure as before.⁴⁾ The deuterium concentration in the "wet" sample was evaluated to be 0.21 D/Ba by thermogravimetry. The neutron powder diffraction data $(\lambda = 1.823 \text{ Å})$ of the samples were collected at 77 K, room temperature and 473 K using a high resolution powder diffractometer (HRPD). The data were analyzed by the maximum entropy method (MEM, program PRIMA) as well as the Rietveld method (program RIETAN-2000)^{5,6}.

Figure 1 shows the distribution of neutron scattering length density in the "wet" samples obtained by the final MEM analysis after the REMEDY cycle^{5,6)}. The distribution

attributable to deuterium atoms is almost independent of temperature and basically the same as that at 10 K⁴⁾, indicating that the deuterium atoms are located at or very close to the 12*h* site with an O-D distance of 1.0 Å at these temperatures. This is the first determination by neutron diffraction of hydrogen position in a proton-conducting oxide at elevated temperatures. On the other hand, we cannot find any features suggesting diffusion paths of deuterium atoms or disorder of other atoms in the scattering length density distributions.



Figure 1: Scattering length density distributions on the (100) plane of D_2O -dissolved $BaSn_{0.5}In_{0.5}O_{2.75}$ at (a) 77 K, (b) RT and (c) 473 K determined by the MEM analysis⁷).

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Observation of CO₂ Molecule in Clathrate Hydrate by Maximum Entropy Method

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Clathrate hydrates consist of two types of cages (called "large" and "small" cages) formed by water molecules and traps encaging gas molecules inside each cage. The aim of this study is the precise crystal structural analysis of CO_2 hydrate focused on the motion behaviors of the inclusion CO_2 gas molecule in the cages. The neutron diffraction patterns of CO_2 hydrate were measured by using a high resolution powder diffractometer (HRPD) in the temperature range from 10 K to 200 K. A neutron wavelength of 0.1823 nm was used and diffraction data were collected in the 2θ range from 20° to 165° with a stepangle of approximately 0.05° . The obtained diffraction patterns were analyzed by the Rietveld method using the program "RIETAN-2000^{"1)}. After the Rietveld analysis, the Maximum Entropy Method (MEM) analysis was carried out using the program "PRIMA"²).



Figure 1: Scattering length density map of CO_2 hydrate at 10 K.

Figure 1 shows the scattering length density map of CO_2 hydrate at 10 K analyzed using MEM. Two unit cells are shown in this figure. The small cage is located at the corner and center of the unit cell and the large cage is located at the faces of the unit cell. Carbon of the CO_2 molecule is observed in the small cage though oxygen is not observed. It is indicated that the CO_2 molecule spins freely around its carbon atom. This behavior is independent of temperature from 10 K to 200 K. Both carbon and oxygen, however, are observed in the large cage: oxygen is distributed around the carbon on the parallel plane to the hexagonal facet of the large cage. Figure 2 shows the temperature dependence of the scattering length density map of the large cage. Although the motion of CH_4 in the large cage of methane hydrate is drastically changes from 10 to 116 K³⁾, the motion of CO_2 in those of CO_2 hydrate is independent of temperature.



Figure 2: Temperature dependence of the scattering length density map of the large cage of CO_2 hydrate.

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Neutron Study Suggests Ferroelectric Ice in the Universe

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In the Galaxy, ice is one of the major solid components in low temperature environment. Ice grains have been identified by infrared spectra in interstellar molecular clouds and in gaseous clouds around low-temperature stars. Big icy planets have been discovered beyond our solar system. Huge ice mass exists on planets and moons, such as Neptune, Uranus, Pluto and Charon, in our solar system. Small bodies like Saturn's rings and comets are also composed of icy grains.



Figure 1: Ice XI with proton-ordered arrangement has small circles that show fully occupied protons. Since water molecules are aligned along c-axis (vertical direction), ice XI has ferroelectricity.

Below 200 MPa, crystalline ice becomes a structure, which named as ice I (one) or ice XI (eleven). Whether ice in the Universe exists as ice XI, is an attracted question, because ice XI is ferroelectric (Fig.1). Long-range electrostatic forces, caused by the ferroelectricity, might be an important factor for planet formation. Furthermore, the grains may play important roles in chemical evolution including the formation of prebiotic organic materials. However, in astronomical observations to identify an icy object, it is not clear whether ice XI exists or not on the surface. Features of the infrared spectrum of ice XI are unknown because of the difficulty in creating perfect ice XI in the laboratory.

We have studied the conditions required for the formation of ice XI. In 06' we measured diffraction profiles of ice with many kinds of dopants using a high resolution powder diffractometer (HRPD). We carefully created samples of ice that contained impurities, which assisted the ice XI conversion process a catalyst. The results indicate that ice with an ionized defect (OH⁻) transforms to an enough ice XI after several hundred hours. We studied an irradiated ice. The gamma- and UVirradiation also creates OH⁻. The detailed analysis is in progress.

Normal ice naturally has a small amount of the defect. Thus, without adding the impurity compound, it would take 10,000 years for normal ice to transform into ice XI. While this time scale is much longer than what can be measured in a laboratory, it is not too long in the astronomical time scale. Furthermore, cosmic rays assist the formation. Thus, we expect that ice XI exists in the Universe¹). We reported this research in the press and it was taken up by the mass media²). We hope that it would spur astronomers to find freeroelectric ice XI in the future.

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Analysis of Crystal LiMn₂O₄ Size in Composite Sample by Neutron Scattering

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Lithium metal transition compounds are promising materials for cathodes in lithiumion batteries. In this group of materials, LiMn_2O_4 is an attractive and important material because it is relatively cheaper and less toxic. We report the use of a neutron scattering experiment to analyze the anneal temperature effect on the crystalline size of composite LiMn₂O₄.

The sample was prepared by dry mixing of LiOH and MnO_2 then milled for 3 hours at frequency of 2 Hz to perform a ground product. After that, the mixture was heated at temperature 200°C for 16 hours. To analyze the anneal temperature effect on the crystalline size of LiMn₂O₄ in the composite samples, we divided the whole sample into three parts: sample A annealed at 400°C for 3 hours, sample B annealed at 500°C for 3 hours and sample C annealed at 800°C for 3 hours. Neutron scattering measurements at room temperature have been performed for samples A, B and C by HRPD. The data were collected in the 2θ range from 20° to 150° with step angle of 0.05° .

Figure 1 shows the neutron scattering intensity of powder LiMn_2O_4 composites for samples A, B and C. Rietveld analysis has been performed on the neutron scattering intensities of samples A, B and C using RIETAN-2000¹⁾. The crystal of LiMn_2O_4 is assumed to belong to cubic type structure with a space group $\text{Fd}3\text{m}^{2)}$. The full-width of half maximum of Bragg lines of LiMn_2O_4 in the samples A, B and C shows a tendency to decrease with increasing the annealing temperature. The average crystallite sizes of LiMn_2O_4 were calculated using Scherrer equation. The obtained average size of a crystal LiMn₂O₄ in the composite samples are about 5, 20 and 130 nm for samples A, B and C, respectively. In a former report of LiNiO₂, the temperature dependence of diffuse scattering intensity decreases drastically with increasing annealing temperature. The strong diffuse scattering intensity was related to the amount of starting material LiOH in the composite samples³. However, in the case of LiMn₂O₄, the diffuse scattering intensity does not change so much in samples A, B and C. The amount of starting material LiOH is very small even in sample A.



Figure 1: Neutron scattering intensities of powder $LiMn_2O_4$ composites at room temperature.

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Ferroelectric Phonon Mode in Relaxor $K_{1-x}Li_xTaO_3$

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Relaxor $K_{1-x}Li_xTaO_3$ (KLT) shows rich dielectric properties. The system is quantum paraelectric at x = 0. With substitution of a small amount of K⁺ ions with Li⁺ the system shows relaxor behavior, and then further substitution triggers ferroelectric transition. Although the relaxor behavior is expected to arise from the relaxational behavior of the off-center Li ions, the role of the zone-center transverse-optic ferroelectric (FE) mode is not well understood yet. Last year, we have studied the diffuse scattering and the FE mode in the relaxor KLT with x = 0.05 and found atomic displacements arising from the condensation of the FE mode superimposed on the uniform phase shift, same as the case of $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN), indicating the contribution of the ferroelectric mode.

We have performed neutron scattering experiments at the TAS-2 triple axis spectrometer to study the FE mode in the KLT (x = 0.10) sample which shows the ferroelectric transition at 110 K with an intent to confirm the phonon contribution to the dielectric behavior in KLT.

Dielectric measurements indicate the ferroelectric transition of the x = 0.10 sample at $T_c = 110$ K. This has been confirmed by the neutron scattering measurements showing that the nuclear Bragg peak width and intensity increase rapidly below 110 K, suggesting a transformation of the lattice into a lower symmetry due to the ferroelectric transition. However, the crystal structure probed by the neutron scattering with a tight collimation sequence, 15'-10'-20'-10', is cubic in average even below T_c , implying that only a small portion of the sample is ferroelectrically transformed.

The FE mode has been measured with the collimation sequence of 15'-80'-80'-open. Figure 1 shows the phonon the energy squared as a function of temperature for KLT x = 0.10 and 0.05. We have found that the x = 0.10 sample exhibits an additional phonon mode which hardens below T_c as shown by the open squares. We assign this as an FE mode originating from the ferroelectrically ordered region. Such hardening of the FE mode below T_c has been observed in the displacive ferroelectic materials such as PbTiO₃, and relaxors, PMN and Pb(Zn_{1/3}Nb_{2/3})O₃ (PZN).

We have detected the hardening of the FE mode below T_c in the relaxor KLT for the first time. Combined with similar results for the relaxors PMN and PZN, it is shown that the FE mode has an important role in the perovskite relaxors.



Figure 1: Squared phonon energy of the zone-center transverse optic phonon as a function of temperature for KLT10 % (open symbols) and KLT5 % (black circles).

原子炉:JRR-3 装置:TAS-2(T2-4) 分野:中性子散乱(構造)

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Assessment of Vanadium Alloys

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A sample holder is necessary for neutron powder diffraction measurements. Vanadium is usually used as the sample holder. Since the coherent scattering length of vanadium is not zero but a small negative value (-0.443 fm), Bragg peaks from the sample holder cannot be neglected in the future. In the Japan Proton Accelerator Research Complex (J-PARC) project, high-intensity neutron beams are going to be produced with MW-class high power pulsed proton beams. Therefore, it is important to develop materials for the sample holder. Recently, a metal with a positive coherent scattering length is mixed with vanadium and some new vanadium alloys are synthesized (V-Al, V-Cr, V-Fe and V-Ni alloys). It is necessary to check these vanadium alloys. Therefore, we investigated these vanadium alloys using a high resolution powder diffractometer (HRPD) at JRR-3.

Measured samples were V, V-Al, V-Cr, V-Fe, V-Ni and V-Nb alloys. For the control experiment, we prepared V, which is pure vana-

dium, and V-Nb alloy confirmed as a 'null alloy'. Here, 'null alloy' is an alloy whose coherent scattering length is zero. These samples were supplied by Taiyo Koko Co., Ltd. (Japan). We used bulk samples and typical sample dimensions were $23 \times 23 \times 5$ mm³. These samples are rotated during measurement. The 1st collimator before the Ge monochromator was opened because of high intensity. Each sample was measured for a day and data were collected over the 2θ range of 2.5–160° because of ascertaining the presence of impurity phase.

Neutron powder diffraction patterns are shown in Fig.1. Tick marks in the figure show the peak positions of vanadium. Some Bragg peaks are clearly observed for V. In powder diffraction patterns except V, there is no vanadium peak and no other Bragg peak. Accordingly, we confirmed that these vanadium alloys were 'null alloy'. Next, we should investigate workability for the sample holder.



Figure 1: Neutron powder diffraction patterns of vanadium alloys.

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1. Neutron Scattering 2) Magnetism

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Magnetic structure of single-crystalline RRhGe (R=Tb, Dy) compounds

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RTX (R: rare earths, T: transition metals, X: metalloids) compounds crystallize in the e-TiNiSi-type orthorhombic structure. The magnetic property is characterized as follows:

1. succesive magnetic transitions below Neel temperature.

2. multi-step metamagnetic transitions in the ordered state along the easy magnetization b-axis.

3. incommensurate magentic structure.

Recently, it has been revealed that RRhGe (R=Tb and Dy) compounds also possess successive magnetic transitions below the Neel temperature from magnetic and specific heat measurements.

The purpose of this study is to determine the magnetic structures of magnetically ordered phases for RRhGe (R=Tb and Dy) compounds.

Single-crystalline samples were grown by a Czhoralski method using a tetra-arc furnace in purified Ar atmosphere. The magnetic and specific heat measurements were performed by a SQUID magnetometer and a PPMS. The neutron diffraction measurements were performed at T1-1:HQR spectrometer installed at JRR-3M, JAEA.

Figure 1(a) shows the magnetization of DyRhGe compound as a function of temperature. It is found that antiferromagnetic ordering takes place at 22 K. The powder neutron diffraction patterns of DyRhGe compound at 3 K and 30 K are displayed in Fig. 1(b). The magnetic reflections are clearly observed at 14.6 and 26.8 deg at 3 K. Detailed analysis of the magnetic structure is now in progress.



Fig. 1. Magnetization as a function of temperature (a) and powder neutron diffraction patterns at 3 K and 30 K (b) for DyRhGe compound.

Critical behavior of S=1/2 triangular antiferromagnet Cs2CuBr4

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In Cs_2CuBr_4 , the magnetic Cu^{2+} -ions form the distorted triangular lattice within the bc-plane. For the isostructural compound Cs₂CuCl₄, the magnetic properties are described by a quasi-2D distorted triangular antiferromagnet with small Dzyaloshinsky-Moriya (DM) interaction between Cu²⁺-ions. Since Cs₂CuBr₄ has the same crystal structure, it is expected that the magnetic behavior of Cs₂CuBr₄ should be described by the same Hamiltonian obtained for Cs₂CuCl₄. Below the ordering temperature $T_{\rm N} = 1.45$ K, the magnetic structure is helical incommensurate structure with the ordering vector Q =(0,0.575,0) (Ono et al. 2003). The helical spin structure has the "chiral" degeneracy which comes from the direction of the spin rotation. It is predicted that the additional degeneracy lead the anomalous critical behavior which belong to the new n =2 and 3 chiral universality classes (Kawamura 1998). In order to check the critical behavior of Cs₂CuBr₄, we have performed the elastic neutron scattering experiments.

Single crystal of Cs₂CuBr₄ was grown by the slow evaporation method from the aqueous solution of CsBr and CuBr₂. Neutron elastic scattering was performed at HER triple axis spectrometer. A single crystal with ~ 0.4 cm³ was used for this measurement. The sample was cooled down to T = 0.7 K using the ³He refrigerator.

Figure 1 shows the temperature dependence of the magnetic Bragg peak intensity at Q = (0, 0.575, 0). The Néel temperature was determined as $T_N = 1.47$ K. The solid line is the result of least squares fit to a power law in the reduced temperature given as Intensity $\propto [(T_N - T)/T_N]^{2\beta}$ + Background. Since the magnetic Bragg scattering intensity is proportional to the square of the sublattice magnetization, we can roughly estimate critical exponent β by

using this power law. Obtained exponent, $\beta = 0.346 \pm 0.010$, agrees well with that of conventional n = 2 (XY) universality class, $\beta = 0.346$ (Guillou 1977). The value of β seems to deviate from the value which is predicted in the "chiral" universality scenario ($\beta = 0.253$ for n = 2 and 0.300 for n =3). This fact indicates that the chiral degeneracy should be lifted by DM interaction between Cu^{2+} -ions on the strongest bonds. Since the *a*-axis component (perpendicular to the *bc*-plane) of the D-vectors point to the same direction, the direction of the spin rotation within the triangular plane is determined uniquely. The value of the critical exponent β consequently demonstrates that the DM interaction plays a key role in determining the spin arrangement. At present, it is not clear the reason why no diffuse scattering was observed just above the transition temperature.



Fig. 1. Temperature variation of the magnetic Bragg peak intensity measured at Q = (0, 0.575, 0). Solid line is the result of a fit to a power law described in the text with $\beta = 0.346 \pm 0.010$ and with $T_{\rm N} = 1.47$ K.

Magnetism of S=1/2 Square-Lattice Antiferromagnets (CuX)LaNb2O7 (X=Cl, Br)

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Magnetic systems usually achieve longrange order of spins at low temperatures. However, completely different behaviors can be seen in low-dimensional antiferromagnetic (AFM) quantum spin systems. Due to quantum fluctuations, the systems may not order long range even at 0 K. A characteristic of the spin liquid ground state is an energy gap in the magnetic excitation spectrum. Among them, the S = 1/2frustrated square lattice AFM system is of special importance in the light of Anderson's resonating valence bond (RVB) concept to explain high-Tc superconductivity in doped cuprates [1].

We discovered that a double-layered Dion-Jacobson phase (CuCl)LaNb2O7 can be a very good candidate for the 2D quantum square lattice system. As shown in Fig. 1, the crystal structure is tetragonal (space group P4/mmm), where 2D Cu square lattices are well separated with each other by nonmagnetic double perovskite slabs. Our bulk susceptibility and zero-field inelastic neutron scattering experiments revealed that this system indeed provides a new class of two-dimensional (2D) Heisenberg spin systems that has a spin-singlet ground state with a finite energy gap of 2.3 meV [2, 3]. The magnetic susceptibility of (CuBr)LaNb2O7 is also prepared from topotactic ion-exchange reactions. In contrast to the spin-liquid behavior in the Cl sample, the Br sample shows an antiferromagnetic ordering at 32 K [4], despite nearly identical structural parameters. The neutron diffraction experiment demonstrated that the magnetic structure is described by a stripe ordering or a collinear ordering with a propagation vector of q = $(1/2 \ 0 \ 1/2)$. This observation implies that the next-nearest bond (J2) is dominant over nearest-neighbor bond (J1), as theoretically suggested for the square-lattice J1-J2 model. This is the 4th experimental example of the stripe ordering. Mixed ferromagnetic nearest-neighbor and antiferromagnetic next-nearest-neighbor interactions are of comparable strength (J1/kB= -35.6 K and J2/kB= 41.3 K), placing the system in a more frustrated region of the stripe (collinear) phase than ever reported.

In order to reveal the origin of the anomalous critical field, we have performed in 2005 and 2006 neutron scattering measurements on the copper chlorine system with fields up to 5 T, using the C1-1 spectrometer installed at the guide hall of JRR-3M and the 5 T superconducting magnet. The scattering intensity as a function of energy transfer shows that the 2.3 mode splits into three mode. This is the first direct experimental observation of the softening of the triplet excitation in this compound. The subsequent experiment at higher magnetic field performed on the DCS at the NCNR further supported this view.

We successfully obtained the solid-solution series between (CuCl)LaNb2O7 and (CuBr)LaNb2O7, (CuCl1-xBrx)LaNb2O7 (0 < x < 1), which allows us to investigate the phase diagram between the spin liquid state and collinear ordered state. Inelastic neutron scattering experiments on the 5%-Br substitute sample, i.e., CuCl0.95Br0.05)LaNb2O7 were carried out on the ISSP-PONTA triple-axis spectrometer installed at a 5G beam port of JRR-3M at the Japan Atomic Energy Research Institute. A powder sample of 12.6 g was put into an aluminum cylinder. Most of the data were collected using a fixed final energy Ef of 14.7 meV (kf = 2.67 Å-1) and a horizontal collimation of open-40'-

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S-80'-80' in combination with a pyrolytic graphite (PG) filter placed after the sample to eliminate higher-order beam contaminations. As shown in Fig. 1, the neutron diffraction evidences the long-range magnetic ordering of the collinear type. It means that 5% Br substitution for the Cl site is enough to induce the long range ordering. A similar impurity-induced antiferomagnetic order from the spin-singlet ground state has been observed in the 1D spin-Peierls system CuGeO3 and 1D spin-ladder system SrCu2O3, suggesting that this phenomena is a universal behavior, occurring not only for 1D but also 2D system.

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Fig. 1. Neutron diffraction patterns for (CuCl0.95Br0.05)LaNb2O7, suggesting the magnetic reflection at $(1/2 \ 0 \ 1/2)$ at low temperature below 8K.

Magnetic Structures of (MX)LaNb2O7 (M=Cu, Mn...; X=Cl, Br)

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In recent years, much attention has been given to low-dimensional antiferromagnetic (AFM) quantum spin systems that have a ground state with no long-range magnetic order and an energy gap in the magnetic excitation spectrum. Among them, the S = 1/2 frustrated square lattice AFM system (J1-J2 model) is of special importance in light of Anderson's resonating valence bond (RVB) concept to explain high-Tc superconductivity in doped layered cuprates. Low-temperature topotactic strategies such as intercalation/deintercalation offer effective routes for the design and construction of new twodimensional (2D) magnetic materials.

Topochemical ion exchange reaction has been employed to obtain a doublelayered Dion-Jacobson phase such as (CuCl)LaNb2O7 starting from a nonmagnetic mother compound RbLaNb2O7 [1-4]. As shown in Fig. 1 (a), the structure consists of magnetic [CuCl] planes having an S = 1/2 square lattice arrangement that are widely separated by nonmagnetic double perovskite slabs. Thus it can be a very good candidate for the 2D quantum square lattice system. In 2004, we performed inelastic neutron scattering experiments on (CuCl)LaNb2O7 using the ISSP-PONTA triple-axis spectrometer installed at a 5G beam port of JRR-3M at the Japan Atomic Energy Research Institute. It has been revealed that this system indeed provides a new class of two-dimensional (2D) Heisenberg spin systems that has a spin-singlet ground state with a finite energy gap of 2.3 meV [5, 6]. Quite recently, we prepared isostructural compound (CuBr)LaNb2O7 using a method similar to that to obtain (CuCl)LaNb2O7. In spite of the fact that the lattice parameters are almost the same,

the magnetic properties of the copper bromine system is completely different from the spin-liquid state observed in the copper chlorine system. In contrast to the spin-gapped behavior in the Cl sample, the magnetic susceptibility of the Br sample shows the gapless behavior with an antiferromagnetic ordering at 31 K. In order to reveal the magnetic structure, we demonstrate the powder neutron diffraction profiles measured at 3 K and 45 K. We found two magnetic peaks centered at 2 θ = 15 ° and 20 ° that can be indexed as (1/2 0 1/2) and (1/2 0 3/2), respectively, indicating the so-called collinear type (or stripe) ordering, where arrays of ferromagnetic chain along [100] align in an antiferromagnetic manner in the square lattice (see Fig. 1(a)). The collinear ordering is expected to occur when the magnitude of the next-nearest-neighbor exchange interaction is greater than that of the nearest-neighbor interaction. To date, only three examples have been reported to exhibit collinear ordering among S = 1/2 square lattice systems. Therefore, it would be interesting to examine the nature of the collinearly ordered state and to compare with the spin liquid state in the isostructural (CuCl)LaNb2O7. To further understand the nature of the unusual ground states observed in

the unusual ground states observed in (CuCl)LaNb2O7 and (CuBr)LaNb2O7, it would be quite interesting to compare these compounds with other related materials. Thus, in this study, we performed powder neutron diffraction experiments on the isostructural (MCl)LaNb2O7 (M=Co, Cr, Mn), using the IMR-HERMES diffractometer (T1-3). Neutrons with a wavelength of 1.81386(7) Å were obtained by the 331 reflection of the Ge monmochro-

mator, and the 12'-blank-sample-18' collimation was employed. A powder sample of 4 g was put into a vanadium cylinder. Figure 1(b) demonstrates the neutron diffraction profiles of (CoCl)LaNb2O7 obtained at 8 K and 100 K. The lower temperature data have additional magnetic reflections characterized by the propagation vector (pi, 0, pi), indicating the collinear type of magnetic ordering. The magnetic ordering temperature is obtained to be 55K by measuring the intensity of (1/2, 0, 1/2). The manganese analogue also exhibits the collinear order but at slightly higher temperature, while the neutron diffraction profile of the chromium analogue may indicate incommensurate magnetic structure at low temperatures.

This work has been supported by Grantsin-Aid for Young Scientists (A) (No. 17684018) and Science Research on Priority Area (No. 16076210) from MEXT of Japan, and by the 21st Century COE Program, Kyoto University Alliance for Chemistry.

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Fig. 1. (a) Crsytal and magnetic structure of (MX)LaNb2O7. (b) Neutron diffraction patterns for (CoCl)LaNb2O7 measured at 8 K and 100 K, demonstrating the collinear (pi, 0) type of magnetic long range ordering.

Magnetic ordering and excitations in the Zn-Fe-Sc-RE (RE: rare-earth) icosahedral quasicrystals

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Quasicrystals are characterized by sharp Bragg reflections with a point symmetry that is forbidden in a periodic lattice, such as the five-fold symmetry. For magnetic quasicrystals, non-trivial ordering of spins arranged on a quasiperiodic lattice may be expected in theory. Nevertheless the longrange order has not been observed yet in any magnetic quasicrystals, despite continuous efforts to find the magnetic longrange order made to date. The recently discovered Zn-Fe-Sc-RE (RE: rare-earth) quasicrystals has been expected to have the highest possibility to show magnetic long-range order, since it has highest magnetic ion concentration among magnetic quasicrystals reported to date. In addition, the combination of the 3d and 4f moments may provide longer inter-spin interactions, resulting in the likely situation for the longrange order. Here, we report first neutron scattering study on the new magnetic quasicrystals Zn-Fe-Sc-RE (RE =Ho and Tm). Experiments have been performed at the triple-axis spectrometer 4G-GPTAS with incident energy $E_i = 13.7$ meV. Data shown here were taken with a double-axis mode. A powder sample of Zn-Fe-Sc-RE was prepared by melting constituent elements and heat-treated in an appropriate manner.

Shown in Fig. 1 are powder diffraction patterns taken at the two temperatures T = 3.8 and 30 K. The difference between the two-temperature data sets is also shown by the blue triangles. As the nuclear Bragg reflections are clearly seen in the figure at both the temperatures, the temperature dependence shows very flat behavior, excluding possibility for appearance of the mag-

netic Bragg reflections at the lowest temperature. We also checked existence of the magnetic Bragg reflections in several samples with RE = Ho and Tm, with a few different RE concentration, however, all of them gives negative results. Further exploratory study on the magnetic quasicrystal with higher magnetic ion concentrations is in progress; neutron diffraction study on those materials is obviously necessary to detect definite long-range signal.



Fig. 1. Neutron powder diffraction patterns at T = 3.8 (red) and 30 K (green) obtained at ISSP-GPTAS. Temperature difference [I(3.8 K) - I(30 K)], as a magnetic scattering contribution, is also shown by the blue triangles.

Uniaxial pressure induced first-order phase transition in Pt₃Fe alloy

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The ordered Pt₃Fe alloy has an $L1_2(Cu_3Au)$ -type structure, in which the corner sites are occupied by Fe and the face center sites by Pt, respectively. Since Pt atoms carry no magnetic moments, Pt₃Fe alloy is considered to be a simple cubic antiferromagnet. Below the Néel temperature $(T_{\rm N} \sim 180$ K), Pt₃Fe alloy undergoes an AF-AF phase transition at $T_{\rm S}$ ($T_{\rm S} \sim 80$ K). At the high temperature phase, magnetic structure is a $(1/2 \ 1/2 \ 0)$ -type, but at the low temperature phase, the $(1/2 \ 0 \ 0)$ Bragg peak coexists with decreasing of the (1/2 1/2 0) Bragg peak intensity.

Among simple cubic antiferromagnetic structure, both $(1/2 \ 1/2 \ 0)$ -type and $(1/2 \ 1/2 \ 0)$ -type and (1/0 0)-type structure have ferromagnetic and antiferromagnetic nearest neighbor spin couplings, suggesting existence of spin frustration. Then, we can expect strong effect for the magnetism of Pt₃Fe alloy by an external perturbation field. To study the spin correlations in simple cubic antiferromagnet, we carried out the neutron scattering experiments on a single crystal specimen of Pt₃Fe alloy under uniaxial pressure. The uniaxial pressure was applied along the [0 0 1] axis using a hard coil spring, which destroys the cubic symmetry of the lattice. The measurements were performed at the T1-1 triple axis spectrometer, JRR-3M.

We first measured the temperature dependence of the $(1/2 \ 1/2 \ 0)$ Bragg peak intensity and obtained the results that the Néel temperature increases with increasing uniaxial pressure, indicating that the $(1/2 \ 1/2 \ 0)$ -type magnetic structure is stabilized by uniaxial pressure. Further, we observed that the phase transition at T_N under the high uniaxial pressure looks like of the first-order. In order to conform the first-order phase transition at T_N , the temperature dependence of the $(2 \ 0 \ 0)$ Bragg

peak intensity was carefully studied at the slightly off point (1.994 0 0). Results are given in Fig. 1 together with the data for free state. The data clearly shows the lattice expansion at T_N with decreasing temperature under the uniaxial pressure, indicating that the magnetic ordering accompanies with the lattice deformation, thus, the first-order phase transition. The lattice expansion at T_N is estimated to be 1.3×10^{-4} using the linear thermal expansion coefficient of Pt (8.9×10^{-6} at RT)



Fig. 1. Temperature dependence of the intensities studied at (1.994 0 0) Bragg peak position

Magnetic excitation in the Ni₄ magnetic cluster

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The molecular magnet $[Mo_{12}^VO_{30}(\mu_2 OH_{10}H_2\{Ni^{II}(H_2O)_3\}_4]\cdot 14H_2O$ (Ni₄) has four magnetic Ni^{2+} (S = 1) ions forming an isolated tetrahedral cluster. Earlier macroscopic experiment suggests dominant antiferromagnetic intracluster interactions between the Ni²⁺ spins, with negligible single-ion anisotropy [1]. Thus the Ni₄ was expected to be a good realization of Heisenberg antiferromagnet with strong geometrical frustration effect due to tetrahedral spin arrangement. Owing to the small S, small number of spins involved, and the geometrical frustration, strong quantum effects may be expected in the Ni₄ magnetic cluster.

Two grams of deuterated powder sample of Ni₄ was prepared following the prescription given in the earlier report [1]. The neutron inelastic scattering experiments were performed at the cold-neutron triple-axis spectrometer ISSP-HER installed at JRR-3, JAEA, Tokai. Superconducting magnetic was used to apply vertical magnetic field up to 5 T. The lowest attainable temperature was 1.5 K. A brand-new horizontally focusing analyzer was used with all seven blades operational, and a Be filter is placed in front of the sample to remove the higher order harmonics. Several final energies were used to collect the inelastic spectra depending on the contradicting necessity for the energy resolution and intensity; typically $E_{\rm f} = 4.5$ meV.

Figure 1 shows inelastic neutron scattering spectra at Q = 0.6 Å⁻¹ under the various magnetic fields. (Each spectrum is shifted by 400 counts to increase visibility.) In a zero filed spectrum, there is a peak at $\hbar\omega = 0.6$ meV appearing as a sholder of the huge elastic peak due to the incoherent scattering of the remaining hydrogen. Also seen is a peak at 1.3meV accompanied by a sholder peak at 1.6 meV. The magneic origin for these peaks was confirmed by measuring their temperature and Q dependence. Applying the magnetic field, the peak at 0.6 meV becomes broad, the peak at 1.3 meV shifts to the lower energy side, though the peak at 1.6 meV exhibits negligible change. These chagnes can hardly be explained consistently by the Zeeman effect.

We have also performed inelastic neutron scattering experiments using the DCS spectrometer at NIST Center for Neutron Research. Combining the all $S(Q, \hbar\omega)$ obtained at the two spectrometers, we are now working on the determination of the spin Hamiltonian in this system.

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Fig. 1. Inelastic spectra of Ni_4 under various magnetic field observed at ISSP-HER. See text for details.

Magnetic correlation and excitation in triangle and hexagonal magnetic molecules

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Single molecular magnets attract special attention recently, as they provide a new playground for studying isolated (or weakly coupled) quantum systems. Here, we have investigated four molecular magnets, V₃, Mn₆Sb, Mn₆As and Cu₆Sb using inelastic neutron scattering. These experiments are rather preliminary, as we look for systems of which spin Hamiltonian may be determined by inelastic neutron Chemical formulae of those scattering. systems are $K_{11}H[(VO)_3(SbW_9O_{33})_2]$ $27H_2O$ and $K_{12}[(VO)_3(BiW_9O_{33})_2] \cdot 29H_2O$, $\begin{array}{ll} [nBuND_3]_{12}[Mn_6Cl_6(SbW_9O_{33})_2] & & 6D_2O, \\ [nBuNH_3]_{12}[Mn_6Cl_6(AsW_9O_{33})_2] & & 6D_2O \end{array}$ $[nBuNH_3]_{12}[Cu_6Cl_6(AsW_9O_{33})_2]$ and $6D_2O$ respectively. V_3 forms a triangle cluster, whereas hexagonal cluster geometry was realized in the other systems. From the bulk magnetic susceptibility measurements, V₃ and Mn₆Sb were found to be anitferromagnetic, whereas physical properties of other systems have not been reported to date.

Powder samples of 0.71 g V₃, 0.34 g Mn₆Sb, 0.36 g Mn₆As, and 0.24 g Cu₆As were used in the neutron experiments. The neutron inelastic scattering experiments were performed at the cold-neutron tripleaxis spectrometer ISSP-HER installed at JRR-3, JAEA, Tokai. A brand-new horizontally focusing analyzer was used with all seven blades operational, and a Be filter is placed in front of the sample to remove the higher order harmonics. Several final energies were used to collect the inelastic spectra depending on the contradicting necessity for the energy resolution and intensity; typically $E_f = 3$ meV. The V₃ experiment was performed at 0.9 K using the 1 K refrigerator, whereas the other experiments were done at 4 K using the Orange cryostat.

Inelastic spectra from the four samples at

 $Q = 0.6 \text{ Å}^{-1}$ are shown in Fig. 1. Data acquisition durations for each point were 20 minutes in the V₃ experiment, 4 minutes in the Mn_6Sb , 6 minutes in Mn_6As , 8 minutes in Cu₆As, respectively. In the figure, the spectrum of V_3 is shifted by 800 counts, Mn₆Sb by 800 and Mn₆As by 400. In the V_3 spectra there appears a peak at $\hbar\omega = 0.8 \text{ meV}$ at the lowest temperature. It is found that the peak intensity decreases as *Q* becomes large, and that it disappears at the high temperature T = 30 K. These results indicate that this peak has a magnetic origin. There also appears an slight shoulder at $\hbar \omega = 0.4$ meV, although it is difficult to conclude due to insufficient statistics. For Mn₆Sb, we only observed a symmetric peak around the elastic position, and thus it most likely originates incoherent elastic scattering of hydrogen or a nuclear bragg peak. The spectrum of Mn₆As exhibits a broad shoulder in an energy range of 0.2 < $\hbar\omega < 0.5$ meV. Its temperature dependence suggests that this shoulder has also a magnetic origin. The spectrum of Cu₆As shows only incoherent scattering from hydrogen.

A continuous study is apparently necessary to elucidate their spin Hamiltonians. In future, we will focus on V_3 and Mn_6As where existence of the magnetic scattering was suggested in the present results.



Fig. 1. Inelastic spectra of V_3 , Mn_6Sb , Mn_6As , and Cu_6As observed at ISSP-HER. See text for details.

Spin excitations in chormite spinel

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We are very attracted to the microscopic origin of the beautiful diffuse pattern along the Brillouin zone boundary in the magnetic geometric frustration systems. Some Reversed Monte Carlo simulations and the paramagnetic spin fluctuation theory with RPA well reproduce the patterns in the several frustrated systems. However, we are questioning the context to study the parameters of exchange interactions and anisotropy energy only from the paramagnetic scattering. The microscopic origin of frustration is unresolved.

On the other hand, the spin excitations in the ordered phase directly give the interactions in the Hamiltonian. For example, the partial frustration system CoCr2O4 and the usual frustration system MgCr2O4 and ZnCr2O4 exhibit magnetic long-range order in the lowest temperature phases. In CoCr2O4, the spiral component of spins forms short-range order at the lowest temperature, but the ferrimagnetic component of spins form long-range order. It is worth investigating the relation between the spiral component and the fluctuation of the ferrimagnetic component. MgCr2O4 and ZnCr2O4 exhibit the antiferromagnetic long-range order described by several propagation vectors. By daring to select the ordered phases in those frustrated systems, we can investigate the spin dynamics and the interactions.

In this year (2006), we performed the inelastic scattering experiments below TN=13 K on the single crystal of MgCr2O4. MgCr2O4 is suitable compared to CoCr2O4, because the former is described by 4 sublattices of spins and less than the 6 sublattices in the latter. In spite of the antiferromagnetic order, the same Q-dependence characterizing the geometric frustration was observed at the finite energy around 4.5 meV. We observed other excitation modes by the three instruments, and will also continue the experiments in the next year to measure the overall picture of S(Q,E).



Fig. 1. Fig. Q-dependence of magnetic inelastic scattering in MgCr2O4 The upper and lower data were measured at T=20 K and E=1 meV and t T=6 K and E=4.5 meV, respectively. The horizontal focusing analyzer was used.

Inelastic neutron scattering in the antiferroquadrupole material, PrPb₃

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The rare-earth compound PrPb₃ crystallizes in the AuCu₃-type structure and the crystalline electric field (CEF) ground state is a Γ_3 non-Kramers doublet.[1] The Γ_3 doublet carries quadrupolar moments O_2^0 and O_2^2 , and it actually exhibits a secondorder transition at $T_{\rm O}=0.4$ K.[2] In our work, we performed neutron diffraction experiment in magnetic field and revealed the distribution of field-induced magnetic moments with the propagation vectors of $k_1 = [1/2 \pm \delta, 1/2, 0]$ and/or $k_2 = [1/2, 0]$ $1/2\pm\delta$, 0] ($\delta\sim1/8$).[3] The field-induced magnetic moments are aligned with a sinusoidal (incommensurate) structure below $T_{\rm O}$, suggesting that the quadrupoles be aligned with the same structure. In inelastic neutron scattering experiments, the CEF excitations were observed, however, it was found that the CEF excitation has a strongly dispersive relation with no temperature dependence.[4]

In the present work, we performed inelastic neutron scattering experiments on PrPb₃ at temperatures ranging from 1.3 K to 30 K. The experiments were performed using the HER(C1-1) with E_f =3.6 meV. We used a single crystalline sample with high quality grown by the Bridgman method.

Fig. 1 shows the constant–Q spectrum at $Q=(5/8 \ 1/2 \ 0)$ at the temperatures of 1.3 K \leq *T* \leq 30 K. At *T*=1.3 K, inelastic peaks were observed at *E*=1.4, 1.7 and 2.4 meV. Surprisingly, the spectra at 1.3 K and 4.2 K show almost no change. In addition, we had found that the the spectra would not change at all even below T_Q in another experiment. These behavior probably shows

that the inelastic peak would not result only from the CEF, since the number of the peaks should be inconsistent with the one expected from the CEF levels reported by Gross *et al.*[1] Moreover, increasing temperatures, the intensity of the peaks at E=1.4and 2.5 meV apparently decreases. On the other hand, the peak at E=1.7 meV still remain even at T=30 K. These temperature dependence of the intensity can not be explained by the CEF levels.

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Fig. 1. Constant-Q spectrum at Q=(5/81/20) at the temperatures of 1.3 K \leq T \leq 30 K.

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Magnetic Field Dependence of Two Kinds of Magnetic Correlations in Random Magnet Fe65(Ni0.78Mn0.22)35

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In a previous neutron scattering study, we found that the short-range ferromagnetic and antiferromagnetic correlations coexist in wide concentration and temperature ranges of a random magnet system Fe65(Ni1-xMnx)35 [1]. This result showed that the magnetic phase diagram determined by macroscopic measurements does not properly represent the magnetic state of a competing magnetic interaction system. In order to clarify the microscopic magnetic state of the competing magnetic interaction system, we observed the magnetic field dependence of the neutron scattering patterns arising from ferromagnetic and antiferromagnetic correlations in Fe65(Ni0.78Mn0.22)35.

According to the reported magnetic phase diagram, the alloy of this composition transforms from a paramagnetic phase to a spin-glass phase around 80K[2]. Spin-wave excitations with ferromagnetic character have been observed in the temperature range 10-300K[3].

As reported in ref.1, the magnetic diffuse scattering pattern arising from ferromagnetic correlation is composed by a Lorentzian (LOR) and a squared Lorentzian (SQL) components. On the other hand, signals from antiferromagnetic correlation is well traced only by a LOR function. As increasing magnetic field, the diffuse scattering pattern from ferromagnetic correlations decreases, whereas the change of the signal from antiferromagnetic correlations is small.

Figure 1 shows the field variations of the amplitude and the width of the SQL component of the ferromagnetic diffuse signal which is the major part of scattering signal.

The field variations of these parameters indicate that the magnetic clusters disappear sequentially from larger size with increasing magnetic field. The present result shows that the ferromagnetic and the antiferromagnetic clusters coexist separately in this alloy.

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Fig. 1. Magnetic field variations of the amplitude and the width of a squared Lorentzian scattering function arising from ferromagnetic correlation measured at various temperatures.

Magnetic Structure of RPdSn(R=Tb ,Dy and Ho) Compounds

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Ternary equiatomic rare-earth compounds, RPdSn (R = Tb, Dy and Ho), crystallize in the orthorhombic (Pnma) TiNiSitype structure. TbPdSn and HoPdSn exhibit a multi-step metamagnetic transition at low temperatures[1]. In the present work, we have carried out the neutron diffraction studies to reveal the magnetic structure of TbPdSn, DyPdSn and HoPdSn. The single crystals were grown by the Czochralski method using a tri-arc furnace. The neutron diffraction measurements were made using the HQR spectrometer of JRR-3M of JAEA at Tokai.

Figure 1(a) shows the contour maps of the diffraction intensity around the (0 0.26 3) Bragg position in the rotated plane from the reciprocal b*-c* by seven degrees around the b*-axis at T=9.5 K and T=14.5 K, respectively of TbPdSn. The propagation vector determined by the powder diffraction data. The obtained propagation vectors k = (0.004, 0.266, 0.003) at 16 K and the k = (0.005, 0.266, 0.107) at 3.5 K are in good agreement with those reported by Andre et al[2].

Figure 1(b) shows neutron diffraction data for HoPdSn in the b*-c* reciprocal plane at 1.8 K. The weak magnetic reflections appear at the at the Bragg positions (0 1.5 l) and (0 2.5 l) for l = 2n+1. The first magnetic scattering is given by (1/3, 1/2, 1/3) and is corresponding to powder neutron results well if it is assumed that these peaks are the third harmonic scattering.

Figure 1(c) shows the powder neutron diffraction pattern of DyPdSn at 1.6 K and 14K. There are three magnetic reflections at 1.6 K. With increasing temperature these magnetic reflections vanish at Tt = 4.8 K. However, the magnetic reflection is not found in the reciprocal a*-b*, a*-c* and b*-c*

planes for DyPdSn single crystal.

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Fig. 1. (a) the contour maps of TbPdSn, (b) neutron diffraction data of HoPdS and (c) the powder neutron diffraction pattern of DyPdSn

Neutron Diffraction Studies on a Dy7Rh3 Single Crystal

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The rare earth compound Dy7Rh3 crystallizes in the hexagonal Th7Fe3 type structure with the space group P63mc. From the magnetic measurements, it was shown that the compound possesses the two magnetically ordered states, an antiferromagnetic one between TN = 59 K and TC = 34 K and a ferrimagnetic or canted one below TC[1]. We have also determined the magnetic propagation vector of $\mathbf{k} = (0 \ 0 \ 0.366)$ in the ferrimagentic phase by the powder neutron diffraction[2]. In this study, more detailed neutron diffraction measurements have been carried out on a Dy7Rh3 single crystal in the a* - c* reciprocal plane using the HQR spectrometer of JRR-3M in the temperature range from 10 to 70 K.

Fig.1(a) shows the magnetic and nuclear reflections in the a* - c* reciprocal plane at 10 K. The magnetic reflections appear at the positions indexed by the propagation vector $\mathbf{k} = (0 \ 0 \ 0.375)$. Since a small spontaneous magnetization was observed both along the c-axis and in the c-plane, the conical or canted magnetic structure is proposed. Fig.1(b) shows the integrated intensity of the magnetic reflection $(0\ 0\ 0)$ + and the z component of the propagation vector k as a function of temperature. The integrated intensity shows a peak at about 20 K and an anomaly at TC, while the kz is almost constant with temperature up to TN. In the intermediate antiferromagentic state above TC, the positions of magnetic reflections are almost the same as that in the lower temperature phase. The absence of magnetic component at the nuclear positions may be explained by the fact that the spontaneous magnetization is only 0.1 Bohr magneton below TC. Magnetic structure analysis for the two magnetic phases is

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Fig. 1. Magnetic and nuclear reflections in the a* - c* reciprocal plane at 10 K (a); the integrated intensity of the (0 0 0)+ reflection and kz component of the propagation vector as a function of temperature(b).

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Zero-Field Random-Field Effect in Diluted Triangular Lattice Antiferromagnet CuFe1-xAlxO2

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Delafossite compound CuFeO2 is one of the model materials of triangular lattice antiferromagnet (TLA), and its magnetic properties were extensively investigated in the last fifteen years. Recent studies on the diluted system CuFe1xAlxO2 (x<0.050) revealed that various magnetically ordered phases are induced in the low-Al3+-concentration region, owing to partial release of spin frustration.[1] In contrast, in the high Al3+concentration region of x > 0.040, only the oblique-partially-disordered (OPD) state, whose local spin structure is a sinusoidally amplitude-modulated structure with incommensurate wave number, shows up, and the local magnetic structure does not changes depending on the amount of nonmagnetic impurity.[2] However, our preliminary neutron diffraction measurements revealed that the width of the diffraction profile broadens with increasing Al3+ concentration. We thus investigate how the spin correlation in CuFe1-xAlxO2 is modified depending on amount of nonmagnetic impurity, by high-Q resolution neutron diffraction measurements.

In present experiments, we performed neutron diffraction measurements using the single-crystal CuFe1-xAlxO2(x=0.10) at the triple-axis spectrometer HQR(T1-1) installed at JRR-3M, The incident neutron wavelength is 2.44[A] and collimation open-'40-'40-'60 was employed. We firstly obtained the diffraction profiles of (qOPD,qOPD,1.5) and (qOPD,qOPD,4.5) magnetic reflections with qOPD^{-0.19} along six directions illustrated in Fig.1 (e). Next, we numerically calculated the diffraction profiles for these directions by convoluting a functional form of S(q) with the measured resolution function, and fitted them to the measured profiles simultane-

ously. Trying several functional form of S(q), we found that the scattering function of the magnetic reflection is described as the sum of a Lorentzian term and a Lorentzian-squared term with anisotropic widths. The Lorentzian-squared term dominating at low temperature is indicative of the domain state in the prototypical random-field Ising model. Taking account of the magnetic structure in OPD phase, we conclude that the effective random field arises even at zero-field, owing to the combination of site-random magnetic vacancies and the sinusoidal magnetic structure. The details of the present study will be seen in the coming paper.[3]

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Fig. 1. (a)-(d)Scattering profiles at T=2K. The dotted, dashed and solid lines depict the profiles calculated with Lorentzian-(LRZ), Lorentzian-squared-(LSQ) and LSQ+LRZ-type of S(q), respectively. (e) scan directions corresponding to (a)-(d)

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Magnetic Structure in the Multiferroic Phase of Frustrated Magnet CuFe1-xAlxO2

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Geometrically frustrated triangular lattice antiferromagnet CuFeO2 has been extensively studied for last fifteen years. Recently, Kimura and co-workers has discovered the spontaneous electric polarization in the low-temperature field-induced phase of CuFeO2, and argued that CuFeO2 provides an opportunity to study a new class of multiferroic materials.[1] To understand the microscopic mechanism of the multiferroic nature, detailed magnetic structure in the ferroelectric(FE) phase is indispensable. Quite recently, we performed neutron diffraction measurements with a horizontal field cryomagnet at HMI, and revealed that the magnetic structure in the FE phase is a proper helical structure propagating along <110> axis.[2,3] This measurements is, however, restricted to the (hhl) zone, in which the proper helical structure cannot be distinguished from the sinusoidal structure with the moments canted by 45[deg] from the c axis toward <1-10> direction.[4] Thus, the information beyond the (hhl) zone is indispensable to confirm the proper helical structure.

Fortunately, the small magnetic reflections corresponding to the magnetic ordering of the FE state were found to coexist with the four-sublattice(upup-down-down) magnetic state in the ground state of the slightly diluted sample CuFe1-xAlxO2(x=0.012), owing to a slight macroscopic inhomogeneity of the Al-concentration. We thus surveyed the three-dimensional hkl-dependence of the magnetic structure factor of the FE state in zero field, using the x=0.012 sample and four-circle diffractometer FONDER(T2-2) installed at JRR-3M. The incident neutron wavelength is 1.24[A] and the closed-cycle He-gas refrigerator is used to provide access to the temperature down to T=2.5K.

From observed magnetic structure factors, we estimated the Spin Orientation Factors (SOF), and found that the hkl-variation of observed SOF is well explained by the proper helical model, even beyond (hhl) zone, as shown in Figs. 1(b)-(e).

A naive application of the theory for ferroelectricity in noncollinear magnets[5] to the proper helical structure does not lead to a finite uniform electric polarization. Nevertheless, the present results imply that a spin noncollinearlity is relevant to the multiferroic nature in CuFe1-xAlxO2.

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Fig. 1. (a)Typical diffraction profile at T=2.5K. (b)-(e)Index I-variation of and the SOFs. The solid, dotted and dashed lines denote the calculated values for a proper helical, +45[deg]-canted sinusoidal and -45[deg]-canted sinusoidal structure, respectively.

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The magnetic field effect of ZnCr2O4

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ZnCr2O4 is a three-dimensional geometrical spin frustration system with a normal spinel structure, in which magnetic Cr3+ ions occupy the B-site and the nearest neighbor Cr3+ spins couple antiferromagnetically. ZnCr2O4 undergoes the first order phase transition to an antiferromagnetic phase accompanied by a tetragonal lattice distortion of the order of 0.2% at 12.5K. The magnetic structure in the ground state of ZnCr2O4 was studied by several authors in the past in the aspect of a fundamental magnetic system. However, the results are not clear due to the complex magnetic structure. Last year, we have performed the neutron scattering measurements with a ZnCr2O4 single crystal specimen. [1] The (hh0) (h= n/2, n= odd) series magnetic Bragg peaks disappeared when the magnetic field was applied along the [111] axis. It means that the magnetic structure turns into a new structure with higher symmetry than that in the ground state under a small magnetic field. In order to obtain further knowledge of the magnetic structure of ZnCr2O4 in the ground state, we performed the neutron scattering using isotropic powder ZnCr2O4 specimen under a magnetic field.

A powder sample was prepared by solid state reaction between stoichiometric amounts of ZnO and Cr2O3 in air. Experiments were performed on the T1-1 triple axis spectrometer installed at JRR-3M with a vertical magnetic field.

In elastic neutron scattering experiments, field cooled (FC) and zero field cooled (ZFC) states were measured. Figure shows the $(2 \ 1 \ 1/2)$ magnetic Bragg peak obtained with and without magnetic field (H=4.5T). As a result, the disappearance of a magnetic Bragg peak was not observed in any series of indices. For the single crystal specimen, since the (hh0) magnetic peaks com-

pletely disappeared under the magnetic field, present data indicate that the (111) plane has a special meaning for the magnetic structure under the magnetic field.

In inelastic neutron scattering experiments, Q-dependence was measured by the constant E mode at E=2.5meV and 4.5meV. At E=2.5meV, dispersion was observed around the strong magnetic Bragg peaks. At E=4.5meV, however, dispersion was not observed. In addition, inelastic diffuse peak shifted towards the low angle side when the temperature was raised. From these experiments, we can conclude that the spin axis inclines gradually under the magnetic field and the magnetic structure with higher symmetry is stabilized. Reference

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Fig. 1. The magnetic Bragg peak at (2 1 1/2) in elastic neutron scattering.

Thermodynamic anomaly specific to PD phase of spin frustration system CuFeO2

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Delafossite compound CuFeO2 has been extensively investigated as one of model materials for triangular lattice antiferromagnets (TLA). Although CuFeO2 is considered to be a Heisenberg spin TLA with S=5/2 of orbital singlet Fe3+, a sinusoidally amplitude-modulated magnetic state with a temperature dependent incommensurate magnetic propagation vector (q, q, 3/2) is thermally induced from 4sublattice ground state as a partially disordered (PD) state characteristic to Ising spin TLA.[1]

We have reported anomalous thermal behavior specific to the PD phase and suggested that changes in microscopic magnetic state with variation of the propagation wave number q is accompanied by additional latent heat in the PD phase. [2] In present study, to investigate accurately how change in the propagation wave number q reflecting the microscopic magnetic state correlate with extra heat absorption and generation during thermal cycles found in the specific heat measurement, we performed neutron diffraction experiments with varying the temperature as was in the specific heat measurement, using HQR spectrometer at JRR3M in JAERI (Tokai) for single-crystal sample of CuFeO2. The incident wavelength of neutron is 2.44[A] and collimation of open-'40-'40-open is employed.

As shown in Fig.1, starting 1st-heating process from T~11.65 K, variation of the wave number q well follows the T-increasing-Guide-line shown in the inset of Fig.1. In subsequent1st-cooling process, with decreasing the temperature from the highest temperature ~11.85 K, the point q(T) depicted by blue cricle moves horizon-tally on the wave number q v.s. Temperature (q-T) plane, meets and follows the T-decreasing-Guide-line. In subsequent 2nd-

heating process starting from T~11.65 K, the point q(T) moves horizontally, meets and follows the T-increasing-Guide-line on T-q plane. In such a way, we measured the trajectory of the point q(T) on q-T plane up to 3rd temperature-cycle for various temperature width dT and confirmed that the trajectory of the point q(T) extracted from knee-points in the temperature response of the sample in the specific heat measurement with the relaxation technique is well coincide with that from present neutron diffraction measurements. From these results, we concluded that extra heat absorption and heat generation in the PD phase occur for decreasing and increasing of the propagation wave number q, respectively, suggesting a kind of Devil's Staircase for the PD state of CuFeO2.

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Fig. 1. Trajectory of the wave number q for temperature-cycles with the temperature width of dT=0.20 K. [inset] Tempetature dependence of the magnetic propagation wave number q in PD state,.

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Phase Stability and Site Occupancy for the L21-type phase in Co2YGa (Y = Ti, V, Cr, Mn and Fe) Alloys

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Many Co2YZ L21 (full-Heusler)-type half-metallic ferromagnets (HMFs) have been extensively studied from both theoretical and experimental points of view due to their potential applications in spindependent devices such as magnetic random access memories (MRAMs). From the recent studies [1-3] on Co-, Ni-, and Cubased X2YZ L21-type alloys, it has been confirmed that the phase stability of L21type alloys strongly depends on the kind of elements occupying the Y (4a) site and that the order-disorder transition temperature from the L21 to B2-type phase Tt(B2/L21) tends to decrease with increasing electron number of the Y element in the periodic table, except for in the case of Cr. The Tt(B2/L21) of Co2CrGa is the lowest among the Co2YGa (Y = Ti, V, Cr, Mn and Fe) alloys. In the present study, the site occupancy in the L21-type phase of Co2YGa alloys was investigated to clarify the correlation between the phase stability and the site occupancy.

The specimens were prepared by induction melting under an argon atmosphere. After alloying, each ingot was annealed at 1373 K for 72 hours and quenched in ice water. Powdered specimens were additionally annealed at 773 K for 2 hours. Neutron powder diffraction experiments were carried out using the Kinken powder diffractometer, HERMES [4], of the Institute for Materials Research (IMR), Tohoku University, installed in the JRR-3M reactor at the Japan Atomic Energy Agency (JAEA), where the wavelength was 0.182646 nm. The neutron diffraction data were analyzed with the Rietveld method using the RIETAN2000 program [5].

Figure 1 shows the observed and calcu-

lated neutron diffraction patterns and their differences between them at 300 K in the paramagnetic state for the Co2TiGa alloy which has a Curie temperature at TC=137 K. It was confirmed from the Rietveld analysis that the lattice constant a = 0.5858 nm, that the 8c site is entirely occupied by Co atoms, and that the 4a site is occupied by the Ti atoms with the site occupancy g =0.96. In order to simplify this analysis, we introduced an assumption that the Co (8c) site is not occupied by Ga atoms [6], which is supported by the thermodynamic calculation based on the Bragg-Williams-Gorsky (BWG) approximation [7]. The high site occupancy obtained for the L21-type phase in the Co2TiGa alloy is consistent with the high phase stability that is suggested by the fact that the order-disorder transition temperature from the L21 to B2-type phase Tt(B2/L21) is very high at 2390 K [3].

The observed and calculated neutron diffraction patterns and the difference betwen them at 573 K in the Co2CrGa alloy are shown in Fig. 2; the TC of this alloy is known to be 495 K [3]. Structural parameters including the site occupancy were refined under the same assumption as that for the Co2TiGa alloy. We have obtained the following results; the lattice constant a = 0.5805 nm, the 4a site is occupied by Cr atoms with g = 0.86, the 4b site is occupied by Ga atoms with g = 0.88, and the 8c site is occupied by the Co atoms with g =0.99. It was confirmed that while the site occupancy of the 8c site by the Co atoms in the Co2CrGa alloy as well as that in the Co2TiGa alloy is almost perfect, the site occupancies of the 4a and 4b sites are lower than those in the Co2TiGa alloy.

According to the BWG approximation [6],

the Tt(B2/L21) of the stoichiometric X2YZ alloy is simply indicated by the following relation under the assumption that the occupancy of the 8c site by the X atoms is perfect at the ordering temperature Tt(B2/L21) [8]:

Tt(B2/L21) = 3W(YZ)/2k,

where W(YZ) is the interchange energy of the Y-Z bond between the second nearest neighbors and k is the Boltzmann constant. The above equation means that there is a linear relation between Tt(B2/L21) and W(YZ). Therefore, it can be concluded that the difference of the site occupancy between Co2TiGa and Co2CrGa can be attributed to the difference of the W(YZ), which can be evaluated from the Tt(B2/L12) of Co2CrGa (1056K) and Co2TiGa alloys (2390K) by Eq 1. Further systematic quantitative analysis of the site occupancy in Co2YGa (Y = V, Cr, Mn and Fe) alloys is needed to clarify the relation between the phase stability and the site occupancy.

In conclusion, the site occupancies of the Co2TiGa and Co2CrGa alloys were investigated and it was found that for the Co2TiGa alloy, the 4a, 4b and 8c sites are almost entirely occupied by Ti, Ga and Co atoms, respectively. On the contrary, for the Co2CrGa alloy, the 4a and 4b sites are occupied by the Cr and Ga atoms with g = 0.85 and 0.88, respectively. These results can be explained by the difference of the order-disorder transition temperature Tt(B2/L21) from L21 to the B2-type phase for these two alloys.

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Fig. 1 The observed and calculated neutron powder diffraction patterns at 300 K for the Co₂TiGa alloy and the difference between the two.



Fig. 2 The observed and calculated neutron powder diffraction patterns at 573 K for the Co_2CrGa alloy and the difference between the two.

Fig. 1.

Magnetic Ordering of β -MnOs alloys

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It has been known that pure β -Mn has no long-range magnetic ordering down to the lowest temperatures [1]. In the β -Mn alloys, the alloying transition elements are usually substituted for Mn atoms in 8c and/or 12d sites of the β -Mn structure (P4132) [2], and the magnetic properties significantly depend on the substituted site of the elements. For example, in the β -MnFe, β -MnCo and β -MnNi alloys where most of the additional atoms occupy the 8c site, the magnetism has been determined by NMR examination to be antiferromagnetic [3]. However, no experimental evidence for the long-range antiferromagnetic ordering has been reported in the previous neutron diffraction study [4]. We have been investigated various physical properties of β -MnTM (TM =Os, Ru and Ir) alloys because the TM can be substituted for a wide concentration range in the β -Mn, almost up to 40 at. %. In the present investigations, we performed neutron powder diffraction (NPD) investigations for β -Mn1-xOsx alloys with x = 0.06 and 0.25 in order to confirmed existence or absence of the magnetic ordering.

The alloys were prepared by arc melting and the obtained ingots were annealed at 1273 K and then quenched in ice water. The NPD experiments were carried out using the Kinken powder diffractometer, HER-MES [5], of Institute for Materials Research (IMR), Tohoku University, installed in the JRR-3M reactor at the Japan Atomic Energy Agency (JAEA), where the wavelength was 0.182646 nm. The obtained NPD data were analyzed with the Rietveld method using RIETAN2000 program [6].

Figure 1 shows the NPD patterns measured at 8 K (a) and 200 K (b) and the difference of them (c) for x = 0.25. The diffraction pattern at 200 K can be simply

indexed as the nuclear peak of the basic β -Mn structure. It was confirmed by the Rietveld analysis that the lattice constant is a = 0.6486 nm, and that the site occupancies of Mn atoms in the 8c and 12d sites are g = 0.37, and 0.93, respectively, i.e., most of the Os atoms occupy in the 8c site. On the other hand, many additional peaks are observed in the diffraction pattern at 8 K (a). According to our previous investigation, an anomaly in the thermo-magnetization curve has been observed around 160 K. This means that these additional peaks are due to the magnetic ordering. From this magnetic diffraction pattern, it would be thought that the magnetic structure is classified as a non-collinear-type in antiferromagnetic structures. The detailed magnetic structure is now under consideration.

Temperature dependence for the intensity of a large magnetic peak for x = 0.25, indicated by an arrow in the Fig. 1 (c), is shown in Fig. 2. It is evident that the magnetic peak disappears at around 160 K almost coinciding with the temperature in which the anomaly was confirmed in the magnetic measurements. Therefore, it is concluded that the anomaly is attributed to the Neel temperature.

Figure 3 shows the NPD patterns at 4 K (a) and 50 K (b) and the difference of them (c) for x = 0.06. It was determined by the Rietveld analysis that the obtained peaks are indexed as the β -Mn structure with a = 0.6315 nm, and that the 8c and 12d sites are occupied by the Mn atoms with g = 0.91 and 0.97, respectively. No magnetic peak is observed in the diffraction patterns obtained at 4 K (a), although an anomaly in the magnetic measurements was detected at around 40 K. These results are similar to that of the β -MnCo alloy [4].

According to the theoretical calculations,

the magnetic moments for a Mn atom in the 8c and 12d sites are completely different and evaluated to be about 0.2 and 1.25 mB/Mn-atom, respectively [7]. The absence of the magnetic ordering of the pure β -Mn alloy is thought to be caused by the geometrical frustration of the Mn atoms in the 12d site forming a triangular lattice [8]. It would be concluded that the lattice expansion and/or the distortion of the triangular lattice given by the substituted alloys in the 8c site bring about the long-range antiferromagnetic ordering.

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Fig. 1 Neutron powder diffraction patterns at 8 K (a) and 200 K (b) and the difference (c) for x = 0.25.



Fig. 2 Temperature dependence of the magnetic peak intensity for x = 0.25.



Fig. 3 Neutron powder diffraction patterns at 4 K (a) and 50 K (b) and the difference (c) for x = 0.06.

Fig. 1.

Neutron Diffraction Studies on R7Rh3Dx

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The rare earth intermetallic compounds R7Rh3 crystallize in the hexagonal Th7Fe3 type structure with the space group P63mc. They are easily hydrogenized to have R7Rh3H30 with the Th7Fe3 type structure remained [1]. We have shown that the magnetic property of Tb7Rh3 is drastically modified by the hydrogenation. Furthermore, electrical conduction changes from semimetallic to metallic by the hydrogenation. In this study, we have performed the powder neutron diffraction measurements on R7Rh3Dx (R=Dy and Ho) to investigate the location of deuterium atoms and the magnetic structure of the deuteride. Deuterization of R7Rh3 samples was carried out in the pressure up to 10 kbar at 25 and 100 degree Celsius in the high pressure vessel [2]. The concentration of deuterium in the deuterides was determined by the gas chromatography. The neutron diffraction measurements have been carried out by using the HERMES spectrometer of JRR-3M in the temperature range from 10 to 100 K. The neutron wave length was 0.18265 nm.

Figure 1(a) shows the powder neutron diffraction profiles of Ho7Rh3 and Ho7Rh3D17 at 70 K. All the peaks in Ho7Rh3 can be indexed on the basis of the Th7Fe3 type structure. In Ho7Rh3D17, the peaks shift to lower angle side, indicating that the lattice expands by the deuterization. The structural determination for the hydrides is in progress. Figure 1(b) indicates the powder neutron diffraction profiles of Ho7Rh3 and Ho7Rh3D17 at 4 K. In the Ho7Rh3 a strong magnetic reflection is observed at the position of 2 theta = 6.4degree. As we proposed an incommensurate helical structure with the propagation vector $\mathbf{k} = (0 \ 0 \ 0.377)$ in the lower antiferromagentic phase of Ho7Rh3 [3]; the observed profile can be indexed with this helical structure.

On the other hand, in Ho7Rh3D17, only a week peak is observed at 2 theta = 2.6 degree. This peak may be a magnetic reflection from the Ho7Rh3D17. The analysis of the magnetic structures of R7Rh3Dx is also in progress.

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Fig. 1. Powder neutron diffraction profiles of Ho7Rh3 and Ho7Rh3D17 at 70 K (a) and 4 K (b).

Activity Report on Neutron Scattering Research: Experimental Reports 14 (2007) Report Number: 120

Neutron Diffraction Experiments with 30T Pulsed Magnets

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Magnetic field is an important parameter which can control magnetic moments directly. On the other hand, neutron scattering provides a direct probe of space-time correlation of spins. Thus, neutron scattering under high magnetic fields is eagerly anticipated.

Currently, the highest magnetic field for neutron scattering experiments was B=25T performed by Motokawa et al. using a repeating pulsed magnet in KENS in KEK, Japan[1-2]. However, experiments over B=10 T are still limited; easier and more diffusive techniques are ambition. Therefore, aiming at performing neutron scattering experiments under B=40T, we are developing techniques for neutron scattering experiments with long pulsed magnets. In 2006, we have succeeded in performing neutron diffraction experiments under 30T pulsed magnetic field on AKANE.

One of the results is observation of spinflop transition at 10T in MnF2[4]. The magnet coil[3], in which the single crystalline sample of MnF2 was fixed, was set in a liquid He refrigerator. The scattering plane was the a*-c* plane so that we could measure the (1,0,0) antifferomagnetic reflection under magnetic fields applied along the c-axis. The wave length of the neutrons was 2.0A; the collimation condition was G-Open-S-B-B. The detector was fixed at the peak top position of the (1,0,0) reflection. During the pulsed magnetic fields experiments, neutrons counts and coil currents were measured with an oscilloscope to resolve time structure. Fig.1 shows time dependence of neutron counts at the peak top obtained after 100shots. Since the interval between each pulse of 17min. was needed, the actual measurements duration was about 28hr. Since the background was negligible small under the present conditions, the scattering in Fig.1 was due to the

(1,0,0) magnetic reflection. As shown in Fig.1, the intensity of the (1,0,0) magnetic reflection decreased when magnetic fields over 10T were applied. Note that the intensity recovered when the magnetic field became lower than B=10T, indicating that the decrease of the intensity was not due to the heating by the coil current. Thus, this indicates that we succeeded in observing the spin-flop transition of MnF2 at B=10T. We have also succeeded in observing magnetic reflection over 22T in CuFeO2 with 30T pulsed magnetic fields.

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Fig. 1. Time Dependence of neutron counts at the peak top position of (1,0,0) magnetic reflection at T=4.2K obtained after 100 shots (upper panel)

Electric Control of Spin Helicity in TbMnO₃

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In а magnetoelectric compound TbMnO₃, sinusoidal incommensuа rate antiferromagnetic ordering of the Mn^{3+} moments takes place at $T_N = 42$ K with a magnetic wave vector with $q \sim 0.27$. The ferroelectric polarization along the c axis (P_c) emerges upon the magnetic phase transition from collinear to cycloid spin structure at $T_C = 27$ K. We report here the quantitative elucidation of such magnetically induced ferroelectricity in terms of the spin ellipticity as the order parameter and show the successful electric control between the clockwise (CW) and counter-clockwise (CCW) spin helixes.

Spin polarized neutron diffraction measurements were performed with a tripleaxis spectrometer PONTA at JRR-3. A single crystal was mounted on a sapphire plate in a closed-cycle helium refrigerator and irradiated with a spin-polarized neutron beam with a kinetic energy of 36.0 meV. A Heusler monochromator was utilized to obtain the spin-polarized neutron beam. The spin of the neutron beam could be flipped by a spin-flipper, so as to be parallel or anti-parallel to the scattering vector Q_s with a guide-field of about 10 gauss applied by a Helmholtz coil.

All the neutron diffraction measurements were performed without application of electric field after cooling the sample from 50 K in a poling field. Peak profiles of magnetic satellite reflections $(4 + q \ 1)$ and $(4 - q \ 1)$ with $q \sim 0.27$ were obtained by rotating the sample around the vertical axis, which approximately corresponded to the L scan in the reciprocal space.

Figure 1(a) shows the profiles of magnetic satellites at $Q_s = (4 \pm q \ 1)$ for the ferroelectric state at 9 K after cooling in an electric field of $E = \pm 160 \text{ kV/m}$. In the case of

 $P_c > 0$, the intensity of the satellite (4 + q 1)is approximately 9 times as high with neutron spin (S_n) anti-parallel to the scattering vector Q_s as that with parallel S_n . As for the satellite (4 - q 1), the opposite relation is observed. These behaviors are typical of a spiral magnet with a single helicity, where the spiral plane is almost perpendicular to the scattering vector. Here, it is to be noted that the spiral plane of TbMnO₃ is perpendicular to the *a* axis. When the direction of the cooling electric field is reversed, it is clearly shown that the opposite helicity domain becomes dominant. In other words, that the spin helicity can be successfully controlled by a poling electric field. The revealed relation between the spin helicity and electric polarization is depicted in Fig. 1(b).



Fig. 1. (a) Profiles of magnetic satellites $(4 \pm q 1)$ with $P_c > 0$ and $P_c < 0$ at 9 K. (b) Relation between the spin helicity and the direction of electric polarization in TbMnO₃.

A puzzling magnetic phase in HoCu2Si2

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The ternary compound HoCu2Si2, having the tetragonal ThCr2Si2-type crystal structure (space group: I4/mmm), orders antiferromagnetically below TN=6.0 K [1]. An additional magnetic transition has been recently observed at Tt=5.1 K from measurements of magnetic susceptibility and specific heat [2]. The antiferromagnetic structure, reported from powder neutron diffraction study [3], is characterized by the wave vector k= (1/2, 0, 1/2), having Ho moments parallel to the [100] direction. The magnetic structure for Tt<T<TN has been, however, unknown yet.

In order to investigate the magnetic structure for the intermediate temperature region Tt < T < TN, neutron diffraction studies have been performed on a HoCu2Si2 single crystal using a double-axis mode of the triple axis spectrometer HQR installed at JAERI, Tokai, Japan. The a-axis of the single crystal was vertically oriented to obtain the distribution of neutron intensities in the a*-c* reciprocal plane.

The single crystal has been grown by the tri-arc Czochralski method. The single phase nature has been confirmed by X-ray powder diffraction

At low temperatures below Tt, an appearance of antiferromagnetic reflections associated with the propagation vector k1=(1/2, 0, 1/2) has been confirmed. These reflections disappear above Tt. In intermediate temperature region Tt<T<TN, new antiferromagnetic reflections appear around (1/2 0 1/2), indexed by (1/2+d1, 0, 1/2+d2) and (1/2-d1, 0, 1/2-d2) (d1=0.030, d2=0.033). They are associated with the propagation vector k2=(0.530, 0, 0.533). No higher order harmonics are observed, suggesting that this magnetic structure is not an anti-phase one but amplitude modulated one. The temperature dependence of peak intensity for antiferromagnetic reflections is shown in Fig. 1. The $(1/2 \ 0 \ 1/2)$ intensity rapidly decreases around Tt with increasing temperature. On the other hand, the $(0.530 \ 0 \ 0.533)$ intensity develops around Tt and disappears above TN. Thermal hysteresis is observed around Tt, indicating the transition at Tt is of the first order. An analysis for magnetic structure of the intermediate temperature is now in progress.

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Fig. 1. Temperature dependence of antiferromagnetic reflections in HoCu2Si2

Neutron Diffraction Study on La2-xCaxCoO4

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Perovskite Co oxide, La1-xAxCoO3(A=Ca, Sr, Ba), has attracted considerable interest because their fascinating physical properties. F. Fauth et al reported the diffraction and transport properties of La0.5Ba0.5CoO3 [1]. From the neutron and synchrotron diffraction powder studies, they have observed the Jahn-Teller (JT) distortion of the CoO6 octahedra below Tc. The JT-effect is favored for the intermediate spin state (IS) configuration, (t2g)5(eg)1. Thus, they concluded that ferromagnetic transition and IS state are strongly correlated each other in La0.5Ba0.5CoO3.

Recently, we reported neutron diffraction experiments of La1.5Ca0.5CoO4 and CE-type spin and charge configurations are probably realized. In the CE-type spin configuration, double-exchange interaction between Co2+(HS) and Co3+(IS) is realized and it is expected that JT-distortion is formed below TN. In order to clarify the JT effects in a half-doped material, we performed neutron powder diffraction experiments using the diffractometer, HER-MES, installed on T1-3 port of JRR-3M reactor. La1.5Ca0.5CoO4 has two-magnetic domains, so we use a single magnetic domain of La1.85Ca0.15CoO4.17 which is an almost half doped material.

The structure analysis for La1.85Ca0.15CoO4.17 at 7, 50 and 100K concluded that its space group is P4/mmm which corresponds to the isotropic oxygen displacement model ($\sqrt{2}$ atet $\times \sqrt{2}$ atet \times c). Figure 1 shows the temperature dependence of Co-O apical oxygen distance. In neutron experiments of La1.5Sr0.5CoO4, it's found that Co2+-O distance is longer than Co3+-O distance [2]. We assumed that the Co(1)-O(2) and Co(3)-O(5) distances correspond to that of Co2+-O and Co3+-O, respectively. As can be seen in

Fig.1, temperature dependence of the apical oxygen distortion coincides with that of the antiferromagnetic order. This result suggests that magnetic transition and JT-distortion are also strongly related each other in La-Ca system. Magnetic diffuse peaks due to an antiferromagnetic ordering of Co2+ are observed at (0.5, 0, 0.5) and (0.5, 0, 2.5). These peaks are indexed in the crystallographic unit cell. This indicates that the magnetic peaks are two-dimensional Bragg diffraction because of the layered crystal structure.

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Fig. 1. Temperature dependence of Co2+(3+)-O bond length

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Anisotropic magnetic diffuse scattering in a helical magnet ErNi2Ge2

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Magnetic frustration is one of the central issue of the magnetism for decades. Origins of the magnetic frustration are roughly classified into two categories, the geometrical frustration and the frustration in the exchange couplings such as in the ANNNI system. A rare-earth intermetallic compound ErNi2Ge2 is a latter type manget, showing a long-periodic magnetic structure[1].

In Ref.[1], they reported that ErNi2Ge2 has a sinusoidal modulated structure with the magnetic wave vector $\mathbf{k} = (0,0,0.757)$ and its magnetic moment forms an angle 64 deg. with the c-axis. However, it is not consistent with our magnetization measurements using single crystalline samples, which evidently indicate that the ab-plane is a magnetic easy plane and the magnetization component along the c-axis is less than 1/10 of that in the ab-plane.

In order to resolve this inconsistency, we have performed neutron scattering experiments using single crystalline samples on the triple-axis spectrometer T11 installed at the JRR-3M. A quantitative analysis of intensities of several magnetic reflections indicates that the moments lie in the abplane, rather than forming an angle 64 deg. with the c-axis, and form the helical modulation, not the sinusoidal one. This magnetic structure is consistent with our magnetization measurements and our crystalline electric field(CEF) analysis.

Furthermore, we found a characteristic magnetic diffuse scattering, as shown in Fig. 1. Below TN, the peak profile is composed of a long-range sharp peak and a short-range broad one. The broad one can be fitted with a Lorentzian. Interestingly, this magnetic diffuse scattering has a remarkable anisotropic nature, namely, the peak profile is broaden along the [1,0,0]and the [1,1,0]-axis, whereas it is sharp along the c-axis enough to be considered as a resolution limit. These results indicate that the antiferromagnetic order of ErNi2Ge2 is composed of the long-range and the short-range orders. And also, they suggest that the short-range orders consist of one-dimensional long-range helices along the c-axis.

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Fig. 1. Temperature variation of the magnetic scattering of ErNi2Ge2. Black solid lines represent the fitting results. Blue ones are the Lorentzian components.

Neutron scattering in O_2 adsorbent magnet

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Oxygen molecule is a simple magnetic element that carries S = 1 spin. While metal ions are constituents of various types of magnetic compounds, O₂ based magnets has been restricted to monolayer O₂ molecule adsorbed on the surface of several materials such as Aluminum or graphite [1, 2]. The adsorbed O₂ forms spin framework that reflects the surface structure of mother compound. For example S = 1 trangular lattice is realized in the O₂ adsorbed graphite. However the small amount of the adsorbed spins makes the magnetic property measurement difficult. Hence the metal based compound has been major substances for the study of magnetism.

Recently the adsorption of O_2 molecule in the nanochannel of some microporous compounds were reported [3]. In contrast with the surface adsorption, the oxygen molecules are intercalated deep inside the host compound and the adsorption is realized in the bulk crystal. Hence the O_2 based magnet with the bulk size is experimentally realized. In this pioneering work we observed the magnetic excitation of $O_2 S = 1$ spins in the O_2 adsorbed microporous compound [Cu(II)₂(bza)₄(pyz)]_n (bza and pyz are benzoate and pyrazine, respectively) by neutron scattering technique.

Crystal structure analysis by x-ray diffraction showed that the adsorbed O_2 molecule forms isolated trimer [3]. Preliminary magnetic susceptibility measurements is consistent with the spin trimer model with $J \sim 2.0$ meV [4]. If this is the case a narrow band excitation would be observed at $\hbar \omega \sim 2.0$, 4.0, and 6.0 meV with the intensity modulation in inelastic neutron scattering (INS). [5]. Hence we performed initial experiment at PONTA spectrometor installed at 5G beamline.

However, we observed no intrinsic signal in the energy transfer range between 1 meV and 20 meV. This means that preliminary model is inconsistent with experiment. Then we performed the second experiment at HER spectrometer at C11 in guide hall. We repeat the measurements for both O₂ adsorbed and not adsorbed samples in the same experimental configuration.

Figure 1 shows a typical constant *q* scan. Well defined sharp peak was observed at $\hbar \omega = 0.40$ meV. We confirmed the disappearance of the peak in not adsorbed sample. The peak position was independent of *q*. The intensity decrease with the increase of *q* gradually and monotonically. The $\hbar \omega = 0.4$ meV mode is the only excitation that we observed in the energy range of 0.15 meV < $\hbar \omega$ < 20 meV. Furthermore we did not observe any sign for the intensity modulation.

The results mean that the observed peak is due to magnetic excitation from O_2 spins of S = 1. The *q* independence means that the spin system is isolated. The absence of the intensity modulation means that the interaction between O_2 spins is too weak to be detected in INS. The only possible explanation for the excitation is that a single ion anisotropy of an O_2 spin of S = 1.

In summary we succeeded in the observation of the magnetic excitation in O_2 adsorbent magnet.

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Fig. 1. Constant q scan in the O₂ adsorbed $[Cu(II)_2(bza)_4(pyz)]_n$.

Neutron scattering in $Ba_2MnGe_2O_7$

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Ba2MnGe2O7 is a 2D square-lattice antiferromagnet with Mn^{2+} spin of S =5/2. The crystal structure is tetragonal with space group P - 421m, a = 8.4952 Å, and c = 5.5256 Å. The isostructural compound Ba₂CuGe₂O₇ [1] is well known as spiral magnet with Dzyaloshinskii-Moriya and KSEA interaction. The remarkable difference is found in the energy scale of exchange constants J. In Ba₂MnGe₂O₇ J \sim 0.05 meV is estimated by magnetic susceptibility measurements. The boundary energy is calculateed to be 0.5meV from spinwave approximation. Hence the spin dispersion can be measured by cold neutron scattering experiment. This exchange energy corresponds to the saturation field of about 9 T. This means that the spin dispersion can be fully tuned by the magnetic field by using available superconducting magnet. To study the behavior of spin wave in the strong magnetic field [2], we planned to characterize the following magnetic properties: (i) magnetic sturcture analysis, (ii) inelastic cold neutron scattering in zero field, and (iii) inelastic cold neutron scattering in magnetic field.

We had grown good-looking single crystal of Ba2MnGe2O7 by floating zone furnaces. In prior to neutron experiment powder XRD was performed to confirm the absence of impurity. We observed beautiful 4-fold axis in Laue picture. Rocking curve with sharp line width was also obtained. After these careful sample characterization, we started neutron experiment at PONTA spectrometer in 5G beamline to collect magnetic Bragg diffractions. To our surprise we found that the intensities of fundamental nuclear Bragg peaks were very weak. For example the intensity of (110) reflection, which is the 2nd strongest peak, of the sample the dimension of 5 \times

 5×5 mm³ was only 2000 cps. Furthermore, we found a few more $(1 \ 1 \ 0)$ reflections in arbitrary directions, even though each rocking curves were in resolution limited.

Hence we had to conclude that our sample was multi-domain crystal even ghouth the bulk sample seems to have good plane and beautiful Laue picture was obtained by using x-ray. textbf The lesson that we learned is that preliminary crystal check must be done by using neutron beams. Xray diffraction is not enough to check the big crystal for neutron use.

In the given maschine time we changed our plan and we did the neutron scattering study in O_2 absorbent magnet: the proposal ID 6459. Now we are trying to grow the single crystal of Ba₂MnGe₂O₇ by using different growth conditions.

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Neutron scattering in O_2 adsorbed CPL-1

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In some metal-organic compounds O₂ molecules are adsorbed in nano-scale microporous structure [1, 2]. Since S = 1 spins are localized at O2 molecules, of which the electronic structure is ${}^{3}\Sigma_{g}^{-}$, and the array of the O₂ molecules is determined by the geometry of microporous in host compounds, O₂ adsorbed microporous compound is a new research field for designing quantum spin magnets. So far magnetism of artificially controlled oxygen molecules has been restricted to surface adsorption on graphite [3] or Aluminum. The amount of oxygen is very small: monolayer or multilayer at best. In contrast in microporous compound, bulk amount of adsorbed oxygen form bulk S = 1 quantum spin magnet. Here we report the observed spin dynamics of O2 molecules adsorbed in the prototypical microporous compound CPL-1 $(C_{16}H_{12}Cu_2N_6O_{10})$ by thermal neutron inelastic scattering technique.

The crystal structure of O_2 adsorbed CPL-1 is determined by x-ray powder diffraction [2]. A saturated amount of adsorption of O_2 molecules is two moles per one mole of CPL1. Since O_2 molecules forms ladder structure, the spin-gap is expected in the O_2 based magnet. Indeed the magnetic susceptibility [2] and magnetization measurements [4] suggests the spin gap of $60 \sim 88$ K (5.2 \sim 7.6 meV). Hence we utilize the thermal neutron scattering technique to study the spin dynamics.

20 g of the powder sample of CPL-1 (protonated sample) was prepared by Takamizawa *et al.* The sample is put in Al can (ϕ 20 mm × 80 mm) with specially designed sample probe for O₂ adsorption experiment. The spacer of 10 mm height is put in the bottom of Al sample can for the extra O₂ reservoir. The O₂ pressure was maintained at 0.8 MPa down to 90 K for the adsorption [2]. ORANGE type cryostat was used to achieve the temperature of 1.5 K. The neutron inelastic experiment was performed at PONTA spectrometer at 5G beam line in JRR3 in JAEA Tokai. The sollar collimation of open - 80' - sample -radial collimation - open with $E_F = 14.7$ meV was used. PG filter was put after sample and horizontally focusing analyzer was used to obtain better statistics. We paid special attention to background subtraction. Since we have large background due to protons in the host compound, we performed the exactly same scans for both with and without O₂ molecule. This means that it takes two times as much as usual experiment. Though large background with peak structure is observed in the constant q scan without O₂, the enhanced intensity is clealy observed in O₂ adsorbed sample. Three peaks are observed at 5meV $\leq \hbar \omega \leq$ 16 meV in the subtracted data. Among them the peaks at $\hbar\omega \sim 10.5$ and 14 meV are supposed to be non-magnetic origin because they are temperature independent. In contrast the sharp peak at $\hbar \omega \sim 8$ meV is suppressed by the increasing temperature. In addition, the peak position is q independent in wide q range and the peak intensity is suppressed with the increase of *q*. These results mean that the 8 meV peak is due to magnetic excitation of isolated spin clusters. Constant energy scan at $\hbar \omega = 8$ meV is shown in Fig. 1. The scan at 6meV is used as background. There seems a maximum around 1.0 meV. In addition peak structure around 3 meV probably exists but seems smeared out due to poor statistics.

The most probable model for the observed spin cluster is S = 1 spin dimers due to adsorbed O₂ molecules. From crystal structure consideration, the intradimer distance is 3.206 Å [4] and the inter-dimer distance is 4.688 Å. The empirical relation between the spin exchange constant and inter-molecule distance of oxygen suggests that the latter is reasonably weak and can be neglected. Hence we draw the spin dimers neutron cross section including presumed O₂ form factor (dashed-dotted line in Fig. 1) [5]. In spite of rough calculation, the curve reproduce maximum at $q \sim 1.0$ Å⁻¹.

In summary we observed spin dynamics of O₂ molecules adsorbed in microporous compound CPL-1.

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Fig. 1. Constant *E* scan.

Magnetic and Neutron Diffraction Study on Ni2In type Mn65(Sn1-xTx)35 T=(Ga,Ge)

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The hexagonal Ni2In type (P63/mmc) Mn65(Sn1-xTx)35 T=(Ga,Ge) compound shows a single phase in the range of 0.2?x?0.5 for T=Ga and 0?x?0.8 for T=Ge. The sample of x=0 has a collinear ferrimagnetic structure showing glass-like phase at lower temperature range. We made the magnetization measurements and the ac susceptibility χ ac measurements for Mn65(Sn1-xTx)35 T=(Ga, Ge) compound.

The concentration dependence of lattice constants a and c at room temperature is shown in Fig.1(a). The ferrimagnetic Curie temperature increases monotonously for Mn65(Sn1-xGax)35 system and decreases for Mn65(Sn1-xGex)35 system.

In order to determine the distribution of the atoms in the Ni2In type crystal structure, the neutron diffraction (ND) experiments were carried out for several samples at paramagnetic state and the data was analyzed with the Rietveld refinement methods. The refined pattern at T=295 K for x=0.5 of Mn65(Sn1-xGax)35 system is shown in Fig.1(b). The determined distribution of atoms among the sublattice is as follows; 2(a) site is occupied by Mn(1.0) , 2(d) site is occupied by Sn(0.50) and Ga(0.50).

Fig.1(c) shows the observed ND intensity at T=20K for x=0.5 of Mn65(Sn1-xGax)35 system. In the lower angle of ND pattern, the magnetic super lattice line (0 0 1/2), (1 0 1/2) is clearly observed in the low temperature, which means the existence of the magnetic unit cell with two times of the chemical one in the c direction. ND pattern for x=0.3 and x=0.5 of Mn65(Sn1-xGex)35 system showed only weak and broad magnetic reflection. In the temperature range of the cluster glass for Mn65(Sn1-xGex)35 system, large size and small size of ferrimagnetic and ferromagnetic clusters may exist coupling each other. The nonmagnetic 2(c) site atoms play important rule to formation of the magnetic super lattice in the hexagonal Ni2In type Mn65(Sn1xTx)35 T=(Ga,Ge) compound.



Fig. 1. Fig. 1 (a) The concentration dependence of lattice constants a and c at room temperature for Mn65(Sn1-xTx)35 T=(Ga, Ge) compound

Inelastic Neutron Scattering Measurements on a Quadrupolar Ordering in Yb monopnictides

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The compound YbSb is well-known as a mixing-type quadrupolar ordering occurs at 5 K. One of the most anomalous properties of Yb monopnictides (YbN, YbP, YbAs and YbSb) is the unexpected splitting of the first excited states (Γ 8) of the crystal field splitting. Keller et al. proposed that the unexpected splitting is explained by the occurrence of a quadrupolar ordering around 80 K in YbN, YbP and YbAs.[1] In order to study the quadrupolar ordering in Yb monopnictides, inelastic neutron scattering experiments on the powder samples of YbSb and a single crystal of YbAs were measured.

The Γ 6 - Γ 8 excitation was observed around 17 meV using the triple axis spectrometer 6G(TOPAN) with a fixed kf. The energy spectra were measured down to 0.7 K including the quadrupolar ordering state. The energy spectra has almost no change at 5 K, that is consistent with the results of the molecular field calculation assuming O20-type ordering. The energy spectra between 0 and 3.5 meV were also measured by the triple axis spectrometer C1-1(HER). A strong q-dependence of the intensity at 0.4 meV was observed below 5 K. The q-dependence is enhanced with lowering the temperature. The qdependence is probably ascribed to the dispersion of the excitation in the quadrupolar ordering state. Further studies at lower energy are required.

Now we turn to the experimental results on a single crystal of YbAs.

Figure 1 shows the q-dependence of the energy spectra of YbAs at 3.3 K. The measurements were carried out on the triple

axis spectrometer 6G(TOPAN) with a fixed kf. The structure in the figure shows the transition between Γ 6 ground states and Γ 8 excited states.

The intensity at (2, 0, 0) is smaller than that at (3, 0, 0). This means the intensity of the zone center is smaller than that of the zone boundary. This situation is similar to PrOs4Sb12 that has a quadrupolar ordering. In the case of YbAs, the quadrupolar ordering around 80 K is still controversial. If there is no quadrupolar ordering around 80 K, our results indicate the importance of the quadrupolar interactions between 4f electrons. Further studies using the single crystal of YbAs is promising.

The observed q-dependence suggests that the theoretical approach beyond the molecular field approximation is required in order to understand the magnetic properties of Yb monopnictides.

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Fig. 1. Energy spectra at Q = (3, 0, 0) and (2, 0, 0).

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Successive magnetic phase transitions of DyB4

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A tetragonal rare-earth compound DyB4 has been attracting interest as a system where the quadrupolar moment of Dy might be fluctuating because of the geometrical frustration, which is geometrically equivalent to the Shastry-Sutherland model. The Dy lattice can be regarded as a combination of square and triangular connections because the nearest neighbor and the next nearest neighbor connections have almost the same distance.

DyB4 interestingly exhibits two phase transitons at TN1=20.3 K and at TN2=12.7 K. It is already established by neutron powder diffraction that an antiferromagnetic order occurs at TN1 with magnetic moments align along the c-axis and propagate along the [100] direction. What is intriguing is that the entropy of Rln2 still remain and that the elastic softening and absorption are enhanced in the temperature region TN2 < T < TN1. These results indicate that the quadrupolar degeneracy still remains even below TN1. We performed resonant x-ray scattering experiments and have revealed that the magnetic components within the ab-plane are short range ordered in this intermediate temperature region [1]. Below TN2, the inplane moments order with the corresponding quadrupolar moment <Ozx>, resulting in a uniform structural distortion from tetragonal to monoclinic.

Observation of the short range ordering by resonant x-ray scattering and the elastic softening suggests that the in-plane moments are fluctuating in a relatively long time scale; it looks ordered by x-ray but paramagnetic by ultrasonic measurement. By investigating this phenomenon by neutron diffraction, with intermediate time scale ~THz, we expect that we could clarify if the in-plane moments are really fluctuating and its fluctuation rate. We have performed neutron diffraction experiment on a single crystalline DyB4. The sample was grown by the floating-zone method using 11-Boron isotope to avoid absorption by 10-Boron in natural boron. The experiment was performed using a triple-axis spectrometer TOPAN, installed at the 6G port of JRR-3 in JAEA. The collimators of 15'-30'-30'-Blank was used with PG filter at neutron energy of 30.5 meV. Since the absorption by natural Dy is extremely large, the diffraction in this sample occurs in a very thin region at the surface less than 0.5 mm. Therefore the comparison of the scattering intensity among different diffraction peaks are impossible. Only the relative variation with temperature are analyzed.

Calculated magnetic structure factor from the magnetic structure model shows that the relative contribution to the intensity by the in-plane moment becomes large with increasing the c-axis component of the scattering vector. The (200) reflection involves no contribution from the in-plane component and reflects only the c-axis component. Then, we have measured the temperature dependences of (100), (101), (102), (103), and (200) reflections and analyzed the results.

Figure shows the temperature dependences of the (200) and (103) reflections. The (200) magnetic reflection arises only from the c-axis component, while the 94% of the structure factor of the (103) magnetic reflection is due to the ab-plane component. The lines in the figure are the calculated temperature dependences for each reflections, assuming the c-axis and ab-plane component illustrated in the bottom figure. The experimental results are well reproduced. This result shows that the in-plane component is indeed very weak in the intermediate temperature region, and it is ordered below TN2. Unfortunatelly, because the structure factor of the (103) reflection contains contribution from c-axis component by 6%, we could not tell if the in-plane component in TN2 < T < TN1 is zero or not although it is certainly less than 10%.

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Fig. 1. Temperature dependence of (200) and (103) reflections of DyB4. Lines are calculated temperature dependences. Bottom shows the c-axis (z) and ab-plane (x) components of the magnetic moment assumed for the calculations.

Chiral Helimagnetism in CuB2O4

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Helical magnet copper metaborate CuB2O4 has been paid attention from the viewpoint of chiral helimagnetic ordering. It shows various magnetic phase transitions at low temperature: paramagnetic state above TN (= 20 K), commensurate phase with weak ferromagnetic ordering in the range of T^* (= 10 K) < T < TN and incommensurate phase with helimagnetic ordering below T*. In the temperature close to the incommensurate-to-commensurate transition, neutron diffraction experiments show higher order satellite, which is an evidence for the formation of magnetic soliton lattice [1]. With increasing an applied magnetic field perpendicular to the helical c-axis, incommensurate phase II is observed in the region which was supposed to be commensurate magnetic structure [2]. The magnetic property of CuB2O4 can be interpreted by the lattice chiral XY model: commensurate-to-incommensurate transition is understood by the formation of chiral magnetic soliton lattice [3]. In order to detect chiral helimagnetic ordering, polarized neutron diffraction technique is powerful by comparing asymmetric magnetic satellite intensities between up-spin (+) and down-spin (-) neutron. Therefore, we performed polarized neutron diffraction experiments in the incommensurate phase.

The single crystal was grown by the spontaneous crystallization technique; slow cooling of CuO, Li2CO3 and B2O3 [3], using enriched 11B2O3 to avoid the large neutron absorption due to 10B. The polarized neutron diffraction experiments were performed at PONTA (5G), JRR-3M reactor in JAEA (Tokai). The experimental condition was 8 K under an applied magnetic field parallel to the scattering vec-

tor, due to aligning the neutron polarization parallel to the scattering vector. We observed incommensurate satellite peaks around (0,0,2), indexed as (0,0,2+q) and (0,0,2-q). As shown in Fig.1, we observed no difference between up-spin and downspin neutron intensities, which indicates no chiral magnetic ordering. However, symmetry operation based on its space group, I-42d, allows antiferrochiral helimagnetic ordering, which alternates right and left handed screws. In case of the antiferrochiral helimagnetic ordering, observing (1,1,4+q) and (1,1,4-q) reflections, which is not parallel to magnetic propagation vector (0,0,q), is needed. Therefore, in order to investigate antiferrochiral helimagnetic ordering, additional experiments are now in progress.

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Fig. 1. Observed satellite intensities around (0,0,2) at 8 K.

Magnetic Structure Analysis in CuB2O4

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Helical magnet copper metaborate CuB2O4 has been paid much attention because its strange behavior of magnetization can be interpreted by lattice chiral XY model; magnetic properties are understood by a formation of magnetic soliton lattice [1]. It shows various magnetic phase transitions at low temperature: paramagnetic state above TN (= 20 K), commensurate phase with weak ferromagnetic ordering in the range of T^* (= 10 K) < T < TN and incommensurate phase with helical magnetic ordering below T*. In the weak ferromagnetic phase, magnetic structure analysis with 4 circle diffractometer shows the commensurate structure with the propagation vector k0 = (0,0,0) [2]. However, the determined structure is inconsistent with NMR data [3] because of a few number of reflections with long incident wavelength of 2.36A. In order to argue the magnetic structure of incommensurate phase, it is important to determine magnetic structure of commensurate phase, because the lattice chiral XY model indicates that the strucure of the incommensurate phase reflects that of the commensurate phase.

Last year, we performed the neutron diffraction experiment at 4 circle diffractometer FONDER (T2-2), JRR-3M reactor in JAEA (Tokai) with short incident wavelength of 1.24A. However, we did not observe any magnetic scattering because of a small size of the sample, several magnetic domains under zero field and a small magnetic moment of Cu.

Therefore, in order to re-perform the experiments, we improved 2 points; 4 times larger size of the sample and field cooled measurement of 800 Oe along the <1,-1,0> by sandwiching permanent magnets, which were enough to saturate the spontaneous magnetic moment.

The single crystal, of which size was 5 x 4 x 7 [mm3], was grown by the spontaneous crystallization technique; slow cooling of CuO, Li2CO3 and B2O3, using enriched 11B2O3 to avoid the large neutron absorption due to 10B. The measurements were performed at 10 K and 30 K. Subtracting the intensities of 30 K from that of 10 K, we determined magnetic scattering intensities. We observed clear difference of scattering intensities between 10 K and 30 K. As shown in Fig.1, comparing (1,1,0) and (1,-1,0), magnetic scattering is observable only in (1,-1,0), which indicates that the magnetic domain of (h,h,0) reflection was well suppressed by the applied magnetic field. Now we are analyzing the magnetic structure with observed 40 reflections.

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Fig. 1. Magnetic scattering in (1,1,0) and (1,-1,0)

Magnetic Structure in the Shastry-Sutherland Lattice TmB4

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Rare-earth tetraborides RB4 have a tetragonal crystal structure with a space group P4/mbm which is characterized by the 2dimensional orthogonal dimers in the cplane. Such dimer systems are equivalent to the Shastry-Sutherland lattice (SSL) [1] where nearest-neighboring dimers geometrically frustrated. The frustration effect in ErB4 manifests itself as a plateau in the magnetization process M(B) at the half of the full moment of 9 mB/Er for B//c and B//a at 2 T and 10 T, respectively [2]. The frustration in DyB4 is caused by not only magnetic interaction but also the quadrupolar interaction [3]. A magnetization plateau appears for B//c, but neither magnetic plateau nor metamagnetic transition occurs for B//a. In order to investigate the origin in the magnetic anisotropy and rare-earth dependence on the magnetic plateau for B//a, we have searched other candidates with geometric frustration in magnetic or quadrupolar interaction among the RB4 series. The previous study of TmB4 indicates an antiferromagnetic order at 11.7 K by the measurements of temperature dependences of electrical resistivity and magnetic susceptibility [4]. We have studied the magnetization process and phase diagram of TmB4.

High-quality single crystal TmB4 was grown by floating zone method using a four-xenon lamps image furnace [5]. Magnetic susceptibility c(T) from 2 K to 300 K and M(B) up to 5 T in were measured by a Quantum Design-SQUID magnetometer. Electrical resistivity was measured by a DC 4-probe method. Specific heat C(T) measurement was performed by a relaxation method using a QD-PPMS system. Magnetoresistance R(B, T) was also measured by using a AC- transport puck of PPMS system up to 14 T. High field magnetization within the c-plane (a-axis) was measured by a long pulse magnet (pulse width ~10 ms) up to 50 T. From these experimental results, TmB4 exhibits three phase transitions at TN1=11.7K, T*=11K and TN2=10K. The phase transitions at TN1 and TN2 were already reported by Fisk et al. However, the phase transition at T* has been found by our single crystal study. c(T) shows highly anisotropic behavior for B//a and B//c. The effective moment was close to that of Tm3+ free ion. However the paramagnetic Curie temperature qP for B//c shows positive sign (+27.5 K) although those within c-plane were negative (-146.5 K). This behaviour can be fit by supposing the crystalfield excited states at 20 K and 40 K, respectively. In viewing of the crystal structure where Tm-Tm dimers stack along the c-axis and orthogonally aligned along with the [110] direction, antiferromagnetic correlation may be dominant within the cplane and ferromagnetic interaction dominant along the c-axis.

The M(B) for B//c has not only a 1/2 plateau at 2-3 T but also a 1/8 plateau at 1.7-1.4 T in the descending process. This hysteresis for a 1/8 plateau was observed in the temperature range from 1.8 up to 8 K. This hysteresis region is named as phase III hereafter. The phase III may be a state with a long period modulation by magnetic frustration for the phase III.

In order to clarify this prediction, we have performed neutron powder diffraction on the Kinken powder diffractometer for high efficiency and high resolution measurements, HERMES, of Institute Material Research, Tohoku University, installed at the JRR-3 reactor in JAEA, Tokai. Neutrons with a wavelength of 1.8265A were obtained by the 331 reflection Ge monochromator. The powder sample Tm11B4 of about 7 gram was filled in a vanadium cylinder with a diameter of 7 mm. Furthermore this cylinder was sealed in the aluminum can cell with a helium gas atmosphere. The cell was cooled down to 3K by using a closed cycle He gas refrigerator. The experiments were performed at 3K (antiferro-magnetic phase, IV), 10.7K (unknown phase, III), 11.7K (unknown phase, II) and 20K (paramagnetic phase, I).

Figure 1 shows the powder pattern for the four phases of TmB4. The pattern at 30 K was used for the nuclear scattering standard. Phase IV shows simple antiferromagnetic pattern with a propagation vector k4=(1, 0, 0). This is consistent with the previous report. The Phase III has been assigned with propagation vector k4 and an additional long period modulation vector k3=(0.13, 0, 0). Furthermore, the phase II was also indexed with the k4 and k2=(0.012, 0.036, 0) and k2=(0.012, 0.012, 0). However, we have not succeeded in obtaining complete fitting parameter because some unknown peaks were observed at this experiment.

Magnetization process M(B//c) in TmB4 shows 1/8 and 1/2 plateaus at 1.7-1.4 T and 2-3 T, respectively. M(B//a) shows a 1/2 plateau at 32 T. The anisotropy in the transition field is much higher than that in ErB4. From the magnetization, magnetoresistance, and specific heat measurements, a complex phase diagram in TmB4 was obtained. These characteristic behavior may be originated from geometric frustration in not only magnetic dipole interactions but also electric multipole interactions.

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Fig. 1. Fig. 1 Neutron powder diffraction patterns for the four phases of TmB4. The bottom shows a simulation of powder diffraction only by the nuclear peaks.

Competing magnetic correlations in the paramagnetic phase of HoB4

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A tetragonal rare-earth compound system of RB4 has been attracting growing interest as a system where both the quadrupolar and magnetic degrees of freedom are active in the geometrically frustrated lattice, which is equivalent to the Shastry-Sutherland model. We reported on the short-ranged magnetic correlation in DyB4. We observed a broadened peak profile of the resonant x-ray scattering in the intermediate phase where the quadrupolar moments are considered to be fluctuating [1]. HoB4 exhibits similar phase transitons as in DyB4 at TN1=7.5 K and at TN2=5.9 K. Results of first neutron diffraction experiment has already been reported by us that an incommensurate magnetic order takes place at TN1 and a first-order-like phase transition at TN2 into a commensurate structure described by q=(100) [2]. Resonant x-ray scattering shows that the low-temperature phase below TN2 is similar to that of DyB4, where both the magnetic and quadrupolar moments are fully ordered with monoclinic distortion. In the present experiment, we concentrated our attention to the broad diffuse scattering in the intermediate phase TN2<T<TN1 and in the paramagnetic phase TN1<T.

We have performed inelastic neutron scattering experiments on a single crystalline HoB4. The sample was grown by the floating-zone method using 11-Boron isotope. The measurement was performed on a triple-axis spectrometer TOPAN, installed at the 6G port of JRR-3 in JAEA. The collimators of B-30'-30'-B was used with PG filter at final neutron energy of 13.5 meV. Scans over a wide reciprocal lattice space were made on the (HOL) plane.

One of the surprising results is that a very broad magnetic diffuse scattering occur around $(0\ 0\ 0.5)$ and $(1\ 0\ 0)$ simultaneously. These scatterings remain up to about 20 K.

Figure 1 shows the intensity map at T=9 K in the paramagnetic phase. In the region TN2<T<TN1, which is defined as phase II, satellite reflections develop at (d d $0.5 \pm d'$) $(d=\pm 0.022, d'=0.07)$ on the diffuse scattering around (0 0 0.5). It should be noticed that another strong diffuse scattering exists around (1 0 2), which is equivalent to (1 0 0), the order parameter in phase III below TN2. This result indicates that two order parameters are competing; one is antiferromagnetic order with q=(d d $0.5 \pm d'$), presumably due to RKKY interaction, and the other is antiferromagnetic and quadrupolar order with monoclinic distortion as in DyB4 with $q=(1 \ 0 \ 0)$. It is also noticed that this behavior of phase transition is quite similar to that of HoB2C2.

Measurements of excitation spectra exhibit two clear peaks at 1 meV and 2 meV. The intensity becomes strong expecially around (1 0 0) and (0 0 0.5) and the peak energy seems to go soft with decreasing temperature to TN2, while the energy at other wavevectors do not change. The detail of this softening behavior will be studied next.

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Fig. 1. Intensity map of HoB4 at 9K in the paramagnetic phase.

Anomalous magnetic transitions of TbCu2Si2

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Anomalous magnetic behaviors have been reported on a TbCu2Ge2 single crystal [1]; It has the tetragonal ThCr2Si2-type crystal structure (space group: I4/mmm), orders antiferromagnetically below TN=12.3 K and shows an additional magnetic transition at Tt=9.3 K. A one-step metamagnetic transition appears around 17 T along the hard magnetization direction at low temperatures and persists above TN up to Tm=25 K where a broad peak appears in temperature dependence of magnetic susceptibility. Recently it has been reported that the TbCu2Si2 single crystal compound shows very similar magnetic behaviors to those of TbCu2Ge2 [2]; it orders antiferromagnetically below TN=11.9 K and has additional magnetic anomalies at Tt=9.1 K and Tm=25 K. The origin of those anomalies has unknown yet.

In order to investigate those transitions, neutron diffraction study has been performed on the TbCu2Si2 single crystal using the triple axis spectrometer HQR installed at JEARI, Tokai, Japan.

At low temperatures, antiferromagnetic reflections associated with the propagation vector k=(1/2, 0, 1/2) have been observed. This result is agreement with that reported by Pinto et al. [3]. The antiferromagnetic structure is characterized by the propagation vector k and has Tb moments parallel to the [110] directions in the basal plane. Above Tt, no new magnetic reflection could be detected. Temperature dependence of the antiferromagnetic peak (1/2 0 1/2) intensity shows in Fig.1. The intensity decreases gradually with increasing temperature and disappears above TN=12 K. No distinctive anomaly can be seen around Tt. A reorientation of the Tb moments from [110] to [100] in the basal plane at Tt has been proposed from the result of resonant and non-resonant X-ray magnetic scattering [4]. There is, however, no clear evidence for the spin reorientation from this neutron measurement. With respect to the transit1on at Tm, no magnetic reflection could be observed; existence of magnetic correlation could not be found. The origin of transition at Tt and Tm is now puzzling yet. Further study is need.

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Fig. 1. Temperature dependence of antiferromagnetic $(1/2 \ 0 \ 1/2)$ peak intensity in TbCu2Si2

Magnetic Structure of CrB2 in Magnetic Field

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CrB2 is an itinerant anti-ferromagnet with TN = 88 K, of which crystal structure is AlB2-type (P6/mmm).

In the magnetically ordered state of CrB2, a cycloidal magnetic structure, in which the magnetic moments of 0.5 μ B turn in the c*-[110] plane with the propagation vector of 0.285[110], was proposed by Funahashi et al[1]. However, NMR data is inconsistent with the cycloidal model, Spin echo 11B NMR spectra suggest commensurate structure[2]. Why the inconsistent data are obtained between NMR and neutron data? NMR experiments were performed with magnetic field however, neutron diffraction experiments were performed without magnetic field.

Therefore, in order to obtain the consistent data of CrB2, we performed the neutron diffraction experiments with an applied magnetic field at 3 circle diffractometer PONTA (5G), JRR-3M reactor in JAERI (Tokai).

The single crystals of CrB2, whose size are length 22 \times diameter 5 [mm3] and length 7 \times diameter 5 [mm3] were grown by the conventional floating zone method with Ar atmosphere, using enriched 11B to avoid the large neutron absorption due to 10B.

The measurements were taken at 1.8 K and applied magnetic field up to 5.9T. We applied magnetic field along the [001] and [1-10] axes, and observed (hh0). As shown Fig1, the propagation vector and scattering intensity did not change along the [001] axis by changing the magnetic field, and also along the [1-10] axis. We concluded that the magnetic structure did not change against the magnetic fields up to 5.9T. The result shows commensurate 120 ° state might be stabilized with larger magnetic field.

In conclusion, we have determined the cycloidal magnetic structure under magnetic field up to 5.9T.

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Fig. 1. Observed intensity at 1.8K,H//[001]

Competition of magnetic correlations in the paramagnetic phase of HoB4

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A tetragonal rare-earth compound system of RB4 has been attracting growing interest as a system where both the quadrupolar and magnetic degrees of freedom are active in the geometrically frustrated lattice, which is equivalent to the Shastry-Sutherland model. We reported on the short-ranged magnetic correlation in DyB4. We observed a broadened peak profile of the resonant x-ray scattering in the intermediate phase where the quadrupolar moments are considered to be fluctuating [1]. HoB4 exhibits similar phase transitons as in DyB4 at TN1=7.5 K and at TN2=5.9 K. Results of first neutron diffraction experiment has already been reported by us that an incommensurate magnetic order takes place at TN1 and a first-order-like phase transition at TN2 into a commensurate structure described by q=(100) [2]. Resonant x-ray scattering shows that the low-temperature phase below TN2 is similar to that of DyB4, where both the magnetic and quadrupolar moments are fully ordered with monoclinic distortion. In the present experiment, we concentrated our attention to the broad diffuse scattering in the intermediate phase TN2<T<TN1 and in the paramagnetic phase TN1<T.

We have performed inelastic neutron scattering experiments on a single crystalline HoB4. The sample was grown by the floating-zone method using 11-Boron isotope. The measurement was performed on a triple-axis spectrometer TOPAN, installed at the 6G port of JRR-3 in JAEA. The collimators of B-30'-30'-B was used with PG filter at final neutron energy of 13.5 meV. Scans over a wide reciprocal lattice space were made on the (HOL) plane.

One of the surprising results is that a very broad magnetic diffuse scattering occur around $(0\ 0\ 0.5)$ and $(1\ 0\ 0)$ simultaneously. These scatterings remain up to about 20 K.

Figure 1 shows the intensity map at T=9 K in the paramagnetic phase. In the region TN2<T<TN1, which is defined as phase II, satellite reflections develop at (d d $0.5 \pm d'$) $(d=\pm 0.022, d'=0.07)$ on the diffuse scattering around (0 0 0.5). It should be noticed that another strong diffuse scattering exists around (1 0 2), which is equivalent to (1 0 0), the order parameter in phase III below TN2. This result indicates that two order parameters are competing; one is antiferromagnetic order with q=(d d $0.5 \pm d'$), presumably due to RKKY interaction, and the other is antiferromagnetic and quadrupolar order with monoclinic distortion as in DyB4 with $q=(1 \ 0 \ 0)$. It is also noticed that this behavior of phase transition is quite similar to that of HoB2C2.

Measurements of excitation spectra exhibit two clear peaks at 1 meV and 2 meV. The intensity becomes strong expecially around (1 0 0) and (0 0 0.5) and the peak energy seems to go soft with decreasing temperature to TN2, while the energy at other wavevectors do not change. The detail of this softening behavior will be studied next.

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Fig. 1. Intensity map of the magnetic diffuse scattering of HoB4 at 9 K in the paramagnetic phase.

Magnetic structure analisys of incommensurate phase in multiferroic RMn₂O₅

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RMn₂O₅ shows a colossal magnetoelectirc effect in which magnetization is induced by electric field or inversely electric polarization is induced by magnetic field. The key ingredient in the CME effect is multiferroics in which (anti)ferromagnetic and ferroelectric orders coexist and connect with each other. It has been experimentally shown that this system shows successive magnetic transitions of incommensuratecommensurate-incommensurate phases with decreasing temperature, where the bulk electric polarization is induced only in the commensurate phase. However, the relation between the microscopic magnetism (magnetic structure) and bulk dielectrics in this system has been not fully understand yet. We thus performed magnetic structure analyses using single crystals for the low temperature incommensurate phase to compare the magnetic structure of the incommensurate phase with that of the commensurate phase solved previously.

The measurements were performed at four circle neutron diffractometer FONDER installed at T2-2 beam port in JRR-3M. In this report, we introduce the results only for YMn₂O₅. Integrated intensities of magnetic reflections were collected at T = 7.5 K. Total number of observed magnetic reflections are more than 200 including zero intensity. Note that the averaged crystal structure at T = 7.5 K was also solved successfully to obtain the absolute quantities of magnetic structure factor. Since the incommensurate magnetic peaks are located at $\pm q_M = (1/2 \pm \delta_x 0 1/4 - \delta_z)$, the reciprocal scan along Q_x was carried out, which can integrate a pair of magnetic peak intensities accurately. Figure 1 shows observed structure factors as absolute quantity in $(h \ 1 \ l)$ zone taken at (a); 25 K (commensurate phase) and (b); 7.5 K

(incommensurate phase). It is seen that the distribution of amplitude for the structure factor at incommensurate phase is similar but is not completely same as that at commensurate phase, indicating that the magnetic structure in the incommensurate phase is different from that in the commensurate phase. Detailed structure analysis is in progress.



Fig. 1. Observed magnetic structure factors in $(h \ 1 \ l)$ zone at (a); 25 K (commensurate phase) and (b); 7.5 K (incommensurate phase).

Spin dymamics of multiferroic compound of HoMn₂O₅

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RMn₂O₅ shows a colossal magnetoelectirc effect in which magnetization is induced by electric field or inversely electric polarization is induced by magnetic field. The key ingredient in the CME effect is multiferroics in which (anti)ferromagnetic and ferroelectric orders coexist and connect with each other. It has been experimentally shown that this system shows successive magnetic transitions of incommensuratecommensurate-incommensurate phases with decreasing temperature, where the bulk electric polarization is induced only in the commensurate phase. The microscopic magnetism in the view point of magnetic structure has been studied intensively to clarify the relation between the microscopic magnetism and bulk dielectrics in this system. However, there is only a few studies about the spin and lattice dynamics, which might be correlated with each other in this multiferroic system. In the present study, we have tried to detect "electromagnons", of which excitations can combine with the dielectric order parameter, to clarify the microscopic origin of the colossal magnetoelectric effect.

The experiments were performed using a single crystal of HoMn₂O₅ at TOPAN, AKANE and HER spectrometers installed at 6G, T1-3, and C1-1 beam ports in JRR-3M, respectively. In this paper, we introduce the summary of results taken at TOPAN. The constant-Q scans were carried out around magnetic zone center $Q \sim (0.5 \ 0 \ 1.75)$ at $T = 3 \ \mathrm{K}$ (incommensurate phase), 25 K (commensurate phase), and 50 K (paramagnetic phase). Figure 1(a) shows the energy spectra at $Q = (0.7 \ 0 \ 1.75)$ taken at three temperatures. It is seen that there are temperature dependent signals in the spectra around ω = 3 \sim 5 meV. In order to know the

details about these spectra, we took the temperature variation of the signals at $\omega = 3, 4, 5$ meV. As seen in Fig. 1(b), the signals gradually change with changing temperature. However, in the data of $\omega = 3$ and 4 meV, the intensities starts to deviate from each other below \sim 18 K, where the magnetic order changes from commensurate to incommensurate. These signals are almost Q-independent, indicating that the excitation is a crystal field excitation associated with 4f-moment of Ho³⁺ ion. These results suggest that the correlation between neighbored Ho³⁺ moments changes at the transition from the commensurate phase to the incommensurate phase.



Fig. 1. (a); Energy spectrum at $Q = (0.7 \ 0 \ 1.75)$ taken at $T = 3 \ K$, 25 K, and 50 K. (b); Temperature dependences of excitation signals at $\omega = 3, 4, 5 \ \text{meV}$ taken at $Q = (0.7 \ 0 \ 1.75)$.

Field-induced ordered state in the rare-earth compound Pr_{0.97}La_{0.03}Pb₃

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Very recently, we have found that quadrupoles are aligned with long periodic structures in quadrupole ordering states in the rare-earth compound PrPb₃.[1] In our work, we performed neutron diffraction experiments on in magnetic fields along the [001] direction. We revealed that field-induced magnetic moments should be distributed with the propagation vectors of $k_1 = [1/2 \pm \delta, 1/2, 0]$ and/or $k_2 = [1/2, 1/2 \pm \delta, 0]$ ($\delta \sim 1/8$), indicating that quadrupoles are aligned with a sinusoidal (incommensurate) structure below the quadrupolar ordering temperature In the dilute system $Pr_{1-x}La_xPb_3$, $T_{\rm O}$. it has been reported that $T_{\rm O}$ would go down below 0.1 K even at the composition x=0.02.[2] It was expected from the La composition dependence of T_Q that the quadrupolar ordered state would disappear at around the composition of x = 0.025. On the other hand, in specific heat measurements on Pr_{0.97}La_{0.03}Pb₃, an anomaly would appear only in magnetic fields.[3]

In the present work, in order to confirm the existence of the field-induced ordered state and reveal the order parameter, we performed neutron diffraction experiments in magnetic fields. We measured a single crystalline sample with high quality which was prepared by the Bridgman method with using a Molybdenum crucible. In the neutron diffraction experiments, the sample was cooled down with a ³He-⁴He dilution refrigerator, and the magnetic field was applied up to 5 T with a superconductor magnet.

We found superlattice reflections at

 $q_1 = (1/2 \pm \delta \ 1/2 \ 0)$ and/or $q_2 = (1/2 \ 1/2 \pm \delta)$ 0) ($\delta \sim 1/8$) only in the magnetic fields above 1 T. Fig. 1 shows the field dependence of the square root of the integrated intensity at around Q = (1/2 3/8 0) and the field dependence of the peak position (k)at T=0.23 K. Apparently, the square root of the intensity was induced linearly from the field of ~ 1 T, indicating the antifferomagnetic component should be induced linearly by increasing the fields above 1 T. The peak position k changes continuously around k=0.38, which means that quadrupoles are probably distributed with the incommensurate structure. From these results, it should be noted that the fieldindeucd ordered state in Pr_{0.97}La_{0.03}Pb₃ is the same as the one found in the ordered phase in PrPb₃.

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Fig. 1. Field dependence of the square root of the intensity(\bigcirc) and the peak position(\square) of the field-induced magnetic reflection at *T*=0.23 K.

Magnetic and Crystal Structures of Tm2CrS4

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Y2CrS4 shows an antiferromagnetic transition at 65 K due to the ordering of Cr2+ ions. Its powder neutron diffraction patterns at both 90 K and 10 K could be refined by using the orthorhombic Er2CrS4type structure (Pca21, No. 29) [1,2] while the magnetic structure was determined by using the pattern at 10 K. Recently we measured magnetic susceptibility of Tm2CrS4 and found magnetic anomalies at ca. 60 K and lower temperatures.

In this study, neutron diffraction measurements of Tm2CrS4 were performed at 80 K, 50 K, 40 K, 15 K, 10 K, and 3 K, on the high efficiency and resolution powder diffractometer, HERMES, of Institute for Materials Research, Tohoku University, installed at the JRR-3M Reactor in JAEA (Tokai). The wavelength of a neutron incident is 1.8265

Any distinct crystallographic phase transition was not observed between 80 K and 3 K. At 80 K, lattice parameters were determined to be a = 12.4337(13), b = 7.4470(8), and c = 12.4082(13), and decreased with decreasing temperature. Rietveld refinements confirmed that the crystal structure was isomorphous with Y2CrS4 at all measured temperatures.

Below 60 K, some magnetic peaks were observed and the peak intensities were gradually increased with decreasing temperature. This suggests that paramagnetic chromium and thulium ions were ordered together. These magnetic peaks could be indexed on the same crystallographic unit cell. In order to determine the magnetic structure, the magnetic peaks have been analyzed with the following assumptions. (1) Magnitudes of magnetic moments of chromium and thulium ions are the same for respective kinds of ions. (2) Magnitudes of magnetic moments for chromium were fixed to be 3.27 Bohr magneton obtained by the refinement of neutron diffraction patterns at 10 K for Y2CrS4 [1,2]. (3) The directions of all magnetic moments are collinear. These assumptions have led to a magnetic structure as shown in Fig. 1. In this structure, magnetic moments of chromium and thulium ions order antiferromagnetically in each set of the 4a sites. The directions of all magnetic moments are parallel to the c axis. The refined magnetic moment of Tm is 4.57(4) Bohr magneton, which is smaller than 7 Bohr magneton expected as the trivalent free ions.

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Fig. 1. Magnetic structure of Tm2CrS4.

Neutron Diffraction Study of Magnetic Transitions in M2(OD)3X

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Recently we found a new geometric frustration system Cu2(OH)3Cl and Co2(OH)3Cl with a 3-dimensional network of corner-sharing tetrahedrons of the Cu2+ and Co2+ spins, respectively 1-3. We found coexisting antiferromagnetic order and spin fluctuation in Cu2(OH)3Cl 2, and a kagome-ice-like partial ferromagnetic order in Co2(OH)3Cl 3, which raise great interest on this new material system. Further, we proceeded to investigate the magnetic structures in other transition metal hydroxyhalide compounds Ni2(OH)3Cl, Mn2(OH)3Cl, and Mn2(OH)3Br.

Neutron diffraction experiment was carried out at T1-3 (Hermes) using powder sample of Ni2(OD)3Cl, Mn2(OD)3Cl, and Mn2(OD)3Br.

Strong magnetic reflections were observed for Ni2(OD)3Cl, Mn2(OD)3Cl, and Mn2(OD)3Br, respectively, at low temperatures. They agree well with antiferromagnetic transitions observed with magnetic susceptibility measurements at TN = 5 K, TN = 3.4 K and TN = 3.3 K, respectively, for Ni2(OD)3Cl, Mn2(OD)3Cl, and Mn2(OD)3Br. Determination of their respective magnetic structures are in progress.

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Fig. 1. Neutron diffraction patterns for Ni2(OD)3Cl, Mn2(OD)3Cl and Mn2(OD)3Br, respectively.

Magnetic structure and crystalline-electric-field splitting in the tetragonal rare-earth compound CeB_2C_2

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The rare-earth borocarbide CeB₂C₂ exhibits long-range magnetic order at T_{N} = 7.3 K where incommensurately modulated structure with the modulation vector q_M = (0.161, 0.161, 0.100) is stabilized [1]. Magnitude of the ordered moment was inferred to be very small. With applied magnetic field of about 1 T in the basel plane, CeB_2C_2 is known to exhibit metamagnetic behavior, recovering the magnetic moment of more than 0.9 μ_B [2]. In order to elucidate the magnetic structure of the ordered incommensurate phase, and to gain insight into the origin of metamagnetic transition, we have performed both the neutron elastic and inelastic scattering experiments.

Single crystals of Ce¹¹B₂C₂ were grown by the floating zone method. A single crystal was mounted in a liquid-He cryostat with a superconducting magnet and cooled down to T = 2.0 K (below T_N).

First, we observed field dependence of the Bragg intensities. The magnetic field was applied along the [110] direction. Shown in Fig. 1(a) is the field dependence of the integrated intensity observed at the incommensurate peak position $Q = (\delta, \delta, 1 - \delta')$ with $\delta = 0.166$ and $\delta' = 0.110$. Also shown as Fig. 1(b) is the field dependence at Q = (2, 2, 1). In both the figures, an abrupt change was observed at H = 0.9 T. Since the incommensurate peak intensity decreases whereas the intensity at the lattice peak position Q = (2, 2, 1) increases, we may conclude that the metamagnetic transition observed in the M - H curve is due to the abrupt change of the magnetic structure from the low-field incommensurate phase to the field-induced ferromagnetic/ferrimagnetic structure. Detailed magnetic structure

analysis is now in progress.

K. Ohoyama *et al.*, J. Phys. Soc. Jpn. **72** (2003) 3303.
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Fig. 1. Field dependence of the integrated intensity measured at (a) $Q = (\delta, \delta, 1-\delta')$ and (b) Q = (2,2,1).

Magnetic Structures of Square-Lattice Antiferromagnets (MX)LaNb2O7 (M=Cu, Mn...; X=Cr, Br)

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In recent years, much attention has been given to low-dimensional antiferromagnetic (AFM) quantum spin systems that have a ground state with no long-range magnetic order and an energy gap in the magnetic excitation spectrum. Among them, the S = 1/2 frustrated square lattice AFM system (J1-J2 model) is of special importance in light of Anderson's resonating valence bond (RVB) concept to explain high-Tc superconductivity in doped layered cuprates. Low-temperature topotactic strategies such as intercalation/deintercalation offer effective routes for the design and construction of new twodimensional (2D) magnetic materials.

Topochemical ion exchange reaction has been employed to obtain a doublelayered Dion-Jacobson phase such as (CuCl)LaNb2O7 starting from a nonmagnetic mother compound RbLaNb2O7 [1-4]. As shown in Fig. 1 (a), the structure consists of magnetic [CuCl] planes having an S = 1/2 square lattice arrangement that are widely separated by nonmagnetic double perovskite slabs. Thus it can be a very good candidate for the 2D quantum square lattice system. In 2004, we performed inelastic neutron scattering experiments on (CuCl)LaNb2O7 using the ISSP-PONTA triple-axis spectrometer installed at a 5G beam port of JRR-3M at the Japan Atomic Energy Research Institute. It has been revealed that this system indeed provides a new class of two-dimensional (2D) Heisenberg spin systems that has a spin-singlet ground state with a finite energy gap of 2.3 meV [5, 6]. Quite recently, we prepared isostructural compound (CuBr)LaNb2O7 using a method similar to that to obtain (CuCl)LaNb2O7. In spite of the fact that the lattice parameters are almost the same,

the magnetic properties of the copper bromine system is completely different from the spin-liquid state observed in the copper chlorine system. In contrast to the spin-gapped behavior in the Cl sample, the magnetic susceptibility of the Br sample shows the gapless behavior with an antiferromagnetic ordering at 31 K. In order to reveal the magnetic structure, we demonstrate the powder neutron diffraction profiles measured at 3 K and 45 K. We found two magnetic peaks centered at 2 θ = 15° and 20° that can be indexed as (1/2 0 1/2) and (1/2 0 3/2), respectively, indicating the so-called collinear type (or stripe) ordering, where arrays of ferromagnetic chain along [100] align in an antiferromagnetic manner in the square lattice (see Fig. 1(a)). The collinear ordering is expected to occur when the magnitude of the next-nearest-neighbor exchange interaction is greater than that of the nearest-neighbor interaction. To date, only three examples have been reported to exhibit collinear ordering among S =1/2 square lattice systems. Therefore, it would be interesting to examine the nature of the collinearly ordered state and to compare with the spin liquid state in the isostructural (CuCl)LaNb2O7. To further understand the nature of the unusual ground states observed in

the unusual ground states observed in (CuCl)LaNb2O7 and (CuBr)LaNb2O7, it would be quite interesting to compare these compounds with other related materials. Thus, in this study, we performed powder neutron diffraction experiments on the isostructural (MCl)LaNb2O7 (M=Co, Cr, Mn), using the IMR-HERMES diffractometer (T1-3). Neutrons with a wavelength of 1.81386(7) were obtained by the 331 reflection of the Ge monmochro-

mator, and the 12'-blank-sample-18' collimation was employed. A powder sample of 4 g was put into a vanadium cylinder. Figure 1(b) demonstrates the neutron diffraction profiles of (CoCl)LaNb2O7 obtained at 8 K and 100 K. The lower temperature data have additional magnetic reflections characterized by the propagation vector (pi, 0, pi), indicating the collinear type of magnetic ordering. The magnetic ordering temperature is obtained to be 55K by measuring the intensity of (1/2, 0, 1/2). The manganese analogue also exhibits the collinear order but at slightly higher temperature, while the neutron diffraction profile of the chromium analogue may indicate incommensurate magnetic structure at low temperatures.

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Fig. 1. (a) Crystal and magnetic structure of (MCl)LaNb2O7. (b) Powder neutron diffraction profles of (CoCl)LaNb2O7 at 8 K and 100 K.

Magentic structures of R2Pd2X (X=In, Sn)

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We have performed neutron powder diffraction measurements on R2Pd2Sn (R=Dy, Ho, Er) where the magnetic R atoms form the Shastry-Sutherland lattice (SSL). All the compounds show two or three successive magnetic transitions at low temperatures. In the lowesttemperature magnetic phase, all the compounds are found to have a doubled c-axis magnetic lattice constant, different result from a typical SSL compound DyB4. In the intermediate magnetic phases, incommensurate magnetic Blagg peaks were observed; therefore the phase transition from the intermediate to the lowest temperature phases is an incommensurate to commensurate lock-in magnetic transition.

Polarized Neutron Inelastic Scattering Study of Spin Fluctuation in $La_{2-x}(Sr,Ba)_xCuO_4$

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The recent discovery of universal magnetic excitation in the high- T_c cuprates, which shows a novel hour-glass shape dispersion, has provided an important insight into the magnetic origin of the superconductivity. Among the several pictures proposed to explain the hour-glass dispersion, the stripe model is expected to be an important candidate. We have performed inelastic polarized neutron scattering on stripe-ordered La_{1.875}Ba_{0.125}CuO₄(LBCO 1/8) and compared the results with those of $La_{1.92}Sr_{0.08}CuO_4(LSCO 8 \%)$ which has no stripe order. The purpose of this experiment is to understand the effects of the stripe order on the low energy magnetic excitations and hence have an insight into the origin of the universal magnetic excitation.

The experiments have been performed at the TAS-1 triple axis spectrometer operated in a uniaxial polarization mode. Vertically and horizontally focused Heusler monochromator and analyzer were used. Inelastic measurements were done with a fixed final neutron energy of 14.7 meV, and a spin-flipper and a PG filter were placed after the sample.

Figure 1 shows profiles observed at the energy transfer 4 meV in the vertical-field (VF) spin-flip (SF) and the horizontal-field (HF) SF channels along the A-C trajectories shown in the bottom figure. Remarkably, it is shown that for LSCO 8 % the HF-SF signal is almost double of the VF-SF signal indicating isotropic spin fluctuations, whereas for LBCO 1/8 both the channels show comparable cross sections indicating anisotropic spin fluctuations where those along the *c*-axis are suppressed. We have also confirmed by the polarized neutron diffraction that the Cu spins

are confined in the CuO₂ plane, that is, the a - b plane, in the stripe-ordered state.

These results demonstrate that the polarization of the low energy spin fluctuation is different between the samples with and without the stripe order. A possible explanation is that the in-plane gap of the excitation which is observed in the non-doped La_2CuO_4 is recovered in the stripe-ordered sample. Further polarized and unpolarized neutron experiments are in progress to confirm this.



Figure 1: Polarized neutron scattering cross section at the energy transfer of 4 meV observed in the VF-SF and HF-SF channels. The data for LSCO 8 % are measured along the A (circles) and B (squares) trajectories, while those of LBCO 1/8 are measured along the C trajectory. The bottom figures show the scan trajectories in the momentum space and the definition of the polarization axes.

Successive Phase Transitions of LuBaCo₄O₇ with Kagome and Triangular Lattices

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Spin systems on the pyrochlore, triangular and kagome lattices are well-known examples of geometrically frustrated systems and expected to exhibit various interesting properties induced by strong magnetic fluctuations. RBaCo₄O₇ (R = Ca, Y and rare-earth elements) is one of typical examples of such systems, because it has both triangular and kagome lattices of Co spins.^{1–3)}

Magnetic, thermal and neutron diffraction measurements have been carried out on single-crystal samples of LuBaCo₄O₇. Anomalies of the magnetic susceptibility have been found at temperatures $T_{a1} \sim 70$ K and $T_{a2} \sim 50$ K. We have also found a secondorder structural transition at $T_{c1} \sim 165$ K and a first-order structural transition at $T_{c2} \sim 105$ K (T_{c2} ' ~ 80 K) with increasing (decreasing) temperature.

We have observed reflections at Q-points (h'/20l) and (h'/2h'/2l) (h' = odd; group A)below T_{c1} , and additionally at the Q-points $(h''/3\pm\delta h''/3\pm\delta l)$ (h''/3 = noninteger number; group B) below T_{c2} , in the reciprocal space of the hexagonal unit cell ($a = b \sim$ 6.27 Å, $c \sim 10.24$ Å). We have found that at $T < T_{c2}$, the line shapes of the reflections at the Q-points of group A can be described by Lorentzian-type ones, while at $T_{c2} < T <$ T_{c1} , they have Gaussian-type ones. From the |Q|-dependence of the integrated intensities, the Gaussian and Lorentzian components can be regarded as nuclear and magnetic origins, respectively. The magnetic (Lorentzian) component is dominant below T_{c2} and only the nuclear (Gaussian) component exists at T between T_{c2} and T_{c1} . For the reflections at the **Q**-points of group B, the δ value is T-dependent. These reflections have broad Lorentzian profiles and can be considered to be magnetic.

Below T_{c2} , we can easily find that the intensities of the nuclear superlattice reflections are almost zero and the intensities of the magnetic reflections increase gradually with decreasing T. The profile shape of the magnetic peaks indicates that the magnetic correlation is not long-ranged even at 10 K, and the magnetic correlation length is estimated to be $\xi \sim 100$ Å. From the magnetic structure analyses, the magnetic reflections at the Q-points of groups A and B can be considered to originate from the moments on the kagome and triangular lattices, respectively.

For both YBaCo₄O₇ and LuBaCo₄O₇ systems, the Co moments of the kagome and triangular lattices exhibit short-range orders with different magnetic periods.²⁾ However, several differences have been found between the behaviors of the magnetic reflections of $YBaCo_4O_7$ and $LuBaCo_4O_7$. In $YBaCo_4O_7$, the growth of the magnetic correlation and a similar structural distortion were found to appear simultaneously at its T_{c1} (~ 105 K) with decreasing T, whereas in LuBaCo₄O₇, the short-range magnetic correlation grows only below T_{c2} . The periods of the magnetic modulation of the triangular lattice are also different between these two systems. At low temperatures, the structural distortion of $LuBaCo_4O_7$ system is different from that of YBaCo₄O₇, which induces the significant differences in the magnetic properties between these two systems.

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Direct Observation of the Pressure-Induced Ferromagnetic Order in Valence Transition Material YbInCu₄

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YbInCu₄ crystallizes in the cubic AuBe₅ (C15b)-type structure. At ambient pressure with decreasing temperature, the compound undergoes the first-order isomorphic valence transition at $T_{\rm V} = 42$ K with the increase of the unit-cell volume of about 0.5 %. At $T_{\rm V}$, the 4f states of Yb ions change from high temperature (HT) well-localized states of Yb³⁺ to low temperature (LT) mixed-valent states of Yb^{2.9+}. Recent studies under high pressures have revealed that the nonmagnetic LT phase is completely suppressed and the magnetic HT phase is stabilized in all temperature ranges above $P_{\rm C} = 2.5$ GPa. Furthermore, it is suggested that the long-range magnetic order appears below $T_{\rm C} = 2.4$ K at 2.5 GPa.¹⁾ On the other hand, this compound shows the superconductivity above 0.7 GPa below 1.4 K. This pressure-induced superconductivity survives up to 4 GPa.²⁾ The purpose of our work is to elucidate directly and microscopically the pressure-induced magnetic order. We performed high-pressure neutron diffraction experiments using the triple-axis spectrometer TAS-1. The high-pressure was generated up to 6.2 GPa by a newly-developed hybrid-anvil device.³⁾ The pressure transmitted by the glycerin medium was hydrostatic even at 7.0 GPa. The sample size was about $1.0 \times 0.5 \times 0.25 \text{ mm}^3$. The pressure was applied along the $[01\overline{1}]$ direction of the sample and the diffraction plane was the [100]-[011] one. We used a neutron focusing device in order to increase the effective neutron intensity at the sample position.⁴)

We have successfully observed the distinct increase of the intensities only at the ferromagnetic ($\overline{1}11$) or ($\overline{1}\overline{1}\overline{1}$) reciprocal lattice points below about $T_{\rm C} = 2.5$ K at 4.0 GPa and 6.2 GPa. As an example, we show the temper-

ature dependence of the intensities at 6.2 GPa in Fig. 1. This result indicates that the ferromagnetic order appears at least above 4.0 GPa and $T_{\rm C}$ is hardly affected by the pressure. On the other hand, the estimated magnetic moment in the ferromagnetic order is about 0.68 $\mu_{\rm B}$ and 0.76 $\mu_{\rm B}$ per Yb ion at 4.0 and 6.2 GPa, respectively. These values are quite large compared to the Y-diluted system Yb_{0.8}Y_{0.2}InCu₄, which shows the weak ferromagnetic order of 0.05 $\mu_{\rm B}$ per Yb ion below $T_{\rm C} = 1.7$ K and above 0.8 GPa.⁵)



Figure 1: Temperature dependence of the intensities at the $(\overline{1}\overline{1}\overline{1})$ ferromagnetic point and at the $(\overline{2}\overline{1}\overline{1})$ antiferromagnetic point for P = 6.2 GPa.

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Magnetic Structure of $TbRhIn_5$

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Intermetallic compounds ATX₅ (A: Lanthanoid or Actinide, T: Transition metal, X: In or Ga) with the tetragonal HoCoGa₅type (P4/mmm) crystal structure, so called "115", attract strong interest because of the heavy fermion superconductivity in Ce-115 and Pu-115 or various magnetic structures in U-115 and Np-115. On the other hand, RRhIn₅ (R: Nd, Tb, Dv, Ho)¹⁾ are local antiferromagnets. The magnetic susceptibility shows Curie-Weiss behaviour, where the Néel temperatures are in good agreement with de Gennes factor. A similar two-step metamagnetic transition is observed in RRhIn₅ (R: Nd, Tb, Dy, Ho), when the magnetic field is applied along the *c*-axis (easy axis). We performed neutron scattering experiment in order to determine the magnetic structure of TbRhIn₅. We used triple-axis spectrometers LTAS and MUSASI (low angle beam port) installed in JRR-3 guide hall.

Figure.1 shows the longitudinal scan profile of the $(1/2 \ 0 \ 1/2)$ antiferromagnetic reflection at 2.8 K, which disappeared at 50 K above Neel temperature. Inset shows the temperature dependence of $(1/2 \ 0 \ 1/2)$ peak intensity. We estimated the Neel temperature T_N to be approximately 47.3 K. This value is consistent with the susceptibility measurement.

Figure.2 shows the magnetic structure for TbRhIn₅, determined from the comparison of the integrated intensity of the antiferromagnetic reflections on the $(h \ 0 \ l)$ plane with model calculations. Tb magnetic moments are parallel to the *c*-axis and order with a propagating vector $Q = (1/2 \ 0 \ 1/2)$. The moment direction is consistent with the susceptibility study, when the *c*-axis is the easy axis. We also confirmed the magnetic structure for RRhIn₅ (R: Nd, Dy, Ho). The obtained mag-

netic moment $\mu = 7.7 \ \mu_B/\text{Tb}$ is consistent with $gJ = 9 \ \mu_B/\text{Tb}$. Relatively large error is most likely due to the strong absorption of In with a large sample size with 4 mm length.



Figure 1: The $(1/2 \ 0 \ 1/2)$ antiferromagnetic reflection. Inset is the temperature dependence of the peak intensity.



Figure 2: The magnetic structure of TbRhIn₅.

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原子炉:JRR-3 装置:LTAS(C2-1)・MUSASI(T2-3) 分野:中性子散乱(磁性)

Magnetic Structure of TbMnO₃ Studied with Spherical Neutron Polarimetry

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TbMnO₃ shows a collinear sinusoidal spin ordering below $T_{\rm N} = 42$ K, where the spins point to the *b* axis and modulate along the *b* axis with a wave number $q \sim 0.28b^*$. The spin structure is transformed into a cycloidal spiral structure below $T_{\rm C} = 28$ K, where the spins rotate within the *bc* plane. The component along the *c* axis of the spiral structure is shorter than that along the *b* axis, which results in an elliptically distorted spiral structure¹). Recently, it has been found that TbMnO₃ as well as some other isostructural manganites shows a ferroelectric transition at $T_{\rm C}$, and that its dielectric properties are strongly coupled with its magnetism²).

In the present study, we conducted a detailed study on the change in the spin structure in TbMnO₃ using the spherical neutron polarimetry technique, which should shed light on the origin of the ferroelectricity. Polarized neutron diffraction measurements were carried out using CRYOPAD installed on TAS-1 spectrometer with the incident neutron energies 14.7 meV and 34 meV.

Polarization of the scattered neutron beam was determined as $P_{if} = (I_{+i,+f} - I_{+i,-f})/(I_{+i,+f}+I_{+i,-f})$, where $I_{i,f}$ represents the scattering intensity with initial and final polarizations *i* and *f*, respectively. Figure 1 shows temperature (*T*) dependences of P_{yx} , P_{zx} , $(P_{yy}^2 + P_{yz}^2)^{\frac{1}{2}}$, and $(P_{zy}^2 + P_{zz}^2)^{\frac{1}{2}}$ at a magnetic Bragg point (4, *q*, 1). In the present measurement condition, P_{yx} and P_{zx} reflect the chirality of the spiral spin structure. Because they are nearly equal to zero even at $T < T_{\rm C}$, two chirality domains with clockwise and anticlockwise chiralities are distributed equally in the spiral phase.



Figure 1: Temperature dependences of neutron polarizations measured at a magnetic Bragg point (4, q, 1).

will become unity for a collinear spin structure, while it will become zero for an ideal spiral structure. In Fig. 1, they are nearly equal to unity at $T_{\rm C} < T < T_{\rm N}$. They gradually decrease below $T_{\rm C}$ as a function of T, but they saturate around 15 K and do not seem to reach zero at T = 0 K. These results indicate that the collinear spin structure in $TbMnO_3$ is transformed into a spiral structure below $T_{\rm C}$ by gradually swelling the c component with decreasing T. The transformation into the spiral structure is incomplete at the lowest temperature, resulting in the elliptical spiral structure. The T dependences of $P_{yy}^2 + P_{yz}^2$ and $P_{zy}^2 + P_{zz}^2$ bear a strong resemblance to that of the spontaneous electric polarization $P_{\rm e}$, which develops below $T_{\rm C}^{2}$, suggesting a strong coupling between $P_{\rm e}$ and the spiral spin ordering.

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On the other hand,
$$P_{yy}^2 + P_{yz}^2$$
 and $P_{zy}^2 + P_{zz}^2$
原子炉: JRR-3 装置: TAS-1(2G) 分野: 中性子散乱(磁性)

Unusual Magnetic Structure and the Successive Transition in NpFeGa₅

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NpFeGa₅ exhibits a successive magnetic transition at $T_{N1} = 118 \text{ K}$ and $T_{N2} = 75 \text{ K}^{(1)}$ Our recent study revealed the c-type antiferromagnetic order with q = (1/21/20) below $T_{\rm N1}$. The strong and weak intensities of (1/21/2l) with l odd or even, respectively, indicate the Fe sublattice ordering with the same structure as in the Np sublattice, but the opposite moment direction in a chemical unit cell. We observed an anomaly in the temperature dependence of the antiferromagnetic intensity around T_{N2} . Spin polarization analysis has been carried out in order to clarify the double transition in NpFeGa₅, which is an iso-structural compound of heavy fermion superconductors Ce115 and Pu115.

Figure 1 shows the result of the temperature dependence for the spin-flip (SF) and non-spin-flip (NSF) scattering cross-section of the (1/21/20) reflection with the *c*-axis of the sample and the guide field for the neutron spin state being perpendicular to the scattering plane. The magnetic moment perpendicular to the *c*-axis and the scattering vector Q = [1/21/20] provides the SF cross-section, whereas the NSF scattering cross-section represents the squared moment parallel to the *c*-axis. The SF scattering cross-section was observed at all temperatures below $T_{\rm N1}$ with a weak anomaly at T_{N2} . On the other hand, a clear NSF signal was observed only below $T_{\rm N2}$. These experimental results indicate unambiguously that the magnetic moment is in the basal plane for $T_{N2} < T < T_{N1}$, while the moment is inclined for $T < T_{N2}$.

Figure 2 shows the magnetic structure of NpFeGa₅ both for high and low temperature phases. Our analysis revealed that NpFeGa₅ keeps a collinear structure with a moment



Figure 1: Temperature dependence of the spin-flip (SF) and non-spin-flip (NSF) scattering cross-section of the (1/2 1/2 l) reflection in NpFeGa₅.



Figure 2: Magnetic structures of NpFeGa₅.

inclination angle about 25 degrees from the basal plane. The result of the scattering intensity of the unpolarized diffraction experiment is well reproduced from the model calculation based on the magnetic structures in Fig.2. The magnetic moment at the base temperature would be 0.8 Bohr magneton per Np and 0.3 Bohr magneton per Fe atom, respectively.

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Coulomb Interaction in NpCoGa₅ Probing through Phonon Spectroscopy

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The discovery of superconductivity in the $PuTGa_5$ system attracts an considerable interest with its relatively high $T_{\rm sc}^{(1,2)}$. The overall features including the NMR studies support the idea of magnetically mediated superconductivity in $PuTGa_5^{3,4}$. However, the importance of phonons on the pairing cannot be ruled out at present as in the case of high- $T_{\rm c}$ cuprate. Furthermore, the phonon spectroscopy with the *ab initio* lattice dynamics calculation offers an ability to probe electronic properties^{5,6}). So far, we studied the phonons in an itinerant paramagnet UCoGa₅ as well as PuCoGa₅, and revealed that the results are compatible with the presence of a local Coulomb repulsion U between f electrons in PuCoGa₅ whereas a purely itinerant approach with U=0 agrees well in UCoGa₅^{6,7)}. In order to obtain the deeper understanding on the f-electron state in A-115, we measured phonons in the isostructural itinerant antiferromagnet NpCoGa₅.

Figure 1 shows the representative results of the neutron inelastic scattering spectra along the Γ -Z line at room temperature. Clear peaks corresponding to transverse acoustic (TA) and transverse optic (TO) phonons were observed as shown in Fig. 1(a). The obtained phonon dispersion relation along the Γ -Z line of NpCoGa₅ together with those of UCoGa₅, PuCoGa₅ and theoretical calculations at room temperature are summarized in Fig. 1(b). Note that the TO mode of NpCoGa₅ (Δ) shows a lower energy than that of UCoGa₅ (\bullet)⁷⁾, and higher than that of



Figure 1: (a) Neutron inelastic scattering spectra of NpCoGa₅ at room temperature. (b) The obtained phonon dispersions of NpCoGa₅, UCoGa₅⁷) and PuCoGa₅⁶ along Γ -Z at room temperature. The lines show the result of calculation with U=0 and 3 eVfor UCoGa₅ and PuCoGa₅, respectively.^{6,7}

PuCoGa₅ $(\mathbf{\nabla})^{6}$. This tendency qualitatively agrees with the itinerancy of 5*f*-electrons in an A-115 system: the strong itinerant character of U-115 and rather magnetic in Np-115. Theoretical calculation on NpCoGa₅ are now in progress.

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Polarized Neutron Inelastic Scattering Study of Central Mode in TlCoCl₃

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In this study, we carried out the polarized neutron inelastic scattering experiments for the central mode using the same procedure as that in the previous experiments for the spin-wave excitation continuum performed in the previous $year^{1,2}$ in TlCoCl₃. In contrast to the spin-wave excitation continuum, the intensity of the central mode increases with increasing temperature because the origin of the mode is thermally excited domain walls³). Figure 1 shows the profile of constant-Q energy scans of TlCoCl₃ for non-spin-flip (NSF) scattering in the vertical field (VF) and horizontal field (HF) configurations at Q = (1.45,1.45, 0.6) for T = 10 and 61 K. As shown in Fig. 1, we can clearly see that the intensity of the central mode in the vicinity of E = 3 meV increases with increasing temperature. Each polarized neutron inelastic scattering intensity in the NSF channel in the VF and HF configurations for the scattering (h, h, l)-plane is expressed as the following equations, respectivel v^{4} ,

$$I_{\text{NSF,VF}} = C \cdot S_{xx}(\boldsymbol{Q}, \omega) + I_{\text{nonmag}}, (1)$$

$$I_{\rm NSF,HF} = I_{\rm nonmag}.$$
 (2)

where $S_{xx}(\mathbf{Q}, \omega)$ and I_{nonmag} are the transverse magnetic fluctuation and the nonmagnetic fluctuation, respectively. Hence $S_{xx}(\mathbf{Q}, \omega)$ can be extracted from the difference between $I_{\text{NSF,VF}}$ and $I_{\text{NSF,HF}}$. As shown in Fig. 1, no remarkable difference between $I_{\text{NSF,VF}}$ and $I_{\text{NSF,HF}}$ at T = 61 K can be seen, indicating that $S_{xx}(\mathbf{Q}, \omega)$ is hardly included in the central mode of TlCoCl₃. While, significant difference between $I_{\text{NSF,VF}}$ at T = 10K and that at T = 61 K is seen. This result indicates that the non-magnetic fluctuations including the phonons are enhanced with increasing temperature. In the previ-



Figure 1: Profiles of constant-Q energy scans of TlCoCl₃ for NSF scattering in the VF and HF configurations at Q = (1.45, 1.45, 0.6) for T = 10 K and 61 K.

ous unpolarized neutron inelastic scattering experiments of $CsCoCl_3^{(3)}$, finite intensity of $S_{xx}(\boldsymbol{Q},\omega)$ in the central mode has been concluded from the difference between the intensity at low temperature and that at high temperature. However, the present result in TlCoCl₃ indicates that the difference observed in the previous unpolarized experiments of CsCoCl₃ is not due to the existence of $S_{xx}(\boldsymbol{Q},\omega)$ in the central mode, but the non-magnetic fluctuations such as phonons. While, for the longitudinal magnetic fluctuation $S_{zz}(\boldsymbol{Q},\omega)$, a finite intensity was observed in the central mode of TlCoCl₃, the same as $CsCoCl_3$ (not shown).

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Magnetic Structures in $Mn_3Cu_{1-x}Ge_xN$: Evidence for the Close Relationship with Magneto-volume Effect

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Recently, Takenaka and Takagi reported that the Magneto-Volume Effect (MVE) is broadened against T in Mn₃Cu_{1-x}Ge_xN leading to a giant negative thermal expansion (NTE) coefficient¹⁾. NTE materials have already been used in a wide area of technical applications. While the volume change is negligibly small at ferromagnetic transition $T_{\rm C} =$ 143 K in Mn₃CuN, a large first order phase transition MVE appears at $T_{\rm C} \sim 100$ K at x = 0.15. With increasing x, the magnetic transition temperature increases and the increase in the volume is broadened in T. At $x \sim 0.5$, the large negative thermal expansion coefficient is about $\alpha \sim -2 \times 10^{-5}/\mathrm{K}$ in the temperature range of $270 \le T \le 350$ K, whose amplitude is one of the largest ones in all NTE materials. Basically, the volume can be expanded according to the change in the amplitude of magnetic moment. Although Fruchart and Bertaut classified the magnetic properties of Mn₃AN system by the number of valence electrons on A ion^{2} , there is no simple relationship between the magnitude of MVE and the valence electron number. In order to study the microscopic magnetic properties and MVE, neutron diffraction studies have been carried out.

Polycrystalline samples of $Mn_3Cu_{1-x}Ge_xN$ were prepared by a solid state reaction¹⁾. The experiments were performed on the high-resolution powder diffractometer HRPD $(\lambda=1.8233 \text{ Å})$ and the triple axis spectorometer TAS-2 ($\lambda=2.3590 \text{ Å}$) installed at JRR-3 of JAEA. Their collimations were open (effective value of 35')-20'-6' and 14'-40'-40'-80', respectively. Powder samples of $Mn_3Cu_{1-x}Ge_xN$ weighing ~7 g were set in vanadium holders, which were enclosed in Al cans filled with He gas. They were mounted in a closed-cycle refrigerator below room temperature and in a furnace above room temperature. The obtained results are summarized as a T-x phase diagram of crystal and magnetic structures as shown in Fig. 1. Magnetic transition temperatures determined by neutron diffraction studies and magnetization measurements are plotted by closed circles and open circles, respectively. The present neutron study revealed that cubic crystal structure and Γ^{5g} anti-ferromagnetic spin structure are key ingredients for the large magneto-volume effect in this itinerant electron system, while it is negligibly small in a tetragonal and ferromagnetic phase. This experimental result proposes the necessity of new theoretical framework on MVE, which takes account of the ordered magnetic structure³).



Figure 1: T-x phase diagram of crystal and magnetic structures on $Mn_3Cu_{1-x}Ge_xN$.

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原子炉:JRR-3 装置:HRPD(1G), TAS-2(T2-4) 分野:中性子散乱(磁性)

Evaluation of Magnetization on $Fe_{16}N_2$ Nanoparticles by Polarized Neutrons Diffraction

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Needle-shaped ferromagnetic metals are often used for magnetic recording tapes. It is, however necessary to make small and spherical shape to increase the recording capacity and density. Recently, $Fe_{16}N_2$ round nanoparticles with a diameter of 20 nm were produced by Hitachi Maxell, Ltd.. But it is difficult to obtain exact magnitude by a conventional magnetometer due to the laminated layer around $Fe_{16}N_2$. We performed polarized neutron diffraction measurements to determine net magnetization.

The averaged diameters of samples used in these experiments are approximately 19 and 17 nm. The triple-axis neutron spectrometer, TAS-1, installed at JRR-3 was used in this experiment. The neutron energy was fixed at 14.7 and 80 meV. A magnetic field of 10 kOe was applied to the samples during measurements to saturate the magnetization. The direction of neutron spin was turned for a parallel or anti-parallel state to the saturated magnetization vector by a spin flipper, and the number of neutrons were recorded in each case $(I_+ \text{ and } I_-)$. The magnitude of ferromagnetic moments appear as a difference $\Delta I = I_+ - I_-$. The magnetic form factor was determined using known crystal structure factors and ΔI . The magnitude of magnetic moments was determined from the magnetic form factor and flipping ratios, $fr = I_+/I_-$

Figure 1 shows the ΔI of the sample with a diameter of 19 nm. This measurement was performed with 80 meV neutrons. The simulation in Fig.1 drawn by a solid line, it is assumed that the magnetic form factor of Fe in Fe₁₆N₂ is the same as that in α -Fe. The experimental data are well reproduced by the simulated curve. Thus, it is concluded that the magnetic form factor is very similar to α -Fe.

Figure 2 shows I_+ and I_- in the vicinity of (202) and (220) Bragg peaks of the sample with the diameter of 19 nm. This diffraction pattern was obtained using 14.7 meV neutrons. The flipping ratios were calculated using the height of each Bragg peak. The magnitude of magnetic moments of $Fe_{16}N_2$ can be deduced without any information on the laminated layer from the results of Fig1 and 2. The same measurements were performed for the sample with a diameter of 17 nm. The magnetization measurements using the magnetometer had given different values of saturation magnetization for these two samples. The polarized neutron diffraction measurements, however, revealed that both $Fe_{16}N_2$ nanoparticles have the same magnitude of the magnetic moments of 2.0 μ_B .



Figure 1: Difference $\Delta I = I_+ - I_-$ and simulation.



Figure 2: Experiment by polarized neutrons diffraction at $\lambda = 2.37$ Å.

Magnetic Structure of Fe-N Nanoparticles for Magnetic Recording Tape Studied by Small-angle Polarized Neutron Scattering

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Fe₁₆N₂-based spherical Fe-N nanoparticle has attracted considerable attention as new material for magnetic recording tapes owing to its large magnetic anisotropy and the possibility of the emergence of large magnetic moment. However, evaluation of the local magnetic moment is difficult by magnetization measurement, because the surface of the Fe-N nanoparticle is covered with structurally unknown non-magnetic laminate layer for the oxidation prevention. In order to evaluate the inner magnetic structure of the nanoparticle precisely, we have performed small-angle polarized neutron scattering experiments using the SANS-J-II instrument of JRR-3. We applied a magnetic field of 1 T to samples and measured SANS intensities of I^+ and $I^$ in the cases that the spin polarity of incident neutrons is positive and negative, re-Fig.1 shows scattering profiles spectively. I_{\perp}^{+} and I_{\perp}^{-} along the direction perpendicular to the applied magnetic field, respectively We analyzed these scattering profiles using a model of spherical nanoparticles with a coreshell structure under the assumption of the magnetic moment of 2.1 μ_B /Fe atom. We evaluated the mean radius \bar{r} , non-magnetic layer's thickness Δr , and magnetization of the nanoparticles m and compared them with the results obtained by TEM and magnetization measurements as shown in Fig.2. These characteristic parameters were analyzed as a function of the effective polarization degree of the incident neutrons P_{eff} with the accuracy χ^2 of the profile fitting, because there was the possibility that the spin of the incident neutrons was depolarized by the local magnetic field produced in the sample. χ^2 was minimized at P_{eff} of 50 %, and evaluated \bar{r} and m

are consistent with the results of macroscopic measurements. Analytical accuracy of the internal magnetic structure of the nanoparticles will improve by determining the depolarization correctly in the future.



Figure 1: Sans intensities vs. q.



Figure 2: Evaluated \bar{r} , Δr , and m as a function of P_{eff} .

原子炉:JRR-3 装置:SANS-J(C3-2) 分野:中性子散乱(磁性)

Successive Phase Transitions of $LuBaCo_4O_7$ with Kagome and Triangular Lattices

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Spin systems on the pyrochlore, triangular and kagome lattices are well-known examples of geometrically frustrated systems and expected to exhibit various interesting properties induced by strong magnetic fluctuations. RBaCo₄O₇ (R = Ca, Y and rare-earth elements) is one of typical examples of such systems, because it has both triangular and kagome lattices of Co spins.^{1–3)}

Magnetic, thermal and neutron diffraction measurements have been carried out on single-crystal samples of LuBaCo₄O₇. Anomalies of the magnetic susceptibility have been found at temperatures $T_{a1} \sim 70$ K and $T_{a2} \sim 50$ K. We have also found a secondorder structural transition at $T_{c1} \sim 165$ K and a first-order structural transition at $T_{c2} \sim 105$ K (T_{c2} ' ~ 80 K) with increasing (decreasing) temperature.

We have observed reflections at Q-points (h'/20l) and (h'/2h'/2l) (h' = odd; group A)below T_{c1} , and additionally at the Q-points $(h''/3\pm\delta h''/3\pm\delta l)$ (h''/3 = noninteger number; group B) below T_{c2} , in the reciprocal space of the hexagonal unit cell ($a = b \sim$ 6.27 Å, $c \sim 10.24$ Å). We have found that at $T < T_{c2}$, the line shapes of the reflections at the Q-points of group A can be described by Lorentzian-type ones, while at $T_{c2} < T <$ T_{c1} , they have Gaussian-type ones. From the |Q|-dependence of the integrated intensities, the Gaussian and Lorentzian components can be regarded as nuclear and magnetic origins, respectively. The magnetic (Lorentzian) component is dominant below T_{c2} and only the nuclear (Gaussian) component exists at T between T_{c2} and T_{c1} . For the reflections at the **Q**-points of group B, the δ value is T-dependent. These reflections have broad Lorentzian profiles and can be considered to be magnetic.

Below T_{c2} , we can easily find that the intensities of the nuclear superlattice reflections are almost zero and the intensities of the magnetic reflections increase gradually with decreasing T. The profile shape of the magnetic peaks indicates that the magnetic correlation is not long-ranged even at 10 K, and the magnetic correlation length is estimated to be $\xi \sim 100$ Å. From the magnetic structure analyses, the magnetic reflections at the Q-points of groups A and B can be considered to originate from the moments on the kagome and triangular lattices, respectively.

For both YBaCo₄O₇ and LuBaCo₄O₇ systems, the Co moments of the kagome and triangular lattices exhibit short-range orders with different magnetic periods.²⁾ However, several differences have been found between the behaviors of the magnetic reflections of $YBaCo_4O_7$ and $LuBaCo_4O_7$. In $YBaCo_4O_7$, the growth of the magnetic correlation and a similar structural distortion were found to appear simultaneously at its T_{c1} (~ 105 K) with decreasing T, whereas in LuBaCo₄O₇, the short-range magnetic correlation grows only below T_{c2} . The periods of the magnetic modulation of the triangular lattice are also different between these two systems. At low temperatures, the structural distortion of $LuBaCo_4O_7$ system is different from that of YBaCo₄O₇, which induces the significant differences in the magnetic properties between these two systems.

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Magnetic Excitations in Lightly-Doped $La_{2-x}Sr_xCuO_4$

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Recently, detailed inelastic neutron scattering studies have been performed up to high energies in various systems such $YBa_2Cu_3O_{6.6}$,¹⁾ $La_{1.875}Ba_{0.125}CuO_4^{(2)}$ asand La_{1.84}Sr_{0.16}CuO₄.³⁾ All of them show hourglass-shaped magnetic excitations with the parallel incommensurate correlations at low energies. On the other hand, there are few studies of magnetic excitations in the diagonal incommensurate phase in lightlydoped $La_{2-x}Sr_xCuO_4$, although conventional spin wave excitations were reported in the diagonal stripe phase of $La_{2-x}Sr_xNiO_4$.⁴⁾ We previously tried to measure magnetic excitations in the diagonal incommensurate phase using a twinned crystal of $La_{1.976}Sr_{0.024}CuO_4$.⁵⁾ The results suggest that the magnetic correlations change from being incommensurate to commensurate at \sim 7 meV and \sim 70 K. However, since some the assumptions are needed to analyze the data in twinned crystal, information was limited. It is important to compare the magnetic excitatons in both the parallel and diagonal incommensurate phases in detail to clarify what is the intrinsic magnetic properties in the superconducting phase.

We performed inelastic neutron scattering measurements on TAS-2 and LTAS using an almost untwinned crystal of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ $(x \sim 0.04)$, in which elastic magnetic peaks are observed at $(1, \pm \delta, 0)_{\text{ortho}}$ or $(0, 1\pm \delta, 0)_{\text{ortho}}$, to observe magnetic excitations in the diagonal incommensurate phase. We observed energy and temperature dependences of magnetic excitations in the range of $0 \leq \omega \leq 12$ meV and $4 \leq T \leq 290$ K. The results show that the incommensurability (δ) decreases gradually with increasing energy up to 12 meV, as shown in Fig. 1. This is qualitatively consistent with the behavior in the parallel incommensurate phase. The temperature dependence of the magnetic excitations shows that the incommensurability gradually decreases with increasing temperature and becomes almost commensurate below 12 meV at room temperature.



Figure 1: Typical consant-energy spectra at T = 4 K in La_{2-x}Sr_xCuO₄ ($x \sim 0.04$). The diagonal incommensurate peaks are observed at $(1, \pm \delta, 0)$ or $(0, 1\pm \delta, 0)$.

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原子炉:JRR-3 装置:TAS-2(T2-4), LTAS(C2-1) 分野:中性子散乱(超伝導)

New-Type Phase Transition of Honeycomb Lattice System Li₂RuO₃

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Li₂RuO₃ has layers of the honeycomb lattice of edge-sharing RuO₆ octahedra with a LiO₆ octahedron at the corner of each hexagon of RuO₆. The Ru valence is +4 and the four electrons exist in the 4*d* t_{2g} orbits. Li atom layers are between the honeycomb layers. For this system, we have found a phase transition at temperature $T = T_c \sim$ 540 K.¹) With decreasing *T*, the electrical resistivity exhibits an anomalous increase at T_c , suggesting the "metal-to-insulator"-like transition, and the magnetic susceptibility also shows a sharp decrease.

To clarify the mechanism of the transition, powder neutron diffraction measurements were carried out at room temperature (RT) and 600 K using a high resolution powder diffractometer (HRPD) installed at JRR-3 of JAEA in Tokai, and Rietveld analyses were carried out using RIETAN-2000. Although the space group at RT was previously reported to be $C2/c^{2,3)}$, several superlattice peaks which cannot be explained by C2/c were observed. To reproduce these reflections, we adopt the space group $P2_1/m$. The result of the Rietveld fitting with $P2_1/m$ is rather well. As the possible space group at 600 K, we have adopted C2/m, the minimal non-isomorphic supergroup of $P2_1/m$, because this space group allows the secondorder transition at $T_{\rm c}$. (From the experimental data, it is not easy to definitely distinguish if it is the second-order one or the first-order one.)

At 600 K, Ru atoms form an almost ideal honeycomb structure. At RT, a significant reduction (by ~ 13 %) of the bond lengths was found between two of the six Ru-Ru pairs of the hexagon (figure (right panel)). To answer why such drastic changes take place, we consider the coupling of the lattice distortion with the formation of the molecular orbits of



Figure 1: The distortion pattern of Ru-honeycomb skeleton at RT (left) and the energy levels of the molecular orbits of Ru^{4+} - Ru^{4+} pairs (right) below T_c . The electrons in these levels are shown by the arrows presenting the spin directions.

the t_{2g} electrons of Ru⁴⁺-Ru⁴⁺ of edge sharing RuO₆ octahedra. The energy levels of the bonding and corresponding antibonding orbits are shown in the Figure 1(right), where we can see that the nonmagnetic electron configuration is realized below T_c .

Although transitions accompanied with the significant anomalies of the electrical resistivity and the magnetic susceptibility similar to those of the present system have been reported for $La_4Ru_2O_{10}$ with corner-sharing RuO_6 octahedra and for $Tl_2Ru_2O_7$ with a pyrochlore structure, their microscopic mechanisms are different from that presently proposed. Li_2RuO_3 with edge-sharing RuO_6 octahedra is considered to present, as far as we know, a new type of phase transitions associated with the structural distortion induced by the molecular-orbit formation of the *d* electron states.

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原子炉:JRR-3 装置:HRPD(1G) 分野:中性子散乱(構造)

Direct Observation of the Pressure-Induced Ferromagnetic Order in Valence Transition Material YbInCu₄

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YbInCu₄ crystallizes in the cubic AuBe₅ (C15b)-type structure. At ambient pressure with decreasing temperature, the compound undergoes the first-order isomorphic valence transition at $T_{\rm V} = 42$ K with the increase of the unit-cell volume of about 0.5 %. At $T_{\rm V}$, the 4f states of Yb ions change from high temperature (HT) well-localized states of Yb³⁺ to low temperature (LT) mixed-valent states of Yb^{2.9+}. Recent studies under high pressures have revealed that the nonmagnetic LT phase is completely suppressed and the magnetic HT phase is stabilized in all temperature ranges above $P_{\rm C} = 2.5$ GPa. Furthermore, it is suggested that the long-range magnetic order appears below $T_{\rm C} = 2.4$ K at 2.5 GPa.¹⁾ On the other hand, this compound shows the superconductivity above 0.7 GPa below 1.4 K. This pressure-induced superconductivity survives up to 4 GPa.²⁾ The purpose of our work is to elucidate directly and microscopically the pressure-induced magnetic order. We performed high-pressure neutron diffraction experiments using the triple-axis spectrometer TAS-1. The high-pressure was generated up to 6.2 GPa by a newly-developed hybrid-anvil device.³⁾ The pressure transmitted by the glycerin medium was hydrostatic even at 7.0 GPa. The sample size was about $1.0 \times 0.5 \times 0.25 \text{ mm}^3$. The pressure was applied along the $[01\overline{1}]$ direction of the sample and the diffraction plane was the [100]-[011] one. We used a neutron focusing device in order to increase the effective neutron intensity at the sample position.⁴)

We have successfully observed the distinct increase of the intensities only at the ferromagnetic ($\overline{1}11$) or ($\overline{1}\overline{1}\overline{1}$) reciprocal lattice points below about $T_{\rm C} = 2.5$ K at 4.0 GPa and 6.2 GPa. As an example, we show the temper-

ature dependence of the intensities at 6.2 GPa in Fig. 1. This result indicates that the ferromagnetic order appears at least above 4.0 GPa and $T_{\rm C}$ is hardly affected by the pressure. On the other hand, the estimated magnetic moment in the ferromagnetic order is about 0.68 $\mu_{\rm B}$ and 0.76 $\mu_{\rm B}$ per Yb ion at 4.0 and 6.2 GPa, respectively. These values are quite large compared to the Y-diluted system Yb_{0.8}Y_{0.2}InCu₄, which shows the weak ferromagnetic order of 0.05 $\mu_{\rm B}$ per Yb ion below $T_{\rm C} = 1.7$ K and above 0.8 GPa.⁵)



Figure 1: Temperature dependence of the intensities at the $(\overline{1}\overline{1}\overline{1})$ ferromagnetic point and at the $(\overline{2}\overline{1}\overline{1})$ antiferromagnetic point for P = 6.2 GPa.

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Magnetic Structure of $TbRhIn_5$

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Intermetallic compounds ATX₅ (A: Lanthanoid or Actinide, T: Transition metal, X: In or Ga) with the tetragonal HoCoGa₅type (P4/mmm) crystal structure, so called "115", attract strong interest because of the heavy fermion superconductivity in Ce-115 and Pu-115 or various magnetic structures in U-115 and Np-115. On the other hand, RRhIn₅ (R: Nd, Tb, Dv, Ho)¹⁾ are local antiferromagnets. The magnetic susceptibility shows Curie-Weiss behaviour, where the Néel temperatures are in good agreement with de Gennes factor. A similar two-step metamagnetic transition is observed in RRhIn₅ (R: Nd, Tb, Dy, Ho), when the magnetic field is applied along the *c*-axis (easy axis). We performed neutron scattering experiment in order to determine the magnetic structure of TbRhIn₅. We used triple-axis spectrometers LTAS and MUSASI (low angle beam port) installed in JRR-3 guide hall.

Figure.1 shows the longitudinal scan profile of the $(1/2 \ 0 \ 1/2)$ antiferromagnetic reflection at 2.8 K, which disappeared at 50 K above Neel temperature. Inset shows the temperature dependence of $(1/2 \ 0 \ 1/2)$ peak intensity. We estimated the Neel temperature T_N to be approximately 47.3 K. This value is consistent with the susceptibility measurement.

Figure.2 shows the magnetic structure for TbRhIn₅, determined from the comparison of the integrated intensity of the antiferromagnetic reflections on the $(h \ 0 \ l)$ plane with model calculations. Tb magnetic moments are parallel to the *c*-axis and order with a propagating vector $Q = (1/2 \ 0 \ 1/2)$. The moment direction is consistent with the susceptibility study, when the *c*-axis is the easy axis. We also confirmed the magnetic structure for RRhIn₅ (R: Nd, Dy, Ho). The obtained mag-

netic moment $\mu = 7.7 \ \mu_B/\text{Tb}$ is consistent with $gJ = 9 \ \mu_B/\text{Tb}$. Relatively large error is most likely due to the strong absorption of In with a large sample size with 4 mm length.



Figure 1: The $(1/2 \ 0 \ 1/2)$ antiferromagnetic reflection. Inset is the temperature dependence of the peak intensity.



Figure 2: The magnetic structure of TbRhIn₅.

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原子炉:JRR-3 装置:LTAS(C2-1)・MUSASI(T2-3) 分野:中性子散乱(磁性)

Magnetic Structure of TbMnO₃ Studied with Spherical Neutron Polarimetry

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TbMnO₃ shows a collinear sinusoidal spin ordering below $T_{\rm N} = 42$ K, where the spins point to the *b* axis and modulate along the *b* axis with a wave number $q \sim 0.28b^*$. The spin structure is transformed into a cycloidal spiral structure below $T_{\rm C} = 28$ K, where the spins rotate within the *bc* plane. The component along the *c* axis of the spiral structure is shorter than that along the *b* axis, which results in an elliptically distorted spiral structure¹). Recently, it has been found that TbMnO₃ as well as some other isostructural manganites shows a ferroelectric transition at $T_{\rm C}$, and that its dielectric properties are strongly coupled with its magnetism²).

In the present study, we conducted a detailed study on the change in the spin structure in TbMnO₃ using the spherical neutron polarimetry technique, which should shed light on the origin of the ferroelectricity. Polarized neutron diffraction measurements were carried out using CRYOPAD installed on TAS-1 spectrometer with the incident neutron energies 14.7 meV and 34 meV.

Polarization of the scattered neutron beam was determined as $P_{if} = (I_{+i,+f} - I_{+i,-f})/(I_{+i,+f}+I_{+i,-f})$, where $I_{i,f}$ represents the scattering intensity with initial and final polarizations *i* and *f*, respectively. Figure 1 shows temperature (*T*) dependences of P_{yx} , P_{zx} , $(P_{yy}^2 + P_{yz}^2)^{\frac{1}{2}}$, and $(P_{zy}^2 + P_{zz}^2)^{\frac{1}{2}}$ at a magnetic Bragg point (4, *q*, 1). In the present measurement condition, P_{yx} and P_{zx} reflect the chirality of the spiral spin structure. Because they are nearly equal to zero even at $T < T_{\rm C}$, two chirality domains with clockwise and anticlockwise chiralities are distributed equally in the spiral phase.



Figure 1: Temperature dependences of neutron polarizations measured at a magnetic Bragg point (4, q, 1).

will become unity for a collinear spin structure, while it will become zero for an ideal spiral structure. In Fig. 1, they are nearly equal to unity at $T_{\rm C} < T < T_{\rm N}$. They gradually decrease below $T_{\rm C}$ as a function of T, but they saturate around 15 K and do not seem to reach zero at T = 0 K. These results indicate that the collinear spin structure in $TbMnO_3$ is transformed into a spiral structure below $T_{\rm C}$ by gradually swelling the c component with decreasing T. The transformation into the spiral structure is incomplete at the lowest temperature, resulting in the elliptical spiral structure. The T dependences of $P_{yy}^2 + P_{yz}^2$ and $P_{zy}^2 + P_{zz}^2$ bear a strong resemblance to that of the spontaneous electric polarization $P_{\rm e}$, which develops below $T_{\rm C}^{2}$, suggesting a strong coupling between $P_{\rm e}$ and the spiral spin ordering.

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On the other hand, $P_{yy}^2 + P_{yz}^2$ and $P_{zy}^2 + P_{zz}^2$ 原子炉: JRR-3 装置: TAS-1(2G) 分野: 中性子散乱(磁性)

Unusual Magnetic Structure and the Successive Transition in NpFeGa₅

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NpFeGa₅ exhibits a successive magnetic transition at $T_{N1} = 118 \text{ K}$ and $T_{N2} = 75 \text{ K}^{(1)}$ Our recent study revealed the c-type antiferromagnetic order with q = (1/21/20) below $T_{\rm N1}$. The strong and weak intensities of (1/21/2l) with l odd or even, respectively, indicate the Fe sublattice ordering with the same structure as in the Np sublattice, but the opposite moment direction in a chemical unit cell. We observed an anomaly in the temperature dependence of the antiferromagnetic intensity around T_{N2} . Spin polarization analysis has been carried out in order to clarify the double transition in NpFeGa₅, which is an iso-structural compound of heavy fermion superconductors Ce115 and Pu115.

Figure 1 shows the result of the temperature dependence for the spin-flip (SF) and non-spin-flip (NSF) scattering cross-section of the (1/21/20) reflection with the *c*-axis of the sample and the guide field for the neutron spin state being perpendicular to the scattering plane. The magnetic moment perpendicular to the *c*-axis and the scattering vector Q = [1/21/20] provides the SF cross-section, whereas the NSF scattering cross-section represents the squared moment parallel to the *c*-axis. The SF scattering cross-section was observed at all temperatures below $T_{\rm N1}$ with a weak anomaly at T_{N2} . On the other hand, a clear NSF signal was observed only below $T_{\rm N2}$. These experimental results indicate unambiguously that the magnetic moment is in the basal plane for $T_{N2} < T < T_{N1}$, while the moment is inclined for $T < T_{N2}$.

Figure 2 shows the magnetic structure of NpFeGa₅ both for high and low temperature phases. Our analysis revealed that NpFeGa₅ keeps a collinear structure with a moment



Figure 1: Temperature dependence of the spin-flip (SF) and non-spin-flip (NSF) scattering cross-section of the (1/21/2l) reflection in NpFeGa₅.



Figure 2: Magnetic structures of NpFeGa₅.

inclination angle about 25 degrees from the basal plane. The result of the scattering intensity of the unpolarized diffraction experiment is well reproduced from the model calculation based on the magnetic structures in Fig.2. The magnetic moment at the base temperature would be 0.8 Bohr magneton per Np and 0.3 Bohr magneton per Fe atom, respectively.

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原子炉:JRR-3 装置:TAS-1(2G) 分野:中性子散乱(磁性)

Coulomb Interaction in NpCoGa₅ Probing through Phonon Spectroscopy

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The discovery of superconductivity in the $PuTGa_5$ system attracts an considerable interest with its relatively high $T_{\rm sc}^{(1,2)}$. The overall features including the NMR studies support the idea of magnetically mediated superconductivity in $PuTGa_5^{3,4}$. However, the importance of phonons on the pairing cannot be ruled out at present as in the case of high- $T_{\rm c}$ cuprate. Furthermore, the phonon spectroscopy with the *ab initio* lattice dynamics calculation offers an ability to probe electronic properties^{5,6}). So far, we studied the phonons in an itinerant paramagnet UCoGa₅ as well as PuCoGa₅, and revealed that the results are compatible with the presence of a local Coulomb repulsion U between f electrons in PuCoGa₅ whereas a purely itinerant approach with U=0 agrees well in UCoGa₅^{6,7)}. In order to obtain the deeper understanding on the f-electron state in A-115, we measured phonons in the isostructural itinerant antiferromagnet NpCoGa₅.

Figure 1 shows the representative results of the neutron inelastic scattering spectra along the Γ -Z line at room temperature. Clear peaks corresponding to transverse acoustic (TA) and transverse optic (TO) phonons were observed as shown in Fig. 1(a). The obtained phonon dispersion relation along the Γ -Z line of NpCoGa₅ together with those of UCoGa₅, PuCoGa₅ and theoretical calculations at room temperature are summarized in Fig. 1(b). Note that the TO mode of NpCoGa₅ (\triangle) shows a lower energy than that of UCoGa₅ (\bullet)⁷, and higher than that of



Figure 1: (a) Neutron inelastic scattering spectra of NpCoGa₅ at room temperature. (b) The obtained phonon dispersions of NpCoGa₅, UCoGa₅⁷) and PuCoGa₅⁶ along Γ -Z at room temperature. The lines show the result of calculation with U=0 and 3 eVfor UCoGa₅ and PuCoGa₅, respectively.^{6,7}

PuCoGa₅ $(\mathbf{\nabla})^{6}$. This tendency qualitatively agrees with the itinerancy of 5*f*-electrons in an A-115 system: the strong itinerant character of U-115 and rather magnetic in Np-115. Theoretical calculation on NpCoGa₅ are now in progress.

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原子炉:JRR-3 装置:TAS-1(2G) 分野:中性子散乱(磁性)

Softening of Magnetic Excitations Leading to Pressure-Induced Quantum Phase Transition in Gapped Spin System KCuCl₃

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KCuCl₃ is an interacting spin dimer system, which has a singlet ground state with an excitation gap of $\Delta = 2.67 \text{ meV}^{1)}$. KCuCl₃ undergoes a pressure-induced quantum phase transition (QPT) to an antiferromagnetic (AF) state. The critical pressure obtained through magnetization measurements is $P_{\rm c} = 8.2 \text{ kbar}^{2)}$. To investigate the pressure dependence of individual exchange interactions and the change of dispersion relations under pressure, we have performed neutron inelastic scattering experiments on KCuCl₃ under high hydrostatic pressure.

The experiments were performed using TAS-1 and LTAS spectrometers installed at JRR-3 in JAEA, Tokai. In general, it is difficult to carry out neutron inelastic scattering under high pressure because of the small sample space and the attenuation of the neutron beam due to the thick pressure cell. In the present study, we used a newly designed cylindrical high-pressure clamp cell made of mesoalite. The inner diameter of the sample capsule was 8.0 mm and the working height is 22 mm. A KCuCl₃ single crystal was shaped into a column of 7.8 mm in diameter and 14 mm in length with the central axis parallel to the crystallographic *b*-axis. A mixture of Fluorinert FC70 and FC77 was used as the pressure-transmitting medium. A hydrostatic pressure of P = 4.7 kbar was applied at helium temperatures. The pressure was determined from the lattice constants of a NaCl crystal placed in the sample space. A welldefined single excitation mode was observed.

The dispersion relations in the $a^* - c^*$ plane were obtained, as shown in Fig. 1. Softening of the triplet mode due to the applied pressure is clearly observed at all Q values. The excitation gap for P = 4.7 kbar corresponding to the lowest excitation energy was evaluated as $\Delta = 1.52$ meV. Using the random phase approximation, we have analyzed the dispersion relations and obtained the intradimer and effective interdimer interactions. It was found that the intradimer interaction decreases under hydrostatic pressure and the effective interactions between the nearest dimers along the *a*-direction and in the $(1, 0, \overline{2})$ plane increase. These pressure dependences of the exchange interactions give rise to the observed pressure-induced QPT from a gapped ground state to an AF state in KCuCl₃. The present result has been published elsewhere³.



Figure 1: Dispersion relations $\omega(\mathbf{Q})$ in KCuCl₃ measured at P = 4.7 kbar for \mathbf{Q} along (h, 0, 1) and (0, 0, 2h + 1). Dashed line is the dispersion curve at ambient pressure.

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原子炉:JRR-3 装置:TAS-1(2G), LTAS(C2-1) 分野:中性子散乱(磁性)

Neutron Elastic Scattering in Quantum Spin System NH₄CuCl₃

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 NH_4CuCl_3 is a weakly coupled spin dimer system, which has the same crystal structure as $KCuCl_3$ at room temperature¹). With decreasing temperature, NH₄CuCl₃ undergoes structural phase transitions at $T_{t1} = 156$ K and $T_{t2} = 70 \text{ K}^{2}$. The magnetic ground state of NH₄CuCl₃ is gapless in contrast to $KCuCl_3^{(3)}$. NH_4CuCl_3 undergoes 3D magnetic ordering at $T_{\rm N}~=~1.3~{\rm K}^{3)}$. Remarkable feature of NH_4CuCl_3 is that the magnetization curve has two plateaus at onequarter and three-quarters of the saturation magnetization⁴). Although various models for the formation of the magnetization plateaus have been proposed⁵), the mechanism leading to the magnetization plateaus has not been clarified. Recently, magnetic Bragg reflection was observed at $\mathbf{Q} = (0, 0, 1)^{2}$, and its intensity decreases with increasing external field. To investigate the magnetic structure in the ordered phase, we have performed a neutron elastic scattering experiment on NH₄CuCl₃ at zero magnetic field.

The experiment was performed using the TAS-2 spectrometer installed at JRR-3 in JAEA, Tokai. The incident neutron energy was fixed at $E_i = 14.7$ meV, and the horizontal collimation sequence was chosen as guide-80'-80'-open. A single crystal of ~ 0.25 cm³ was used. The sample was mounted in the cryostat with its (010) plane parallel to the scattering plane, so that the reflections in the $a^* - c^*$ plane were investigated. The sample was cooled to 50 mK using a dilution refrigerator.

Magnetic Bragg peaks were observed below $T_{\rm N} = 1.3$ K at $\boldsymbol{Q} = (h, 0, l)$ with the integer h and odd l. These reciprocal lattice points are equivalent to those for the magnetic-field and pressure induced ordered phases in TlCuCl₃^{6,7)}. No Bragg peak indicating superlattice structure along the *a*-axis was observed. Table 1 summarizes the integrated intensities of magnetic Bragg reflections normalized to the (001) reflection. It is noted that Bragg intensities for $\mathbf{Q} = (0, 0, 5)$, (1, 0, 1) and (1, 0, -1) are strong. These intensities for the magnetic-field and pressure induced ordered phases in TlCuCl₃ are less than 0.1. From the magnetization and excitation data^{2,4)}, we can deduce that one-quarter of the spins are ordered below $T_{\rm N}$ and the rest of spins are in the singlet state at zero magnetic field. At present, the magnetic structure of NH₄CuCl₃ cannot be determined uniquely. Neutron elastic scattering experiments taking other scattering plane are needed.

Table 1: Integrated magnetic Bragg peak intensities observed at 50 mK. The intensities are normalized to the $(001)_{\rm M}$ reflection.

| $(001)_M$ | $(003)_{M}$ | $(005)_{M}$ |
|----------------------|----------------------|----------------------|
| 1.000 | 0.000 | 0.425 |
| $(101)_M$ | $(10\overline{1})_M$ | $(103)_M$ |
| 0.385 | 0.302 | 0.109 |
| $(10\overline{3})_M$ | $(201)_M$ | $(20\overline{1})_M$ |
| 0.485 | 0.000 | 0.000 |

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原子炉:JRR-3 装置:TAS-2(T2-4) 分野:中性子散乱(磁性)

Magnetic Structure of $Co_2TeO_3Cl_2$

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 $Co_2 TeO_3 Cl_2$ has so-called delta or sawtooth chains consisting of corner-sharing triangles of Co spins,¹⁾ and two crystallographically distinct Co^{2+} sites exist in this system. If the exchange interaction between the nearest neighbor Co spins is antiferromagnetic, a rather strong magnetic fluctuation is expected.

Measurements of the magnetic susceptibility χ and specific heat C of Co₂TeO₃Cl₂ have revealed that two transitions take place at temperatures T = 73 K (T_{N1}) and 15 K (T_{N2}). At T_{N1} , a small anomaly has been observed in the $\chi - T$ curve. A weak ferromagnetic moment shows up at T_{N2} with decreasing T. In the C/T - T curve, anomalies characteristic of second-order phase transitions are observed at both transition temperatures.

For this system, we have carried out the powder neutron diffraction measurements down to 2.8 K at the high resolution powder diffractometer (HRPD) of JRR-3 of JAEA in Tokai, and carried out Rietveld analyses using RIETAN-2000 at two temperatures $T_{\rm N2} < T < T_{\rm N2}$ and $T < T_{\rm N2}$.

Neutron powder patterns were taken at 85 K (> $T_{\rm N1}$), 25 K (between $T_{\rm N2}$ and $T_{\rm N1}$) and 2.8 K (< $T_{\rm N2}$). At 25 K, superlattice reflections ($h/2 \ k/2 \ l/2$) ($h, \ k, \ l =$ odd) were found and at 2.5 K, superlattice reflections ($h \ k \ l/2$) ($h, \ k, \ l =$ odd) were also found. The integrated intensities and 2θ positions of the peaks appearing at 25 K have been found not to change with T from 25 to 2.8 K. By using the obtained intensities of the magnetic reflections, we have determined the magnetic structures of the ordered phases. At 25 K, only the Co(2) moments order antiferromagnetically with their spins along the *b*-axis, where the ordered moment is 3.6 (± 0.2) $\mu_{\rm B}$.

At 2.8 K, the Co(1) moments not only order nearly parallel to the *a*-axis but also cant towards the *b*-axis by 13.3° due



Figure 1: Magnetic structure of $\text{Co}_2\text{TeO}_3\text{Cl}_2$ at 2.8 K. The open and closed circles indicate the Co(1) and Co(2) sites, respectively. The arrows indicate the directions of magnetic moments. The Co(1) spins cant from the *a*-axis toward the *b*-axis by ~13.3°.

to Dzyaloshinski-Moriya interaction, which causes the weak ferromagnetism observed below $T_{\rm N2}$. The ordered moment is 3.3 (±0.2) $\mu_{\rm B}$. The magnetic structure of Co(2) spins and their ordered moment are unchanged when T is changed through $T_{\rm N2}$. For the noncollinear magnetic structure and the nearly individual orderings of the sublattices of the Co(1) and Co(2) sites, the structural characteristics of the present system with isosceles triangles seems to be important.

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原子炉:JRR-3 装置:HRPD(1G) 分野:中性子散乱(磁性)

Spherical Polarization Analysis of Artificially Confined Spin-Density Waves in Cr/Sn Multilayers

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In Cr/Sn(001) multilayers in which monatomic Sn nonmagnetic layers are periodically embedded, spin-density waves (SDWs) are formed below the Néel temperature like that in bulk Cr. They are, however, quite different to the SDW in bulk Cr. For instance the wavelength of the SDW is defined not simply by the nesting vector of Cr but also by the artificial periodicity introduced by the Sn layers^{1,2}). We performed the spherical neutron-polarization analysis of these anomalous SDW structures by using CRYOPAD(CRYOgenic Polarization Analysis Device)^{3,4} on TAS-1 to get detailed magnetic structural information which could not be obtained with unpolarized neutron experiments⁵).

The samples were $[Cr(10.0 \text{ nm})/Sn(0.2 \text{ nm})] \times 24$ grown on MgO(001) substrates. The incident neutrons were polarized and monochromatized with a Cu₂MnAl polarizing monochromator. The energy of the neutrons was fixed at 14.7 meV. The scans were done through the (001) and (010) reciprocal points, where the nuclear peaks were forbidden, along the [001] (out-of-plane) and [010] (in-plane) directions.

The film had a commensurate antiferromagnetic (CAF) structure at 290 K and changed into the incommensurate SDW (ISDW) state with decreasing temperature. Several satellite peaks corresponding to the ISDW structures appeared in the scan profiles. The position of each peak can be written as $(01 \pm N\Delta)$ or $(00 \ 1 \pm N\Delta)$ where $\Delta = a_{001}/\Lambda$, and Λ is the distance of artificial boundary ($t_{\rm Cr} + t_{\rm Sn} = 10.2$ nm).

The polarization matrix, P_{ij} , was measured at 270 K and 4.3 K⁶⁾. The matrix elements are given in Ref. 5. At (010) peak the outof-plane and in-plane component of magnetic interaction vectors, M(Q), are detected while at (001) only two in-plane components reflect in P_{ij} . The observed P_{yy} is equal to $-P_{zz}$ for (001) at 270 K. On the other hand, $|P_{yy}|$ is larger than $|P_{zz}|$ for (010). This indicates that the sample has a multi-domain CAF structure with M(Q) mostly normal to the plane and that the distribution of the domain is isotropic in the (001) plane at 270 K.

In the ISDW phase at 4.3 K, M(Q) seems to incline towards the in-plane because $|P_{zz}| > |P_{yy}|$ for the first satellite peak of (01 Δ). Significant depolarization is observed in P_{xx} for (00 1+ Δ). This would imply that this peak has both nuclear and magnetic origins. Further investigation is, however, necessary to derive a firm conclusion.

The neutron polarimetry experiments gave us much more detailed magnetic structural information on the ISDW, which could not have been obtained by the conventional unpolarized and polarized neutron diffraction measurements. Measurements of P_{ij} for the other reflections and temperature dependence of P_{ij} are expected to give a better insight into the magnetic nature of this multilayer.

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原子炉:JRR-3 装置:TAS-1(2G) 分野:中性子散乱(磁性)

Neutron Scattering Study of Metamagnetic Phase Transition in HoRhIn₅ Compounds

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The metamagnetic transition of a single crystal of HoRhIn₅ was studied by neutron diffraction. This compound exhibits an antiferromagnetic structure with $\vec{q} = (1/2,0,1/2)$ below $T_N = 15.8$ K. The magnetization curve for $\vec{H} \parallel [001]$ exhibits a characteristic two-step metamagnetic transition at $H_{m1} = 3.4$ T and $H_{m2} = 5.4$ T at T = 2 K¹). Neutron diffraction experiments have been carried out using the TAS-2 and MUSASI spectrometers installed at the research reactor JRR-3 in JAEA. Experiments under high magnetic fields were carried out at (hk0) and (h0l) scattering plane with $\vec{H} \parallel [001]$ by using a vertical or horizontal superconducting magnet.

Figure 1 shows the field dependence of the $(3/2 \ 0 \ 5/2)$ antiferromagnetic peak intensity of HoRhIn₅. The AF1 represents the antiferromagnetic phase for $H < H_{m1}$, and AF2 for $H_{m1} < H < H_{m2}$ is the intermediate phase with the intensity roughly 25% of that for AF1. It means that the antiferromagnetic modulation in AF2 would be half that of AF1. On the other hand, the ferromagnetic moment in AF2 is a half of the saturation value, as a shown in Fig. 2. These results indicate flipping of the Ho moment. The temperature dependence of H_{m1} and H_{m2} obtained in the present work is in good agreement with the phase diagram extracted from the magnetization measurements. The magnetic structure at the intermediated phase AF2 could not been determined yet. Further experiments will be required to clarify the magnetic structure in magnetic fields.

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Figure 1: Field dependence of the intensity of $(3/2 \ 0 \ 5/2)$ antiferromagnetic reflection for HoRhIn₅.



Figure 2: Magnetic field dependence of ferromagnetic moment measured at (110) reflection for HoRhIn₅.

分野:中性子散乱(磁性)

Measurements of the Magnetic form Fators of α -Fe and CoFe Powder by Polarized Neutron Deffractometry

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Ferromagnetic nanoparticles are attracting attention from the viewpoint of applications to magnetic recording materials. Polarized neutron diffraction measurements at ambient temperature using 80 meV neutrons were performed to estimate the value of magnetization of the nanoparticles.

The triple-axis neutron spectrometer, TAS-1, installed at JRR-3 was used to obtain the magnetic form factor. A magnetic field of 10 kOe was applied perpendicular to the scattering vector to saturate the magnetization.

In the polarized neutron diffraction measurements, Bragg peak intensities from the samples with net magnetizations depend on the neutron spin direction with respect to the magnetization direction.

The intensities are written as follows.

$$I_{+} = \left(\frac{d\sigma}{d\Omega}\right)_{+}$$

$$= \{F_{\rm N}(Q) + \bar{F}_{\rm M}(Q)\}^{2} \exp(-2W)$$
(1)

$$I_{-} = \left(\frac{d\sigma}{d\Omega}\right)_{-}$$

$$= \{F_{\rm N}(Q) - \bar{F}_{\rm M}(Q)\}^2 \exp(-2W)$$
(2)

where $F_{\rm N}(Q)$ and $F_{\rm M}(Q)$ are nuclear and magnetic structure factors, respectively, and $\exp(-2W)$ is the Debye-Waller factor. When $F_{\rm N}(Q)$ is known, $F_{\rm M}(Q)$ can be determined from the flipping ratio (*FR*) as follows.

$$FR = \frac{\left(\frac{d\sigma}{d\Omega}\right)_{+}}{\left(\frac{d\sigma}{d\Omega}\right)_{-}} = \left(\frac{F_{\rm N}(Q) + \bar{F}_{\rm M}(Q)}{F_{\rm N}(Q) - \bar{F}_{\rm M}(Q)}\right)^{2} = \left(\frac{1 + \gamma(Q)}{1 - \gamma(Q)}\right)^{2}$$
(3)

$$\gamma = \frac{F_{\rm M}(Q)}{F_{\rm N}(Q)} \tag{4}$$

The magnetic moment was determined by fitting using the well-known magnetic form factor of α -Fe taking the depolarization effect into consideration. The scaled magnetic form factor using the magnitude of magnetic moments determined by the fitting procedure is shown in Fig. 1.



Figure 1: Scaled magnetic form factor of α -Fe

The measured magnetic moment per atom of each sample is shown in Table 1. These results show that the polarized neutron powder diffraction method is a powerful and accurate tool to microscopically determine the magnetization of ferromagnetic nanoparticles.

| sample | reference | result |
|------------------------|----------------|-------------------------|
| α -Fe (19 nm) | $2.2 \ \mu_B$ | $2.14 \pm 0.32 \ \mu_B$ |
| CoFe (35 nm) | $2.47 \ \mu_B$ | $2.42\pm0.17~\mu_B$ |
| CoFe (45 nm) | $2.47 \ \mu_B$ | $2.44\pm0.33~\mu_B$ |

Table 1: Measured magnetic moments

原子炉:JRR-3 装置:TAS-1(2G) 分野:中性子散乱(磁性)

1-2-72

Magnetic-field Induced Magnetic Phase Transitions in Multiferroic Compound of $ErMn_2O_5$

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The recent discovery of a colossal magnetoelectric (CME) effect in manganese oxides of $RMnO_3$ and RMn_2O_5 (R = rare earth $elements)^{(1,2)}$ opens possibilities of new candidates for multifunctional devices such as a magnetically controlled ferroelectric memory. These systems show a multiferroic behavior where an antiferromagnetic order and a ferroelectric order coexist, which is thought to be ingredient essential for realizing the CME effect. However, microscopic mechanisms of the CME effect is not fully understood yet. We have conducted neutron diffraction measurements under high magnetic fields in the multiferroic ErMn₂O₅ and found unambiguous relation between the microscopic magnetism and the field-induced ferroelectricity.

Neutron diffraction measurements were performed using the thermal neutron tripleaxis spectrometer TAS-2. A single crystal of ErMn_2O_5 was mounted on the $(h \ 0 \ l)$ scattering plane with a horizontal-field superconducting magnet, which results in applying a field up to 5 T along the *a*- and *c*-axis. The incident and final energies of neutrons were fixed at 14.3 meV.

Figure 1 summarizes the magnetic field (H)– temperature (T) phase diagrams for magnetic phases, showing that there exists no field dependence when the magnetic field was applied along the *a*-axis while incommensurate – commensurate – incommensurate magnetic phase transitions are induced by applying the field along the *c*-axis. In this figure, the *H* – *T* phase diagram for dielectric property reported in Ref. 3 is superposed, showing that the well-defined ferroelectric state is induced only in the CM phase. This one-to-one correspondence between the magnetic phase diagram and the dielectric phase diagram under



Figure 1: H-T magnetic phase diagram in ErMn_2O_5 , where magnetic field was applied along (a) *a*-axis and (b) *c*-axis. The dielectric phase diagram taken by Higashiyama et al.³⁾ is superposed in this figure. Abbreviations: HT-ICM; High-temperature incommensurate magnetic, CM; Commensurate magnetic, LT-1DICM; Low-temperature one dimensionally modulated incommensurate magnetic, LT-2DICM; Lowtemperature two dimensionally modulated incommensurate magnetic, PE; Paraelectric, FE; Ferroelectric, X and X'; unidentified.

a magnetic field clearly indicates that the electric polarization is magnetically induced and the commensurate magnetic structure is indispensable to the ferroelectricity in the multiferroic RMn_2O_5 system.

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原子炉:JRR-3 装置:TAS-2(T2-4) 分野:中性子散乱(磁性)

1-2-73

Temperature and Electric Field Dependences of Spin Chirality in Multiferroic Compound of $HoMn_2O_5$

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It is well known that the multiferroic compounds of HoMn₂O₅ show a colossal magnetoelectric (ME) effect. This material has successive magnetic transition below 45 K from a high-temperature incommensurate magnetic (HT-ICM) phase to a commensurate magnetic (CM) phase, and finally to a lowtemperature incommensurate magnetic (LT-ICM) phase as the temperature decreases. A recent neutron diffraction $study^{1}$ as well as dielectric measurements²) under a magnetic field have established that a well-defined ferroelectricity is induced only in the CM phase. Our magnetic structure analysis also revealed that there exists spiral spin structure in the CM phase³⁾, which can produce a spontaneous electric polarization by an inverse effect of Dzyaloshinski-Moriya interaction with $\mathbf{S}_i \times \mathbf{S}_j$ products. Thus, we have thus performed polarized neutron diffraction measurements under an electric field to clarify the relation between the rotation direction of the spiral component (spin chrality) and the direction of spontaneous electric polarization, which can confirm whether the transverse spiral structure yields an electric polarization.

Polarized neutron diffraction measurements were performed using the triple-axis spectrometer TAS-1 installed at JRR-3. An incident beam was unpolarized by a PG(002) monochromator while a scattered beam was polarized by a Heusler(111) monochromator. A single crystal of HoMn₂O₅ was mounted on the $(h \ 0 \ l)$ scattering plane. The incident and final energies of neutrons were fixed at 14.7 meV.

Figure 1 shows the temperature dependences of magnetic Bragg reflections with a chiral component (filled symbols) and without a chiral component (open symbols) un-



Figure 1: Temperature dependences of magnetic Bragg reflection with chiral component (filled symbols) and without chiral component (open symbols). Electric-field-cooling was performed below 50 K with + 5 kV/mm. The dielectric phase is paraelectric (PE), ferroelectric (FE), and unidentified (X) phases in HT-ICM, CM, and LT-ICM phases, respectively.

der an electric-field cooling with + 5 kV/mm. This result shows that there is no chiral component in the HT-ICM phase (paraelectric phase) while the chiral component arises in the CM phase (ferroelectric phase). Furthermore, in the CM phase, there is one-to-one correspondence between the electric field dependence of the amplitude of the chiral component and that of the amplitude of electric polarization, suggesting that the spin chirality yields the electric polarization. However, the relevance between the chirality component and the dielectric property in the LT-ICM phase is not clarified yet.

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原子炉:JRR-3 装置:TAS-1(2G) 分野:中性子散乱(磁性)

1-2-74

Magnetic Structure and Phase Diagram of NpIn₃ Studied by Neutron Scattering under Magnetic Field

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NpIn₃ is \mathbf{a} cubic compound with $AuCu_3$ -type structure. The ferromagnetic order was reported in a narrow temperature region for 10 K < T_C < 14 K, while an antiferromagnetic ground state is stable below $T_N = 10$ K. A previous neutron diffraction study¹⁾ reported a longitudinal modulated magnetic order with $q=(3/8 \ 3/8 \ 3/8)$ in the ground state. Two metamagnetic transitions have been reported for three principal directions, $H \parallel <100>$, <110> and <111> from the antiferromagnetic (AF) ground state to the AF+FM phase, which is followed by the FM phase at high fields. Here the order parameter of the intermediate AF+FM phase is unknown yet.

In order to clarify the order parameter and magnetic structure, we studied $NpIn_3$ by neutron scattering under a magnetic field with a triple-axis spectrometer TAS-2 in JRR-3.

The intensity of the $(0 \ 0 \ 1)$ reflection increases below 14 K then decreases rapidly at 10 K down to the background. We observes magnetic reflections, for example (3/8)3/85/8 (Fig.1). These results are consistent with a previous study¹⁾. The intensity of the $(3/8 \ 3/8 \ 5/8)$ reflection decreases rapidly under the magnetic fields above 3 T. We found the reflections $(0 \ 1/2 \ 1/2)$ and $(1 \ 1/2 \ 1/2)$ in the AF+FM phase. A field dependence of the $(1 \ 1/2 \ 1/2)$ peak intensity for various temperature is observed (Fig.2). These data indicate that the $(1 \ 1/2 \ 1/2)$ peak appears in the AF+FM phase. The critical field between the AF and the AF+FM phases is in good agreement with a magnet susceptibility²).



Figure 1: Temperature dependence of the $(3/8 \ 3/8 \ 5/8)$ and $(0 \ 0 \ 1)$ reflections intensity.



Figure 2: Field dependence of the $(1\ 1/2\ 1/2\)$ reflection intensity for various temperature.

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$\begin{array}{c} \mbox{Magnetic Ordering Process in the Layered Triangular Lattice System} \\ \mbox{LuFe}_2 \mbox{O}_4 \mbox{ in Applied Field} \end{array}$

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In $LuFe_2O_4$, the Fe ions are arranged to form the hexagonal double layers and stack in the sequence of (AB), (CA), (BC),... along the rhombohedral unique axis. The average valence of the Fe ions is expected to be $Fe^{+2.5}$ in these materials. More recently the evidence for ferroelectricity arising from electron correlations is found by means of resonant Xray scattering experiment directly determining the ordering of the Fe^{+2} and Fe^{+3} ions¹). Furthermore, the temperature dependence of the electric polarization indicates an intimate relation between the coherence length of the charge-ordered region and the magnetic correlations. We have been studying the magnetic ordering process in zero applied field of $LuFe_2O_4$, which clearly shows charge ordering at RT. A clear sign of 3-D ferrimagnetic ordering at $T_N = 242$ K has been observed. But at around $T_f = 177$ K there is yet another characteristic temperature, where the intensity distribution among the magnetic Bragg peaks changes and the correlation along c^* direction decreases drastically $^{2)}$. Thus the ground state in zero applied field seems to be a some type of spin frozen state. To shed some light on this anomalous spin freezing process we performed both magnetization measurements and neutron scattering experiments under an applied magnetic field along the *c*-axis. Figure 1 (a) depicts the temperature dependence of the Q = (1/3, 1/3, 0) magnetic peak in H = 1 T and 3 T applied field vertical to the scattering plane. Under the applied field of 1 T, T_N is slightly increased and T_f is decreased to about 150 K. Under the applied field of 3 T, T_N increases even more (almost to 260 K) and T_f is now completely suppressed. Figure

1 (b) shows the magnetization measurements in the corresponding magnetic field, and the ferromagnetic component shows exactly the same behaviour as the antiferromagnetic component observed by neutron scattering. These results indicate that the spin frozen ground state in zero field is suppressed by the applied field along the *c*-axis. A neutron scattering experiment using a horizontal field magnet will clarify the low temperature behaviour of the correlation in c^* direction in applied fields, and is planned for near future.



Figure 1: (a) Temperature dependence of Q = (1/3, 1/3, 0) magnetic peak intensity in H = 1 and 3 T applied field. (b) Temperature dependence of magnetization in H = 1 and 3 T applied field.

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原子炉:JRR-3 装置:TAS-2(T2-4) 分野:中性子散乱(磁性)

1. 中性子散乱 3) 強相関電子系

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Incommensurate Magnetic Order in the Pressure-Induced Superconductor CeRhSi₃

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Coexistence between magnetism and superconductivity is the central issue in condensed matter physics. Recently noncentrosymmetric heavy-fermion superconductor CePt₃Si [1] and UIr [2] were reported. From the fundamental point of view of symmetry, the discovery of these materials are very surprising because there are two basic symmetries which are considered indispensable to form Cooper pair: time reversal symmetry and parity. The former is important for Cooper pairing in any case while the latter is mandatory for pairing in the triplet channel. Thus there is no right picture for the non-centrosymmetric superconductivity at present.

Kimura et al. [3] discovered another noncentrosymmetric superconductor CeRhSi₃. Its crystal structure is the BaNiSn₃-type belonging to space group *I4mm* (No. 107) without an inversion center. [4] CeRhSi3 exhibits the antiferromagnetic (AFM) ordering below $T_{\rm N}$ = 1.6 K at ambient pressure. By increasing the pressure, T_N shows a maximum around 0.7 GPa, then gradually decreases. Superconductivity appears in a wide pressure range from 1.2 to 2.3 GPa (and more). Very recently, CeIrSi₃, with the same crystal structure, was reported to be categorized in the pressure-induced superconductor. [5] It shows AFM ordering below $T_{\rm N}$ = 5.0 K at ambient pressure, then $T_{\rm N}$ decreases monotonically with increasing pressure. Superconductivity appears in a wide pressure region from 1.8 to 3.5 GPa. Concerning the magnetic structure, there is only one neutron diffraction work on polycrystalline samples for both materials, [6] which exhibits no magnetic reflections with possible maximum magnetic moment of 0.25 $\mu_{\rm B}/{\rm Ce}$. To determine the magnetic structure which is closely connected with the superconductivity in

CeRhSi₃, therefore, we performed the neutron diffraction measurements using single crystals CeRhSi₃.

Single crystals were grown by Czochralsky pulling method in a tetra-arc furnace. Neutron diffraction experiments have been performed on ISSP triple-axis spectrometers GPTAS (4G) and PONTA (5G) installed at the research reactor JRR-3M of Japan Atomic Energy Agency, with the incident energy of $k_i \sim 2.67$ Å⁻¹ and the configuration of 2-axis mode. Pyrolytic graphite filters were used for both incident and scattered neutron to reduce the higher-order contamination. The crystals were cooled down to 0.75 K.

We have searched magnetic reflections in the major symmetry axes of three scattering planes of (H0L), (HHL) and (HK0). Only in the (H0L)-zone, the magnetic reflections can be observed. Figure 1 (a) and (b) show typical scan profiles through (H, 0, 1.5). One can clearly recognize the Bragg reflections at incommensurate reciprocal points Q = (0.215, 0, 1.5) and Q =(0.785, 0, 1.5), respectively, at 0.75 and 1.5 K (below $T_{\rm N}$), which disappeared at 2.0 K (above T_N). These observation indicate that the above Bragg reflections are of magnetic origin. The magnetic intensity of the former is larger than that of the latter, which roughly indicates that the magnetic moment lies in the a - b plane. This fact is in excellent agreement with an anisotropy of the susceptibility measurement. [7]

Temperature dependence of the peak intensities at Q = (0.215, 0, 1.5) and (0.785, 0, 0.5) are not shown in this report. At Q = (0.215, 0, 1.5), the intensities of ~ 800 counts well below $T_{\rm N}$ gradually decreases with temperature and suddenly drops to ~ 180 counts of background intensity around $T_{\rm N} \sim 1.6$ K. The temperature dependence at Q = (0.785, 0, 0.5) also shows the sim-

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ilar behavior. It should be noted that the obtained Néel temperature of 1.6 K corresponds to the anomaly in both the susceptibility and electrical resistivity measurements using single crystals. [7]

To determine the incommensurate magnetic structure, we have performed radial scans at 17 inequivalent Bragg points. After calculating the integrated intensities of various models, we propose that the longitudinal spin-density wave (LSDW) state is realized below $T_{\rm N}$ in CeRhSi₃. This magnetis structure is in excellent agreement with the dHvA experiments [7], in which dHvA signals in both CeRhSi3 and LaRhSi3 are observed and the different Fermi surfaces lead to that the 4f electrons of CeRhSi3 are itinerant. The samll size of the magnetic moment is $0.16(10) m_B/f.u.$, which indicates that this material is located in the vicinity of quantum critial point (QCP).

Another interesting feature of the magnetic structure is the propagating along *c*-axis of up-up-down-down spin arrangement because Q = (0, 0, 1) is not allowed for the BaNiSn₃-type crystal structure. This is possibly due to the lack of the inversion center along *c*-axis and the legand electrons of Rh and/or Si atoms might play an important role in the magnetic structure.

The neutron experiments were supported by ISSP, University of Tokyo (PACS No. 6418). A part of this work was supported by the Grant-in-Aid for the Ministry of Education, Culture, Sports, and Science of Japan.

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Fig. 1. Peak profiles through (a) Q = (0.215, 0, 1.5) (left) and (b) Q = (0.785, 0, 1.5) (right), which has asymmetric shape due to the sample mosaicity.

Evolution of commensurate magnetic state in the heavy-fermion superconductor $\mbox{CeRh}_{0.6}\mbox{Co}_{0.4}\mbox{In}_5$

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In recent years, there has been growing interest in the physical property near the quantum critical point (QCP) in the heavyfermion systems. The heavy-fermion compound CeRhIn5 orders in an incommensurate antiferromagnetic (AF) phase with the modulation of $q_h = (1/2, 1/2, 0.297)$ [1]. It is revealed in the Co-doped alloys $CeRh_{1-x}Co_{x}In_{5}$ [2] that the AF phase is suppressed with increasing *x*, and then disappears at $x_c \sim 0.7$. At the same time, the superconducting phase appears between x = 0.4 and x = 1. The evolution of superconducting state around x_c implies that these two states are strongly coupled with each other. To investigate the relation between these two phases, we have performed the elastic neutron scattering experiments for CeRh_{0.6}Co_{0.4}In₅ [3].

Single crystals of CeRh_{0.6}Co_{0.4}In₅ were grown by the In-flux method. The samples were shaped into bar (typical size: ~ $3 \text{ mm}^2 \times 20 \text{ mm}$) in order to minimize the effects of the neutron absorption caused by the Rh and In ions contained in the samples. The unpolarized and polarized elastic neutron scattering experiments were performed using triple-axis spectrometers GP-TAS and PONTA located at the JRR-3M research reactor of JAEA, respectively. The measurements were performed in the (*hhl*) scattering plane for both the experiments.

Figure 1 shows the neutron scattering pattern obtained by the $(1/2, 1/2, 1 + \zeta)$ $(0 \le \zeta \le 1)$ scan at 1.4 K, using unpolarized neutron beam. We have found that three nonequivalent Bragg peaks, other than nuclear ones expected from the tetragonal structure, develop at low temperatures. The wave vector characterizing

these peaks are estimated to be $q_{\rm h}$ = $(1/2, 1/2, 0.306), q_1 = (1/2, 1/2, 0.402),$ and $q_c = (1/2, 1/2, 1/2)$. The polarized neutron scattering experiments indicate that all these peaks originate from the magnetic scatterings. The appearance of the Bragg peaks for q_h is attributed to the incommensurate AF order, since pure CeRhIn₅ also shows this type of order. On the other hand, the development of the Bragg peaks relevant to the modulation of $q_{\rm c}$ and $q_{\rm 1}$ indicates that new AF orders evolve with intermediate Co concentration. We are now planning to perform further neutron scattering experiments for entire *x* range to elucidate the nature of these AF phases.

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Fig. 1. The antiferromagnetic Bragg-peak profiles at 1.4 K.

Ferromagnetic and antiferromagnetic orders in $CaRu_{1-x}Mn_xO_3$

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The nature of metal-insulator transition in the transition-metal oxides is one of the intriguing issues in the condensedmatter physics. The distorted perovskite compound CaRuO₃ (the GdFeO₃-type orthorhombic structure; space group *Pnma*) is considered to be paramagnetic metal, and located in the vicinity of the metalinsulator transition. Recently, it is revealed that the ionic substitutions for the Ru site dramatically enhance the magnetic correlation [1, 2, 3, 4]. In particular, we found that the substitution of Mn for Ru induces both the ferromagnetic and antiferromagnetic (AF) components in magnetization *M*, accompanying the variation of the electrical resistivity from metallic to insulating behavior. These features are expected to be attributed to the variations of the d electronic state, and it is therefore interesting to investigate the microscopic properties of the d electrons in the intermediate Mn concentration range. In the present study, we have performed powder neutron diffraction experiments for $CaRu_{1-x}Mn_xO_3$.

polycrystalline The samples of $CaRu_{1-x}Mn_xO_3$ with x = 0.4 0.6 and 0.7 were prepared by the solid-state The neutron diffraction meamethod. surements for powdered samples were performed in the temperature ranges between 15 K and 290 K, using the HERMES spectrometer installed at the research reactor JRR-3M of JAEA. The wavelength of the incident neutron was selected to be 1.8264 Å. Figure 1 shows the neutron powder diffraction profiles at 15 K for x = 0.4, 0.6 and 0.7. We have observed the development of Bragg peaks ascribed to the AF order with the G-type structure. These AF Bragg-peak intensities increase with increasing x, indicating that the AF

structure becomes stable in the Mn-rich concentration range. Furthermore, the intensities of some Bragg-peaks, such as the (101) and (020) peaks, are found to show notable temperature variations. They are roughly in proportional to $M^2(T)$, suggesting that the ferromagnetic order develops in the intermediate x range. These features are roughly consistent with the previous report on the Mn-rich region [5]. The precise analysis on the present neutron diffraction data is now in progress.

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Fig. 1. Neutron powder diffraction profiles of $CaRu_{1-x}Mn_xO_3$ with x = 0.4, 0.6 and 0.7 at 15 K. The open and closed arrows indicate the antiferromagnetic and ferromagnetic Bragg peaks positions, respectively.

Magnetic excitations of high TQ compound YbAl3C3

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YbAl3C3 shows a second-order transition at 80 K on the result of specific heat measurement. We think that this transition indicates an antiferroquadrupolar ordering (AFQ) and we interested in the reason of extremely high transition temperature. It is important to determine crystalline electric fields (CEF) parameters to discuss detail of the AFQ. Therefore, we carried out inelastic neutron scattering experiments of YbAl3C3.

Fig.1(a) shows inelastic neutron spectra of YbAl3C3 and LuAl3C3 at 8 K and 100 K. The well-defined excitations are observed around 14, 20, 33 and 43 meV. The spectra of LuAl3C3 shows phonon contributions around 14 and 43 meV. However, the intensity of the peak around 43 meV of YbAl3C3 decreases obviously with increasing temperature. Therefore, this excitation is attributed to magnetic one. As a result, it is thought that the split of the CEF are 20, 33 and 43 meV.

On the other hand, unexpected magnetic excitations were observed around 1.5 and 2.9 meV in Fig.1(b). It seems that these excitations appear below 80 K. A decrease in temperature splits the excitations into two peaks and the intensities develop dramatically. At this stage, we do not have an understanding of the mechanism that allows such a giant magnetic excitations to form. However, a valence of Yb ion is estimated to be a trivalent state with large antiferromagnetic interaction between Yb ions by magnetic measurements (effective Bohr magneton 4.57, Weiss temperature -94 K). Furthermore, Yb ions form a triangular lattice and no magnetic transition was observed down to 20 mK. We think that such the behavior of low energy excitations suggests a sign of a frustration or a fluctuation between Yb magnetic moments.



Fig. 1. Inelastic neutron spectra of YbAl3C3 and LuAl3C3.

Antiferromagnetic Phase Transition in the Kondo Semiconductor CeOs₄Sb₁₂

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CeOs₄Sb₁₂ has a band gap of around 10 K estimated from the temperature dependence of electrical resistivity, while it shows the large T-linear coefficient of specific heat $\gamma = 200 \text{mJ/K}^2/\text{mol}$ (E. Bauer et al., J. Phys.: Condens. Matter 13 (2001) 4495, H. Sugawara et al., Phys. Rev. B 71 (2005) 125127). Our previous inelastic neutron scattering experiment revealed no clear crystal-filed excitation, in contrast to the Curie-Weiss behavior of magnetic susceptibility in higher temperature region (C. P. Yang et al., J. Phys. Soc. Jpn. 74 (2005) 2862). These facts indicate that CeOs₄Sb₁₂ is a so-called Kondo semiconductor due to the strong *c*-*f* hybridization. It is notable that this material shows a phase transition at 0.9 K under zero magnetic field and the ordering temperature is enhanced by applied magnetic fields. SDW or CDW transitions are suggested from the Sb-NQR result in the ordered phase (M. Yogi et al., J. Phys. Soc. Jpn. 74 (2005) 1950).

In order to identify the nature of ordering in $CeOs_4Sb_{12}$, we performed neutron diffraction experiment at the tripleaxis spectrometer TOPAN (6G) and HER (C1-1). We adopted the dilution refrigerator of ISSP, Univ. of Tokyo. A single crystal sample synthesized by the Sb-flux method was cooled down to 0.1 K.

We succeeded in observing weak antiferromagnetic reflections characterized by a wave vector $\mathbf{q} = (1 \ 0 \ 0)$ below the ordering temperature, as shown in the figure. Assuming the magnetic ordering at the Ceion sites forming the *bcc* lattice, we evaluated the ordered moment value of around $0.05\mu_{\rm B}/{\rm Ce}$. Such a tiny ordered magnetic moment as well as the unusual phase diagram are consistent with the SDW-like antiferromagnetic instability due to the *c*-*f* hybridization as proposed in the theoretical works on Kondo semiconductors (T. Ohashi *et al.*, Phys. Rev. B 70 (2004) 245104, Y. Imai *et al.*, J. Phys. Soc. Jpn. 75 (2006) 033706). On the other hand, the antiferromagnetic peak disappears above 1 T in contrast to the reported phase diagram. The antiferromagnetic region coincides with that of large magnitude of electrical resistivity. Thus, we expect that the electronic state change from the gapped state in the low field region to the metallic one above 1 T correlates with the magnetic state.



Fig. 1. Scan profiles through ${\bf Q}=(1\ 0\ 0)$ of $CeOs_4Sb_{12}.$

Magnetic Excitation in the Antiferro-Type Multipolar Ordering Phase of $PrFe_4P_{12}$

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PrFe₄P₁₂ has recently attracted much attentions because of the heavy electron behavior that is novel for Pr-based compounds (H. Sugawara et al.: Phys. Rev. B 66 (2002) 134411, H. Sato et al.: Phys. Rev. B 62 (2000) 15125). It undergoes a nonmagnetic phase transition at $T_{\rm A} = 6.5$ K (Y. Aoki et al.: Phys. Rev. B 65 (2002) 064446, L. Keller et al.: J. Alloys and Compounds 323-324 (2001) 516). X-ray superlattice reflections characterized by the wave vector $\mathbf{q} =$ (100) were observed below T_A (K. Iwasa *et* al.: Physica B 312-313 (2002) 834). Our neutron diffraction study revealed antiferromagnetic reflections induced by magnetic fields below T_A . These phenomena indicate antiferro-type ordering of the 4f electrons of Pr ions (L. Hao et al.: Acta Physica Polonica B 34 (2003) 1113). Recently, this antiferro-type ordered phase has been interpreted as the Γ_1 -type or scalar-type order of higher-rank multipole that does not break the local symmetry (A. Kiss and Y. Kuramoto: J. Phys. Soc. Jpn. 75 (2006) 103704). In the heavy electron phase, magnetic excitation spectra from the polycrystalline sample are heavily overdamped and quasielastic (K. Iwasa et al.: Acta Physica Polonica B 34 (2003) 1117). This fact indicates that the $4f^2$ electrons of Pr^{3+} ion hybridize strongly with carriers. Since elementary excitation in the multipolar ordering phase is an interesting subject, we performed inelastic neutron scattering measurements for single crystal samples.

Inelastic neutron scattering experiments were carried out on the cold- and thermalneutron spectrometers HER (C1-1) and TOPAN (6G), respectively.

Figure 1 shows energy spectra at $\mathbf{Q} = (0\ 1.9\ 0)$ obtained in the HER experiment. At zero magnetic field at 1.6 K, two sharp peaks appear at 1.5 and 3.2 meV, in con-

trast to the quasielastic response above T_{A} , although it is not shown here. We have already confirmed that these excitations are less dispersive, so that they are originated from the excitations in low-lying crystalfield levels. These peaks are considered to be elementary excitations in the higher multipolar ordering phase. When the magnetic field was applied to 2.75 T corresponding to the intermediate region of the ordered phase, the 1.4 meV peak seems to split in two or three peaks. This phenomenon can be naively understood as a lifting of the crystal-field-level degeneracy. As discussed recently, the Γ_1 -type or scalartype order conserves the local symmetry and the crystal-field level splitting thorough the transition temperature, although the two Pr ions in the bcc unit cell become inequivalent. This scenario is consistent with the observed splitting of the excitation peak.



Fig. 1. Inelastic magnetic neutron scattering profiles at $\mathbf{Q} = (0 \ 1.9 \ 0)$ in the ordered phase of PrFe₄P₁₂.

Inelastic Neutron Scattering from the Heavy-Electron System NdFe₄P₁₂

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Rare-earth filled skutterudite compounds have been extensively studied in terms of strongly correlated electron phenomena. One of the topics is heavy electron state appearing in the system with two or more 4f electrons per rare-earth ion. $PrFe_4P_{12}$ with $4f^2$ configuration of Pr^{3+} is a typical example, which shows the Sommerfeld coefficient for electronic specific heat $\gamma = 1.4 \text{J/mol/K}^2$ and the clear -logT behavior of electrical resistivity (Y. Aoki et al., Phys. Rev. B 65 (2002) 064446, H. Sugawara et al., Phys. Rev. B 65 (2002) 134411). Our inelastic neutron scattering experiment revealed the quasielastic magnetic response indicating the strongly hybridized state (K. Iwasa et al., Acta Physica Polonica B 34 (2003) 1117).

A similar $-\log T$ behavior is also found in NdFe₄P₁₂ with $4f^3$ configuration of Nd³⁺ (H. Sato *et al.*, Phys. Rev. B 62 (2000) 15125). However, it undergoes a ferromagnetic phase transition at $T_{\rm C} = 1.9$ K and the magnitude of ordered magnetic moment was evaluated as $1.6\mu_{\rm B}/\rm Nd$ (L. Keller et al., J. Alloys and Compounds 323-324 (2001) 516), which is much larger than the typical heavy electron materials and seems not to be consistent with the singlet formation due to Kondo effect. Thus, the heavy electron behavior in electrical resistivity of $NdFe_4P_{12}$ with well-localized 4f electrons is a mysterious property. In order to investigate the 4f electron state of this material, we performed inelastic neutron scattering experiments.

The triple-axis spectrometer TOPAN (6G) and HER (C1-1) were adopted to measure energy spectra from a single-crystalline sample.

Figure 1 shows energy spectra at $\mathbf{Q} = (4\ 0\ 0)$ of NdFe₄P₁₂ as a function of temperature. Quasielastic intensities extending beyond 5 meV were detected. Because the

intensity decreases with decrease of temperature, these intensities are considered to be come from structural fluctuation. In the typical heavy-electron systems, magnetic quasielastic intensities have been generally observed, due to interaction between the localized 4f electrons and conduction electrons. In this case, the intensity of broad response increases with decrease of temperature, as the Pauli paramagnetic susceptibility. The observed result of NdFe₄P₁₂ is completely opposed. As written in the other report of this volume, we observed similar phonon spectra in PrRu₄Sb₁₂ and PrOs₄Sb₁₂, in which the filled Pr ions vibrate with large amplitude within the surrounding large cage of Sb. The relaxation mode may be given by the strong interaction between the Pr-ion motion and the electronic state. If the observed quasielastic response in NdFe₄P₁₂ was also come from such electron-phonon coupling, the heavy electron behavior would relate with the observed structural fluctuation spectra. We have to continue the study to clarify the mechanism of appearance of the quasielastic intensity.



Fig. 1. Energy spectra at $\mathbf{Q}=(4\,0\,0)$ of $NdFe_4P_{12}$ as a function of temperature.

Thermoelectric properties and crystal structures of chemically-modified layered thermoelectric materials

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Since the discovery of large thermoelectric power in the layered compounds, misfitlayered cobalt oxides particularly have attracted much interest as candidates for thermoelectric (TE) materials. We have employed a high-resolution neutron powder diffraction technique to investigate the modulated crystal structure of [(Ca1-x Pbx)2CoO3]0.62CoO2 polycrystalline samples. The solubility limit of Pb was determined on the basis of powder X-ray diffraction (XRD) intensities at room temperature using a JEOL JDX-3530 diffractomater (CuK α). Neutron powder diffraction (ND) data were collected at room temperature using the Kinken powder diffractometer for high efficiency and high resolution measurements (HERMES) of Institute for Materials Research (IMR), Tohoku University, installed at the JRR-3M reactor in Japan Atomic Energy Research Institute (JAERI), Tokai. Neutrons with a wavelength of 0.18265 nm were obtained by the 331 reflection of the Ge monochromator. The ND data were collected on thoroughly ground powders by a multiscanning mode in the 2 θ range from 3.0 ° to 153.9 ° with a step width of 0.1 ° and were analyzed using a Rietveld refinement program, PREMOS 91, adopting a superspace group of C2/m(1p0)s0, where the CdI2type [CoO2] subsystem has C2/m symmetry while the RS-type BL [Ca2CoO3] subsystem has C21/m symmetry. The crystal structures and interatomic distance plots were obtained with the use of PRJMS and MODPLT routines, respectively; both were implemented in the PREMOS 91 package. Figure 1 shows Co1-O (upper panels) distances in the [CoO2] subsystem and Co2-O (lower panels) distances in the RStype subsystem of (a) x=0 (left) and (b) x=0.02 (right) plotted against t. Among

these bonds, two apical Co2-O3 bonds are fairly shorter than the other four equatorial Co2-O2 bonds, ranging from 0.17 to 0.195 nm for x = 0 and from 0.165 to 0.19nm for x=0.02. The mean distance of Co2-O3 bonds for x=0 does not change very much as that of Co2-O3 bonds for x=0.02, i.e., both distances are 0.18 nm. This fact indicates that the Co ions in the RS-type subsystem are not replaced by tetravalent lead ions in the x range from 0 to 0.02. On the other hand, the four equatorial Co2-O2 bonds for x=0 (lower left panel) show small modulation amplitudes from 0.205 and 0.275 nm, relative to the x=0.02 (lower right panel) of 0.18 and 0.3 nm. However, the mean distances of the Co2-O2 bonds of the two phases are almost equal, i.e., 0.24 nm. In contrast to the Co2-O bonds, the six Co1-O1 bonds illustrated in the upper panels remain stable with increasing x, where the mean distance of the Co1-O1 bonds is 0.19 nm.



Fig. 1. Fig.1 Co1-O distances in the [CoO2] subsystem and Co2-O distances in the RS-type subsystem.

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Spin Dynamics of Rare Earth Antiferroquadrupolar Ordering Compound HoB2C2

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The RB2C2 (R=rare earth) compounds, which have the tetragonal LaB2C2 type structure with P4/mbm symmetry show diversified magnetic properties caused by coexistence of antiferroquadrupolar (AFQ) and antiferromagnetic (AFM) interactions. In particular, DyB2C2 is the first tetragonal rare earth compound in which an AFQ ordering is realised. Since the exact ground state by crystalline electric field under tetragonal symmetry has no degree of freedom on electric quadrupolar moments, it was thought that no AFQ ordering can be realised in the tetragonal rare earth compounds.

On the contrary, we have proved that some of RB2C2 are AFQ ordering compounds with higher TQ than other typical AFQ compounds. Thus, to understand necessary conditions of AFQ orderings in rare earth compounds, it is indispensable to clarify characters of the AFQ ordering in RB2C2. Of the RB2C2 system, HoB2C2 is particularly unique because of the following points: (i) the AFQ ordering in HoB2C2 is realised at TQ=4.5K below the magnetic ordering temperature, TN=5.9K[2], (ii) anomalous magnetic diffuse scattering is observed above TQ up to 2TQ[4].

We expect that the AFQ orderings in RB2C2 probably yield anomalies of dynamic properties because the lattice and spin systems in RB2C2 must be coupled by the AFQ orderings through the strong LS coupling. In particular, in HoB2C2, characteristic diffuse scattering is observed around the transition temperatures, implying some kind of spin fluctuation. Therefore, to observe magnetic excitations in HoB2C2, we performed inelastic scattering experiments on a single crystalline sample of HoB2C2 on the triple axis spectrometer HER at the C1-1 beam hole of JRR3M of JAERI(Tokai). The collimation condition was g-open-PG filter-S- Radial -B, kf=1.550AA-1 with the horizontal focusing analyzer condition

In the experiments on C1-1, we observed obvious magnetic excitations at T=1.4K below TQ and TN around the (1,0,0) position which is the magnetic zone center. Figure shows the energy spectrum at (1,0,0)in HoB2C2 at T=1.42K . As shown in the figure, an obvious magnetic excitation was observed around 1meV, which shows the energy gap at the zone center. Moreover, in this experiments, we newly found higher magnetic excitation around 3meV. On the other hands, we observed no quasi-elastic scattering within the resolution limit even in the temperature region where the characteristic magnetic diffuse scattering is observed[4]. This indicates that the characteristic magnetic diffuse scattering in HoB2C2 is mainly due to elastic scattering not to some spin fluctuations.

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Fig. 1. Intensity distribution of magnetic excitations along the a^* axis in HoB2C2 at T=1.5K around (1,0,0). Vertical and horizontal axes are the excitation energy and q vector.

Magnetic structure study of the multi-step metamagnet Celr3Si2

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CeIr3Si2 crystallizes in the orthorhombic ErRh3Si2-type structure (Imma, No. 74). The lattice parameters are a=7.1765 A, b=9.7274 A and c=5.5971 A. The results of electrical resistivity, specific heat and magnetic susceptibility measurements reveal that CeIr3Si2 is a Kondo-lattice compound showing two successive magnetic transitions at 4.1 K and 3.3 K. Below 3.3 K, the isothermal magnetization of polycrystalline sample displays four-step metamagnetic transitions at 0.6 T, 0.9 T, 1.2 T and 1.43 T. It should be needed to obtain the magnetic structures between each transition field in order to study the origin of multi-step metamagnetism of CeIr3Si2. We have been performing the elastic neutron scattering of powder sample and singlecrystal one.

At first, we measured the powder neutron diffraction at 300 K, 10 K, 3.7 K and 1.5 K under 0 T. The powder pattern at 300 K agrees with the orthorhombic ErRh3Si2type structure as shown in Fig.1(a). At 1.5 K, we observed a possible magnetic Bragg peak at 2theta=25.8 degree as shown in Fig.1(b).

We also made a measurement using a single crystal sample. No magnetic reflections have been observed on the principal indices at 0.7 K. Therefore, we will perform futher measurements including non-integer indices.



Fig. 1. Powder neutron diffraction patterns of CeIr3Si2.

Investigation of the magnetic excitations in high- T_C cuprates Bi_{2.1}Sr_{1.9}CaCu₂O_{8+ δ}

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The interplay between antiferromagnetic (AF) spin fluctuations and superconductivity is the central issue in the physics of high-transition temperature (high- T_c) superconductivity because of the persistent AF fluctuations in the superconducting phase. Recently, similar magnetic spectra have been reported from two families of high-Tc materials, $La_{2-x}Ba_xCuO_4$ and $YBa_2Cu_3O_{6+x}[1, 2]$, which includes a characteristic hourglass magnetic excita-If spin fluctuations are important tion. for the mechanism of high- T_c superconductivity, they should be universal for all copper-oxide systems. Although two families of high- T_c materials show the similar magnetic excitation spectrum, it is still not clear whether they are the universal feature of all cuprates. One way to resolve this issue is to investigate another high- T_c system $Bi_{2.1}Sr_{1.9}CaCu_2O_{8+\delta}$ (Bi2212). We explored the magnetic spectrum in optimally doped Bi2212. Single crystals of Bi2212 were grown using travellingsolvent-floatingzone method. Neutron scattering experiments were performed on the triple-axis spectrometer PONTA installed at the JRR-3 Reactor of the JAEA. We have aligned 19 single crystals on Al plates. The total mass of aligned crystals is 16.5g (2.5cc), which is 40 times as large as the crystal used in the previous report[3].

Our experiment shows a clear enhancement of the scattering at (π,π) around 36 meV below T_c , however, we could not confirm the Q dependence expected from a magnetic peak. Figure 1(a) shows the difference spectrum at T = 1.2 K ($T < T_c$) and 100 K ($T > T_c$) at $Q = (1/2 \ 1/2 \ -14)$ as a function of energy. Although the difference spectrum have a peak around 36 meV, the peak at (π,π) in the Q-scan (shown by closed circles in Fig.1(b)) disappears at

 $(3\pi,3\pi)$ (open circles). If the peak at E = 36 meV and (π,π) is magnetic in origin, the peak intensity should follow the square of magnetic form factor of Cu²⁺ which decreases from 0.43 at (π,π) to 0.19 at $(3\pi,3\pi)$. Further investigation of the magnetic excitations in Bi2212 will be required by using polarized neutrons.

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Fig. 1. a) Difference spectrum of constant-Q scan at $(1/2 \ 1/2 \ -14)$ at T = 1.2 K $(T < T_c)$ and 100 K $(T > T_c)$. b) constant-Energy spectra at $\hbar \omega = 36 \text{ meV}$ with (*hh*-14) and (*h* - 1 *h* - 1 -14).

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Evolution of spin gap structure in underdoped LSCO

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Neutron scattering studies for high- $T_{\rm c}$ cuprates have revealed that a welldefined gap opens at low temperature in the energy spectra, which is called "spin gap", in LSCO ($La_{2-x}Sr_xCuO_4$) and YBCO (YBa₂Cu₃O_{6+y}). As for LSCO, the spin gap is observed only around the optimum doping concentration 0.15 $\leq x \leq$ 0.18 [1]. On the other hand, the spin gap of YBCO appears in the wide underdoped region $0.5 \le y \le 0.95$ [2]. The invisibility of spin gap in underdoped LSCO is a longstanding issue. To solve the issue, we have carried out a systematic series of inelastic neutron scattering experiments on single crystals of LSCO with *x* lower than optimal doping.

Single crystals of LSCO with x = 0.125, 0.13, 0.135, 0.14, 0.15 were grown by a traveling solvent floating zone method. For these crystals, we estimated the superconducting transition temperature T_c by the shielding signals and the Sr concentration x by the inductively coupled plasma (ICP) analysis. The values of *x* and $T_{\rm c}$ are summarized in Table. 1 and are almost consistent with the previous results. Neutron scattering experiments were performed with the triple-axis spectrometer TOPAN installed at JRR-3M. We selected the final energy of 13.5 meV with the horizontal collimator sequence of 40'-30'-30'-80'. In order to gain sufficient intensity, we mounted single crystals with total weight of more than 2.5 cc (=17 g) for each concen-

| Table 1. <i>x</i> and | $T_{\rm c}$ in La ₂ | 2-xSr _x CuO ₄ |
|-----------------------|--------------------------------|-------------------------------------|
|-----------------------|--------------------------------|-------------------------------------|

| sample | Sr x | $T_{\rm c}$ |
|-----------|----------|-------------|
| x = 0.15 | 0.142(8) | 37.6 K |
| x = 0.14 | 0.130(5) | 36.3 K |
| x = 0.135 | 0.125(5) | 33.7 K |
| x = 0.13 | 0.120(6) | 30.9 K |
| x = 0.125 | 0.115(6) | 25.8 K |
| | | |

tration.

In the low energy region ($\omega \leq 10$ meV), the spin excitation appears at incommensurate (IC) positions $Q = (\frac{1}{2} \pm \delta \frac{1}{2} 0)$, $(\frac{1}{2}$ $\frac{1}{2} \pm \delta 0$ in the high-temperature tetragonal (HTT) notation. Figure 1 shows the energy spectra of the dynamical magnetic susceptibility $\chi''(Q_{\delta}, \omega)$ at the IC peak position $Q = Q_{\delta}$ below 10 K. As for $x \ge 0.135$, the clear spin gap were observed and its structure is almost unchanged. While, for x = 0.125 and 0.13, the spectrum shows an upturn behavior around 3 meV. This sudden change of the spectrum around x =0.13 indicates that the low-energy additive state appears with keeping the gap structure in $x \leq 0.13$. In addition, we found weak elastic magnetic peaks for x = 0.13, and the peaks becomes sharp and strong for x = 0.125, which is coincident with the appearance of the additional state. Therefore, the spin gap appears robust in 0.125 \leq $x \leq 0.15$ and the low-energy additional state emerges near $x \sim 1/8$.

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Fig. 1. Energy spectra of the dynamical magnetic susceptibility $\chi''(Q_{\delta}, \omega)$ at the incommensurate peak position $Q = Q_{\delta}$ below T = 10 K for $La_{2-x}Sr_xCuO_4$ (x = 0.125, 0.13, 0.135, 0.15).

Concurrent Measurements of Neutron Diffraction and AC Susceptibility in the Pressure-Induced Superconducting Ferromagnet UGe₂

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discovered the ferro-Saxena et al. magnetic (FM) superconductor UGe₂ in which superconductivity (SC) occurs at high pressure range between \sim 1.0 and \sim 1.5 GPa. [1]. In the FM phase, there seems to be another phase transition or crossover at T_x (\simeq 32 K at ambient pressure). This characteristic temperature T_x also decreases with increasing P and becomes suppressed to zero at a critical pressure P_x (\simeq 1.2 GPa) where a maximum SC transition temperature ($T_{\rm SC} \sim 0.7$ K) appears. In our previous work [2], we presented the temperature dependence of magnetic Bragg peak intensities under P by the neutron diffraction (ND) technique to reveal the nature of the transition at P_x . We have found that the low-*T* behavior of the uniform magnetization can be explained by a conventional Stoner model, indicating that the FM state below P_x can be understood as the perfectly polarized state.

Very recently, Ban *et al.* reinvestigated a SC phase diagram of UGe₂ by AC magnetic susceptibility measurements. [3] They found that the T_{SC} and volume fraction show a "M-shaped" structure as a function of *P* and suggested that both of two critical points play an important role in the occurrence of SC. These observations are possibly ascribed to the improved homogeneity of the *P* transmitting medium. To examine the correlation between SC and FM in UGe₂, we have to performe ND measurements by simultaneously detecting the superconductivity in UGe₂.

A single crystal was grown by Czochralsky pulling method with a tetra-arc furnace. The *P* was generated by a berylliumcopper pressure cell [4] using Daphne oil 7373 as a *P* transmitting medium, instead of Fluorinert FC-75 used in the previous measurements. [2, 4] Coils of ac susceptibility measurements are wound in the outside of the cylinder. The *P* was estimated by determining the T_{SC} of Sn. Elastic ND experiments has been performed on the tripleaxis spectrometer PONTA (5G) at temperature down to 0.1 K using a dilution refrigerator.

In this study, the pressure was tuned just above P_x , where no FM Bragg peak jump was observe corresponding to T_x . AC susceptibility measurements successfully show the 80 % volume fraction of SC at 0.2 K with T_{SC} of 0.58 K in UGe₂. As shown in fig. 1, there seems little change in the FM bragg peak profiles between at 0.2 K (below T_{SC}) and 1 K (above T_{SC}).

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Fig. 1. FM Bragg peak profiles of through (a) Q = (0, 0, 1) (upper) and (b) its temperature difference between 0.2 K and 1 K (lower).

Magnetic order and magnetic excitations in the Kondo-semiconductor CeOs₄Sb₁₂

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CeOs₄Sb₁₂ is a candidate of a Kondosemiconductor realized in the group of the skutterudite compounds which show various strongly correlated electron phenomena in the same crystal structure. In our previous experiments we found that the compound shows an antiferomagnetic ordering with a tiny magnetic moment of about 0.05 $\mu_{\rm B}/{\rm Ce}$ at the temperatures below about 1 K. We also observed some indication of magnetic excitations with an energy scale of 10 K around the magnetic zone center in our inelastic neutron scattering measurement down to 0.7 K. The purpose of the present work is to get more detailed information on the nature of the unusual magnetic order and magnetic excitations in the compound. We carried out an experiment at the cold neutron triple axis spectrometer C1-1:HER equipped with a large horizontally focused analyzer. The single crystal sample of 13 g was cooled down to 80 mK using the dilution refrigerator. Final neutron energy of 5 meV $(k_f=1.553 \text{ Å}^{-1})$ was employed.

In the inelastic scattering measurements, we observed similar inelastic response with the energy transfer below about 1 meV around Q=(1,0,0) reciprocal lattice point at 80 mK as those observed in the previous experiment. However, the signal intensities were very weak and it was difficult to well characterize them except the features described above from the data obtained within the allocated beam time.

We also measured temperature and magnetic field dependencies of the intensity of the (1,0,0) magnetic Bragg peak in order to get useful information about the ordered state below 1 K. Fig. 1 depicts the observed temperature dependences of the peak intensities at magnetic fields of zero and 0.5 T. Note that the horizontal axis is scaled by the 3/2 power of the temperature. The experimental result shows that the temperature dependence of the magnetic moment associated with the antiferromagnetic order obeys well the 3/4 power law. It was also observed that the intensity of the (1,0,0) magnetic peak decreases linearly with increasing magnetic field and disappears at about 1 T.

These results suggest that the low temperature ordered phase of CeOs₄Sb₁₂ observed below about 1 K is categorized as that of the weak antiferromagnetism in the itinerant electron system that is described by the spin-fluctuation theory by T. Moriya group. However, the fact of the disappearance of the antiferromagnetic Bragg peak at about 1T is puzzling since the reported upper critical magnetic field of the ordered phase determined by the specific heat and resistivity measurements is more than 10 T at low temperatures. Further experiment is necessary to establish overall features of the unusual electronic state of the compound.



Fig. 1. Temperature dependence of the (1,0,0) peak of $\text{CeOs}_4\text{Sb}_{12}$

Spin correlations in electron-doped antiferromagnetic ordered phase of Pr1-xLaCexCeO4

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High-transition temperature (T_c) superconductivity mediated by spin fluctuations is one of central issues in the strongly correlated electron systems. Extensive neutron scattering measurements on hole-doped $La_{2-x}Sr_xCuO_4$ have revealed an evolution of spin correlation by doping and its intimate relationship with the superconductivity [1, 2]. To understand a novel magnetism in carrier-doped Mott insulators and the role in the high- T_c SC mechanism, comparative studies betweeen holedoped and electron-doped systems are indispensable. However, due to the difficulty in preparing superconducting single crystalline samples, experimental studies for electron-doped system have been far behind compared to those for hole-doped system.

Recent neutron-scattering study revealed the existence of the commensurate low-energy spin fluctuations in optimally electron-doped Nd_{1.85}Ce_{0.15}CuO₄ (NCCO)[3] and Pr_{0.89}LaCe_{0.11}CuO₄[4]. These observations indicate that the collective spin fluctuations commonly exist in the SC phase irrespective of carrier type. However, to investigate the universal nature in the electron-doped system further systematical study is important. We therefore performed systematic neutron scattering measurements on the Pr_{1-x}LaCe_xCeO₄ system.

Figure 1 shows the peak profiles with ω =3, 5, and 8 meV for non-superdonducting the sample of $Pr_{0.93}LaCe_{0.07}CuO_4$ ($T_N \sim 100K$). Clear commensurate low-energy spin fluctuations are observed at the antiferromagnetic zone center as is the case of non-doped mother compound. However, the peak-width is slightly broader than the resolution

limited value. This result suggests that the doped electron can affect the spin fluctuations and reduces the spatial coherence length. Further upon doping, the paek-width drastically broadens when the system becomes superconductor and the broadening of the width continuously progresses in the superconducting phase, indicating a close relation between the spin correlations and the superconductivity in the electron-doped system.

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Fig. 1. Constant energy spectra with ω^{a} (a) 3 meV, (b) 5 meV, and (c) 8 meV for $Pr_{0.29}LaGe_{0.07}CuO_4$ measured at 7K.

Spin fluctuations in high-temperature-tetragonal phase of La1.70Sr0.24Ce0.06CuO4

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It is known that incommensurate (IC) spin fluctuations in the underdoped $La_{2-x}Sr_xCuO_4$ shows a close relation with the superconductivity[1]. On the other hand, our neutron-scattering measurement on $La_{1.875}Ba_{0.125}CuO_4$ revealed an enhancement of the low-energy spin correlations in the low-temperature-tetragonal phases, in which the superconductivity is strongly suppressed[2]. Therefore, the superconductivity, the spin fluctuations and the crystal structure are intimately correlated.

In order to clarify the inherent relation between the spin fluctuations superconductivity and the without the effect of lattice distortion, we performed neutron-scattering experiment on In this system, $La_{1.70}Sr_{0.24}Ce_{0.06}CuO_4.$ the bulk structure remains the hightemperature-tetragonal phase with flat CuO₂ planes down to 8K. Since the Ce ion is introduce as Ce⁴⁺, replacement of La⁴⁺ by Ce⁴⁺ results into the reduction of one hole Thus, the effective hole concentration in La_{1.70}Sr_{0.24}Ce_{0.06}CuO₄ considered to be 0.18, corresponding to slightly over-doping.

Figure 2 shows constant-energy (ω) spectra for ω =(a) 2 meV, (b) 5 meV and (c) 8 meV measured below T_c (=22 K). At 5 meV and 8 meV, well-defined IC peaks are observed, while no clear magnetic signal was observed at 2meV, indicating an opening of spin gap in the magnetic excitation spectrum. This observation is consistent with that in the optimally-doped and slightly overdoped region of LSCO with $0.14 \le x \le 0.20[3]$ and quite different from the spin excitations in the overdoped LSCO with x=0.25[4] which shows low energy spin excitations at least down to 2

meV. Thus the observed spin excitation in the La_{1.70}Sr_{0.24}Ce_{0.06}CuO₄ is rather close to that in the optimally-dope sample. This similarity suggests that the doped Ce indeed reduces the hole concentration and the small lattice distortion in the overdoped LSCO does not affect the spin correlations. Thus, the spin correlations at the specific hole concentration of 1/8, which is strongly influenced by the lattice distortion, can be investigated in the 6% Cedoped La_{1.82}Sr_{0.18}CuO₄ without the significant structural effect for the next step.

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Fig. 1. Inelastic neutron scattering spectra of $La_{1.70}Sr_{0.24}Ce_{0.06}CuO_4$ at 8 K.

Spin correlations in electron-doped antiferromagnetic ordered phase of Pr1-xLaCexCeO4

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High-transition temperature (T_c) superconductivity mediated by spin fluctuations is one of central issues in the strongly correlated electron systems. Extensive neutron scattering measurements on hole-doped $La_{2-x}Sr_xCuO_4$ have revealed an evolution of spin correlation by doping and its intimate relationship with the superconductivity [1, 2]. To understand a novel magnetism in carrier-doped Mott insulators and the role in the high- T_c SC mechanism, comparative studies betweeen holedoped and electron-doped systems are indispensable. However, due to the difficulty in preparing superconducting single crystalline samples, experimental studies for electron-doped system have been far behind compared to those for hole-doped system.

Recent neutron-scattering study revealed the existence of the commensurate low-energy spin fluctuations in optimally electron-doped Nd_{1.85}Ce_{0.15}CuO₄ (NCCO)[3] and Pr_{0.89}LaCe_{0.11}CuO₄[4]. These observations indicate that the collective spin fluctuations commonly exist in the SC phase irrespective of carrier type. However, to investigate the universal nature in the electron-doped system further systematical study is important. We therefore performed systematic neutron scattering measurements on the Pr_{1-x}LaCe_xCeO₄ system.

Figure shows the 1 peak profiles with ω =3, 5, and 8 meV for non-superdonducting the sample of $Pr_{0.93}LaCe_{0.07}CuO_4$ ($T_N \sim 100K$). Clear commensurate low-energy spin fluctuations are observed at the antiferromagnetic zone center as is the case of non-doped mother compound. However, the peak-width is slightly broader than the resolution

limited value. This result suggests that the doped electron can affect the spin fluctuations and reduces the spatial coherence length. Further upon doping, the paek-width drastically broadens when the system becomes superconductor and the broadening of the width continuously progresses in the superconducting phase, indicating a close relation between the spin correlations and the superconductivity in the electron-doped system.

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Fig. 1. Constant energy spectra with ω = (a) 3 meV, (b) 5 meV, and (c) 8 meV for $Pr_{0.93}LaCe_{0.07}CuO_4$ measured at 7K.

A phase transition between the itinerant and the localized f-electron states in the heavy fermion antiferromagnet Ce(Ru0.9Rh0.1)2(Si1-yGey)2

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In the heavy fermion systems, f-electrons are hybridized with conduction electrons (cf-hybridization), and hence, localized spins and heavy quasi-particles coexist[1]. This duality of f-electrons can lead an alternation between an itinerant and a localized magnetic orders by changing the strength of the cf-hybridization in the heavy fermion systems[2,3]. The former is a spontaneous magnetic polarization of the heavy quasi-particle band (quasiparticle band regime), whereas the latter is formed by the localized spin via the RKKYinteraction (RKKY-regime).

In the course of searching for such an alternation of schemes of the magnetic order, we have studied the magnetic properties of the pseudo-binary alloy system Ce(Ru0.9Rh0.1)2(Si1-yGey)2. The base material Ce(Ru0.9Rh0.1)2Si2 is known as an archetypal heavy fermion compound which shows a spin density wave (SDW) transition[4]. By substituting Ge for Si, we effectively apply negative pressure to the SDW phase through the lattice expansion, and the magnetic order can be shifted to the antiferromagnetic order formed by the localized f-spins(LAF)[3,5]. Recently, we found a 1st order phase transition between the SDW and the LAF phases in the Ce(Ru0.9Rh0.1)2(Si1-yGey)2 system by the substitution of Ge for Si[6].

In 2006, we have performed neutron scattering experiments under hydrostatic pressure for Ce(Ru0.9Rh0.1)2(Si1-yGey)2 with y = 0.30, showing the LAF transition at ambient pressure, using the 4G spectrometer installed at the JRR-3M. Figure 1 shows temperature dependences of integrated intensities of magnetic reflections with (a) q1 = (0.344,0,0) and (b) q3 = (0,0,0.358). The former and the latter reflections, the q1- and the q3-reflections, correspond to the LAF and the SDW phases respectively. The figure shows that only the q1reflection is found at ambient pressure. On the other hand, the q1-reflection disappears and the q3-reflection appears at high pressure region, P > 0.5GPa. In the intermediate pressure region, 0.30GPa < P <0.5GPa, both the magnetic reflections are found, which indicates the coexistence of the SDW and the LAF phases. This experimental results under hydrostatic pressure strongly suggest the pressure induced 1st order phase transition between the SDW and the LAF phases, reproducing very nicely the chemical pressure effects for the Ce(Ru0.9Rh0.1)2(Si1-yGey)2 system.

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Fig. 1. Temperature dependences of the integrated intensities of magnetic reflections with (a) q1 = (0.344,0,0) and (b) q3 = (0,0,0.358) under hydrostatic pressure.
Charge and magnetic order in La2-xSrxCoO4

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Layered cobaltate La2-xSrxCoO4 (LSCO) has been studied for the spin state transition from high-spin (HS) to intermediate spin (IS). Moritomo et al. observed significant reduction of resistivity with increasing x beyond ~ 0.7 , and reduction of the effective moment from 4.0 μ B to 2.6 μ B [1]. They ascribed these changes to a transition of the spin state of the Co3+ ions from the HS ($x \le 0.6$) to the IS (x \geq 0.8), because the double-exchange interaction between HS state Co2+ and IS state Co3+ ions is expected to stabilize the IS Co3+ state. On the other hand, Zaliznyak et al. claimed that charge ordering is important to realize the IS state [2]. In the recent neutron experiments, they reported that the breathing-type modulation is realized in La1.5Sr0.5CoO4. As a result, an eg doublet of dx2-y2 and d3z2r2 orbitals are split. They concluded that Co3+ ions in La1.5Sr0.5CoO4 are in the IS state at low temperature, which favors the Jahn-Teller (JT) distorted charge-order (CO) phase. Our purpose of this study is to clarify the relationship between IS and CO phase.

Single crystal of La2-xSrxCoO4 ($0.4 \le x \le 0.6$) was grown by the TSFZ method, of which volume was about 1.0 cc each. It was mounted in a cryostat with the b-axis vertical, allowing to observe the (h0l) reciprocal lattice plane. We took a unit cell ($\sqrt{2}$ 2atet $\times \sqrt{2}$ 2atet \times c) as twice as the primitive cell (atet \times atet \times c). The neutron scattering experiments were carried out on the 3-axis spectrometer AKANE (T1-2).

The elastic neutron scattering at Q=(1,0,l) is shown in Fig.1. In the all Sr concentration x, the structural peaks of checkerboard type charge order were observed. Comparing with the recent neutron experiment of La2xCaxCoO4 (LCCO), the peaks were diffusive and not commensurate to the lattice. The broad peak intensities become large with increasing l, indicating that out-ofplane strain of oxygen is larger than inplane strain. From I dependence of charge order peaks, LSCO is expected to modulate a apical oxygen, as a result an eg doublet splitting that generate IS state is realized. It is expected that oxygen displacement ε of LCCO is larger than that of LSCO because of the strong CO peaks of Ca system. Moreover, the CO correlation length of LCCO is about five times larger than that of LSCO system and CO state is realized in a wide Ca concentration range. From above discussion, it is expected that IS state of Ca system is more stable than that of LSCO system. In our magnetic susceptibility measurement on LCCO (0.5<x<0.8), intermediate spin state transition was observed at lower concentration comparing with the Sr system. These neutron and susceptibility results suggest that charge ordered phase plays an important role to stabilize the intermediate spin state of Co3+ ions.

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Fig. 1. Charge order peaks of Q=(101). Sample of x=0.4 is performed at 14K, and x=0.5, 0.6 at 10K.

Rattling in filled-skutterudite compounds

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In clathrate compounds, structure and dynamics of a guest ion inside a large host cage play an important role for those physical properties. Filled-skutterudite compounds are supposed to belong to such family, where a rare-earth ion locates in a relatively large pnictogen icosahedral Recently one of the skutterudite cage. compound PrOs₄Sb₁₂ was reported to be a heavy fermion superconductor[1]. The non-magnetic singlet ground state and the existence of the field-induced antiferroquadrupolar order suggest a novel mechanism for the formation of heavy quasiparticles and unconventional superconductivity in PrOs₄Sb₁₂. In order to clarify the detailed structure without a model, single crystal neutron diffraction experiments were carried out and obtained data were analyzed by using the maximum entropy method (MEM).

Single crystal neutron diffraction experiments have been carried out on the fourcircle diffractometer FONDER, installed at the T2-2 beam port in the guide hall of the research reactor JRR-3. The data were taken at 8 K and room temperature by using the single crystal of $PrOs_4Sb_{12}$ with ~40 mm³. The obtained Bragg reflection intensity was analyzed by maximum entropy method (MEM) with a software PRIMA[2].

A space- and time-averaged nuclear density distribution including a thermal vibration can be obtained by the MEM analysis. Figure 1 shows a cross-sectional drawing of Pr distribution along the [100] direction for 8K and room temperature. The results unveil a widely spread Pr distribution in the Sb cage at room temperature. The Pr density distribution is almost flat in the real space, which reaches roughly 0.5 Å in the full width at half maximum (FWHM). The Pr nuclear density distribution at 8 K becomes sharp, almost isotropic and gaussian-form, although the width distribution at 8 K of 0.15 Å in FWHM is roughly twice broader than those for Os and Sb. Note that the highest density of Pr distribution at 8 K founds at the center of the cage within an experimental accuracy. These features are far from the simple harmonic model, in other words, the present result suggests the strong anharmonicity for the Pr potential in the Sb cage.

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Fig. 1. Cross-sectional drawing of Pr distribution in $PrOs_4Sb_{12}$ along the [1 0 0] direction.

1-3-21

Magnetic structures of PrA2Mn2O7 (A=Ca, Sr)

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Although the competition between the A- and the CE-type antiferromagphase is reported for netic (AFM) LaSr2Mn2O7[1], purely CE-type AFM phase is not reported so far in the halfdoped bilayer manganites system. We have investigated magnetic structures of PrCa2Mn2O7 and PrSr2Mn2O7. Single crystals of PrCa2Mn2O7 (with twin structures because of the orthorhombic distortion) and PrSr2Mn2O7 were prepared by a floating-zone method. Neutron scattering measurements were carried out on the triple axis spectrometer GP-TAS in the JRR-3M. We measured on the pseudo-tetragonal (hhl) reciprocal zone for PrCa2Mn2O7 and the (h0l) reciprocal zone for PrSr2Mn2O7.

Figure 1(a) shows the temperature dependence of the bulk magnetization measured by a SQUID magnetometer and the peak intensity at Q=(1/4, 1/4, 3), which is corresponding to a measure of the order parameter of CE-type AFM. With decreasing the temperature, the peak intensity at Q=(1/4, 1/4, 3) increases monotonically below T_N=143 K, while that at the Q=(0, 0, 3) (characteristic of the A-type AFM) is negligibly small (not shown). On the other hand, the monotonic increase of the peak intensity at the Q=(0, 0, 3) with decreasing temperature is observed for PrSr2Mn2O7 (See Fig. 1(b)).

These results indicate that the magnetic structure of PrCa2Mn2O7 is the CEtype AFM down to the lowest temperature, while that of PrSr2Mn2O7 is the A-type AFM, similarly to the case of NdSr2Mn2O7[2][3].

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Fig. 1. Temperature dependence of in-plane components of the bulk magnetization and peak intensities at selected positions for (a)PrCa2Mn2O7 and (b)PrSr2Mn2O7.

1-3-22

Crystalline Electric Field Excitations in Pr3Pd20Ge6

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Pr3Pd20Ge6 crystallizes in the cubic Cr23C6-type structure (Fm3m) with two inequivalent Pr sites of 4a (Oh) and 8c (Td). The previous experiments of inelastic neutron scattering (INS) [1] and high-field magnetization [2] suggested that the crystalline-electric-field (CEF) lowest level of the Pr 4f electrons is the quadrupole doublet Gamma3 for both the 4a and 8c sites. On the other hand, the elastic constant c44 was found to show a 1/T behavior at low temperatures [3], which cannot be account for sorely by the Gamma3 ground state. We also found that the magnetic susceptibility of this compound shows no tendency of saturation down to 0.1 K, indicating that the 4f electrons should have a magnetic ground state in at least one of the Pr sites [4]. From the detailed CEF analyses on the M(B, T) and C(B, T) results, we proposed that the magnetic Gamma5 triplet sits at the lowest level in the 4a site while the G3 doublet is in the 8c site [4]. This "two-site" CEF scheme semi-quantitatively well reproduces the B and T variations of magnetization and specific heat, particularly the step-like fine structures observed in the low-temperature M(B) curves and a field-induced first order phase transition. The energy separations between the lowlying two levels are estimated as Gamma5(0)-Gamma3(~0.5 meV) and Gamma3(0)-Gamma5(~0.3 meV) for 4a and 8c sites, respectively. These excitations, however, are difficult to be distinguished from each other by the energy resolution in the previous INS measurements. In the present project, we reperformed the INS experiments for a powdered Pr3Pd20Ge6 sample on the triple axis spectrometers PONTA at 5G beam hole and HER at C1-1 of the JRR-3M reactor in JAEA, extending the energy window up to 15 meV and

improving the energy resolution down to ~ 0.1 meV, respectively. We have observed significant fine structures in the INS spectra. Their intensities and temperature dependencies are quantitatively well reproduced by the numerical calculations based on the two-site CEF model. The CEF parameters determined here, however, are slightly larger than those obtained from the magnetization data, but they give more reasonable fits for C(T). The reanalyses on the M(B, T) curves are now in progress.

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Fig. 1. Part of the inelastic neutrn scattering spectra of Pr3Pd20Ge6 obtained by using C1-1(HER). The lines are numerical calculations based on the two-site CEF model. The peaks observed at about 1.2 meV and 2.5 meV are spurious.

High-Pressure Effects in Strongly Correlated 5f Electron Systems

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In order to obtain a reliable pressuretemperature phase diagram of the heavyelectron (HE) superconductor URu2Si2, we reperformed the ac-susceptibility and elastic neutron-scattering (NS) measurements by using a small single-crystalline rod (2 mm in diameter, 6 mm in length) and a Cu-Be clamp-type high-pressure cell (P < 1.1 GPa).

We found that at ambient pressure this sample shows the weakest antiferromagnetic (AF) Bragg reflections reported so far, corresponding to the volume-averaged staggered moment of m_ord ~ 0.011 mB/U. This implies that the AF signal at the low-P range is irrelevant to HO, and that HO breaks different symmetries from those for the high-P AF order. The so-called "smallmoment antiferromagnetic phase" will be unlikely to be present as the uniform order. Under applied pressure, the AF scattering intensity exhibits a sharp increase at P~0.7 GPa at low temperatures. The saturation value of the AF scattering intensity above 0.7 GPa corresponds to m_ord ~ 0.41 mB/U, which is in good agreement with that (~ 0.39 mB/U) observed above 1.5 GPa in our previous high-P NS measurements [1]. The superconductivity is dramatically suppressed by the evolution of AF phase, indicating that the superconducting state does not coexist with the antiferromagnetism, unlike many other HE superconductors. In other words, the intrisic interaction that can mediate the Cooper pairing in this system exists only in the HO state. Since the present investigations clearly demonstrated that a volume fraction of the low temperature AF long range order phase below 0.7 GPa can be minimized, the intrinsic properties of the HO phase, such as the superconductivity will be able to be clarified in near future. Further experimental studies are planning in our group.

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Fig. 1. Overall view of the pressure-temperature dependence of the integrated magnetic Bragg-scattering intensity at Q = (1,0,0) in URu2Si2 obtained by using GPTAS at 4G in JAEA. The lines are guides to the eye.

Neutron scattering study of Pr0.5Sr0.5CoO3

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 $Pr_{0.5}Sr_{0.5}CoO_3$ exhibits metal-insulator transition at 230 K. Ferromagnetism is also induced below 230 K. Recently, Mahendiran and Schiffer suggests the existence of antiferromagnetic order below 100K from magnetization measurements.

We have perfomed neutron diffiraction measurements to explore the magnetic order.

We have performed neutron diffraction measurements with the ISSP triple-axis spectrometer HQR installed at the T11 experimental port of JRR-3M in JAEAI (Tokai). We prepare the 0.5 cc crtstal sample and cooled with a ⁴He gas closed-cycle cryostat.

Figure 1 shows powder diffraction patters of 11 K and 300 K. It indicates that the ferromagnetic order exists in the low temperature. It also indicates that the structural phase transition exists.

Figure 2 shows temperature dependence of ferromgnetic Bragg peak and nuclear peak. It indicates that the ferromagnetic order temperture is 230K nad the phase transition temperature, 120 K.

No antiferromagnetic magnetic peak is observed. Nevertheless, the ferromgnetic moments becomes depressed at 120 K. The structural phase transition may affect magnetic order.

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Fig. 1. Diffraction pattern (Fig.1) and temperature dependence of Bragg intensity (Fig.2)

Role of the electronic spins in a novel superconductor CeCoIn₅

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A series of $CeMIn_5$ (M = Rh, Co and Ir) has the highest superconducting (SC) transition temperature $T_c = 2.3$ K for heavy fermion materials. Such a high SC transition temperature can be realized by strong antiferromagnetic (AFM) fluctuations. Pure CeRhIn₅ exhibits an incommensurate AFM phase below $T_{\rm N} = 3.8$ K, with the modulation of $q_h = (1/2, 1/2, 0.297)$.[1, 2, 3] In this phase, a helical spin density wave (SDW) state is suggested to appear. It is expected that a quantum critical point (QCP) exists at $x \sim 0.75$ with strong magnetic fluctuations, and the AFM phase vanishes here. On the other hand, the superconductivity appears in $x \ge 0.4$. Therefore, the SC phase in this family lies near the QCP, and coexists with the AFM phase in the intermediate x region. In order to understand the role of the magnetic spins for the superconductivity in these systems, we performed neutron scattering measurements on $\text{CeRh}_{1-x}\text{Co}_x\text{In}_5$.

Single crystals of CeRh_{1-x}Co_xIn₅ with x = 0.3, 0.4, 0.6, 0.7 and 0.75 were prepared. Elastic and quasi-elastic neutron scattering experiments were carried out at 4G (GPTAS). (*hhl*) was selected as the scattering plane. The x = 0.3, 0.4 and 0.6 samples were cooled down to 1.5 K by using a ⁴He cryostat, and the x = 0.7 and 0.75 ones were cooled down to 0.7 K with a 1K cryostat. The neutron momenta of k = 3.814 Å⁻¹ and 2.67 Å⁻¹ were selected for the measurements on the x = 0.3, 0.4 and 0.75 samples, respectively.

In the x = 0.7 and 0.75 systems, which are near the QCP, neither magnetically ordered phase nor the magnetic fluctuation is observed. On the other hand, the x =0.6 system exhibits a magnetically ordered state below 2.8 K. Fig. 1 shows the elastic neutron scans at q = (1/2, 1/2, l) for the x = 0.6 system, with *l* ranging from 0.25 to 0.55. For $0.45 \le l \le 0.55$, the scan at q =(1/2, 1/2, 1+l) is shown instead of q =(1/2, 1/2, l) to exclude Bragg peaks from mosaic. The open and closed circles indicate the results obtained at 5 K and 1.5 K, respectively. A Bragg peak is observed at $q_c = (1/2, 1/2, 1/2)$, indicative of the appearance of a commensurate AFM phase. The helical SDW phase, which is observed in the pure CeRhIn₅, with a propagation vector $q_h = (1/2, 1/2, 0.297)$ is already vanished here. Thus, the SC phase coexists with the commensurate AFM phase. The present study suggests the significant relationship between these two phases.

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Fig. 1. Elastic neutron scans for $CeRh_{0.4}Co_{0.6}In_5$. Open and closed circles indicate the results at 5 K and 1.5 K, respectively.

Flux Line Lattice in CeCoIn₅

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CeCoIn₅ is a new heavy fermion superconductor with quasi two-dimensional electronic structure and the superconducting transition temperature $T_c = 2.3$ K. Recently the specific heat[1], ultrasound velocity[2] and NMR[3] measurements pointed out a possibility of an occurrence of a Fulde-Ferrell-Larkin-Ovchinnikov (FFLO) phase. In the FFLO phase, modulation of the magnetic field in the flux line appears along the vortex direction. It is necessary to know the flux line lattice (FLL) structure before observation of the FFLO state.

We performed a SANS experiment on CeCoIn₅ at the C1-2 spectrometer (SANS-U). The single crystal samples (the average size is $3 \times 3 \times 0.5 \text{ mm}^3$) were aligned on the sample holder so that the *c*-axis is parallel to the neutron beam. A ⁴He (orange) cryostat with a 3 T magnet was used, and cool the sample down to 1.6 K. The magnetic field was applied parallel to the *c*-axis and the neutron beam to make the vortices along this direction. The neutron wave length of 7.08 Åwas selected, and the PSD was set to 8 m and 16 m positions.

From a recent report[4], a phase transition from a triangular FLL to a square one at ~0.55 T is suggested. However, it is not easy to observe the FLL in this system, because the absorption factors of Co and In are so high. Totally 12 scattering spots are expected to be observed at the nearest position from the origin in the triangular FLL, because of nonequivalent two directions of the FLL. On the other hand, only 4 spots should be observed in the square FLL, presumably with higher intensity. We tried observation of the square one. Fig. 1 shows a neutron scattering intensity as a function of the radius from the origin on the detector, r, (in pixel) at 1.6 K under 1.5 T. The background has already been subtracted. A small peak is observed at around 29 pixel. In this study, we succeeded in the observation of the FLL in CeCoIn₅ even under a magnetic field of 1.5 T.

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Fig. 1. Neutron scattering intensity at 1.6 K as a function of the radius from the origin of the detector. Uniform background has already been subtracted.

1-3-27

Flux Line Lattice Symmetry in MgB₂-type Superconductor CaAlSi probed by Small Angle Nuetron Scattering

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Since the flux line lattice (FLL) configuration can be dominated by the Fermi surface property and underlying crystal symmetry, investigations of FLL state play an important role to understand the superconducting mechanism. In this work, we have focused on the superconductivity in a MgB₂type superconductor CaAlSi (CAS).

According to the recent report [1], the CAS possesses two types of multi-stacked crystal structures, in which a clear five-layered (5*H*-CAS) or six-layered (6*H*-CAS) superlattice along the *c*-axis was observed. On the other hand, we first fabricated a no superstructured CAS (1*H*-CAS) with AlB₂-like structure [2]. In order to clarify the relationship between the crystal symmetry, structure of superconducting order parameter and vortex lattice symmetry in three phases of CAS, we have performed the first small angle nuetron scattering (SANS) experiments.

The SANS experiment was conducted by using SANS-U spectrometer installed in JRR-3 at Japan Atomic Energy Agency (JAEA), and single crystal of respecetive phase with the dimension $7 \times 7 \times 2 \text{ mm}^3$ was used. The mean wavelength of incident neutron beam monochromatized by a mechanical velocity selector was set to λ_n ~ 6.7 Å with resolution $\Delta \lambda_n / \lambda_n = 10$ %.

Figure 1 shows the representative SANS diffraction patterns in 6*H*-CAS (not shown the data of 1*H*- and 5*H*-CAS) at 2 K applied fields parallel to the crystalline (a) *c*- and (b) *a*-axes. We found that the hexagonal FLL structure under $H \parallel c$ over the entire temperature/field range was observed in the respective phases in CAS, but that they exhibit a no sign of reorientation with increasing temperature/field as in multi-

gaped superconductor MgB₂ [3]. Meanwhile, only 6H-CAS shows a distortion with Bragg peaks lying on an ellipse under H||a| due to the magnetic penetration depth anisotropy.

Consequently, we obtained an usual FLL phase diagram in 6*H*-CAS expected for the uniaxial conventional superconductor described by London theory. The further SANS experiments are also needed to determine the comprehensive FLL phase diagram in 5*H*- and 1*H*-CAS.

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Fig. 1. SANS diffraction patterns from the FLL state in 6H-CaAlSi at 2 K applied fields of 1.5 kOe parallel to the crystalline (a) *c*- and (c) *a*-axes.

Order Parameter of Phase IV in (Ce,La)B6

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Cerium hexaboride CeB6 undergoes successive phase transitions from paramagnetic phase (Phase I) to antiferroquadrupolar ordering with a wave vector \mathbf{k} = [1/2,1/2,1/2] at TQ = 3.3 K (Phase II) and to antiferromagnetic ordering with 4k magnetic structure at TN = 2.3 K (Phase III). This complex magnetic phase diagram comes from the multipolar degrees of freedom in a Gamma8 quartet ground state of Ce3+ ion. By substituting La for Ce in this material, one can change the strength of the multipolar interactions. In the La diluted compound CexLa1-xB6, with decreasing x, TQ rapidly decreases, while TN slightly decreases. Then, a new ordered state called "Phase IV" appears at $x < \sim 0.8$. In Phase IV, various unusual properties such as the large softening of the c44 mode in the ultrasonic measurement, the isotropic cusp in the bulk magnetic susceptibility, the trigonal lattice distortion along the [111] direction, have been reported. Recently the resonant X-ray scattering experiment (Mannix et al, Phys.Rev.Lett. 95(2005)117206) and the theoretical analysis (Kusunose and Kuramoto, J.Phys.Soc.Jpn. 74(2005)3139) have reported that the octupolar ordering with a wave vector [1/2, 1/2, 1/2] occours in Phase IV. In this case, the superlattice reflections at (h/2,k/2,l/2) with high Q-vectors are expected to be detected by neutron scattering because the magnetic form factor of magnetic octopole moment exhibits a maximum at a high Q-vector. Therefore we have performed the neutron diffraction experiment on (Ce,La)B6 in Phase IV. The large single crystal of B11 99.52%

enriched Ce0.7La0.3B6 was grown by the floating zone method. In this sample of Ce 70%, Phase IV is below ~ 1.5K. The sam-

ple was mounted in a 3He-4He dilution refrigerator with (hkk) as horizontal scattering plane. The neutron diffraction experiment was performed on the thermal neutron triple axis spectrometer TOPAN (6G) with the incident energy Ei = 41 meV. We scanned in reciprocal space along the main symmetry directions at lowest temperature of 0.2 K and found the superlattice reflections at (h/2,h/2,k/2). Furthermore the intensity of the superlattice reflections have a tendency to increase as increasing Q-vectors. This result is consistent with the octupolar ordering.



Fig. 1. Profile of Ce0.7La0.3B6 at (3/2,3/2,3/2) at 0.2 K and 2 K

Neutron diffraction study of PrFe4P2 under high pressure

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PrFe4P12 undergoes the non-magnetic phase transition at TA = 6.5 K under ambient pressure. By applying pressure, the non-magnetic ordered phase disappears and the insulating phase appears around Pc = ~ 2.4 GPa (Hidaka et al.: Phys.Rev.B 71(2005)073102, J.Phys.Soc.Jpn. 75(2006)094709). In order to get the microscopic information about the order parameter in this pressure-induced insulating phase, we have performed highpressure neutron diffraction measurements on PrFe4P12 single crystals up to 3.8 GPa at low temperatures under magnetic fields using the triple-axis spectrometer TOPAN at JRR-3M in JAEA and a new hybrid-type pressure cell which is composed of a large sapphire anvil and a tungsten carbide anvil (Osakabe et al., International Conference on Magnetism, Kyoto, Japan, 2006 [PHYS-ICA B, in press]). The pressure cell was set inside a superconducting magnet with the [0,0,1]-axis vertical to the (h,k,0) scattering plane.

We have observed the distinct magnetic Bragg peak with a wave vector q = (1,0,0)in the insulating phase above Pc. Figure 1 (a) shows the profile of the theta-two theta scan around (1,0,0) under 3.8 GPa. The superlattice peak at lowest temperature 1.6 K corresponds to an antiferromagnetic longrange order characterized by q = (1,0,0)with the large magnetic moments of about 2 mB/Pr along the [0,0,1] direction. The result indicates that the 4f electronic states of Pr ions under the cubic crystal field are magnetically degenerate in low energy region. By measurements of the temperature and magnetic field dependences of the antiferromagnetic peak, as shown in Fig. 1 (b),

furthermore, we found slight but distinct anomalies below about 4 K in the insulating phase, suggesting some change of the magnetic structure around 5 K.



Fig. 1. (a) antiferromagnetic Bragg reflection at (1,0,0) under 3.8 GPa and (b) the temperature dependence of the (1,0,0) antiferromagnetic peaks in several magnetic fields under 3.8 GPa in the pressure-induced insulating phase of PrFe4P12.

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Pyrite- and shandite-type transition metal disulfides are both minerals that can be artificially synthesized. While Pyrite-types of MS_2 (M=Fe, Co, Ni,etc.) have been the subject of the intense research due to their variety of interesting physical properties [1, 2], few studies have been made of shandite-type $M_3A_2S_2$ (A=Sn, Pb, In, and Tl; M=Co, Ni, Rh and Pd) [3, 4] with two-dimensional Kagome lattices.

Earlier studies report that shandite-type Co₃Sn₂S₂ is a metallic ferromagnet with $T_{\rm C}$ (=177K), and that Ni₃Sn₂S₂ is a paramagnetic metal [3, 4]. In a solid solution of ferromagnetic metal CoS_2 (T_C =120K) and an antiferromagnetic Mott-Hubbard insulator NiS₂, ferromagnetism is gradually suppressed with Ni substitution [2]. However, the detailed Ni substitution effect in $(Co_{1-x}Ni_x)_3Sn_2S_2$ with 2-D Kagome latticesnot has been examined and the electronic nature is not clear. In this report, we discuss the hitherto unknown electrical and magnetic properties for $(Co_{1-x}Ni_x)_3Sn_2S_2$ [5] in comparison with $Co_{1-x}Ni_xS_2$.

Polycrystalline $(Co_{1-x}Ni_x)_3Sn_2S_2$ samples were carefully prepared by a solid state reaction method in a evacuated quartz tube and characterized by powder x-ray diffraction (XRD), Rietveld refinement using the Rietan 2000 [6], and x-ray photoemission spectroscopy (XPS). Electrical resistivity was measured at 10-300 K by the conventional dc four-probe technique. DC magnetization was measured by a superconducting quantum interface device (Quantum Design, MPMS) at 10-300K. Neutron powder diffraction (NPD) patterns were obtained with Kinken powder diffractometer [7] for high efficiency and high resolution measurements (HERMES) installed at the T1-3 beam hole of the guide

hall at the Japan Research Reactor 3M (JRR-3M) in Japan Atomic Energy Research Institute (JAERI).

Figure 1(a) shows the temperature dependence of magnetic susceptibility (χ) for $(Co_{1-x}Ni_x)_3Sn_2S_2$ in field cooled (FC) conditions. Co₃Sn₂S₂ shows the ferromagnetic transition at 178K, which almost agrees with previous work [4]. With increasing Ni concentration (x), the magnitude of χ and $T_{\rm C}$ are gradually decreased as $Co_{1-x}Ni_xS_2$ [2], and ferromagnetism is suppressed above x = 0.2. However, unlike in the case of $Co_{1-x}Ni_xS_2$, there is no antiferromagnetic phase throughout the full range of composition. This Ni substitution effect indicates that the ferromagnetism on Kagome lattices originates from an exchange split of the Co 3d orbital, so substitution of Ni, which has one more electrons than Co, increases the number of electrons in the 3d orbital and suppresses the ferromagnetism on Kagome lattices.

As shown in the inset in Fig.1(a), the magnetization does not saturate up to 5.5T at 10K, unlike CoS₂. From the *M*-*H* curve we can roughly estimate a small saturation moment (p_s) of $0.2\mu_B$ per Co atom (which is slightly smaller than previous data ($0.29\mu_B$) [4]), while in CoS₂ p_s is $0.85\mu_B$.

 $(\dot{Co}_{1-x}Ni_x)_3Sn_2S_2$ are metallic with room temperature resistivities (ρ) of $10^{-3}\sim 10^{-4}\Omega$ cm and show a kink in resistivity at T_C , as shown in Fig.1(b). While, a hump at T_C appears in CoS₂, which has certain degree of localized moment.

The unsaturated magnetization, a small saturation moment, and the absence of a hump in resistivity indicate that $Co_3Sn_2S_2$ is an itinerant weak ferromagnet. These phenomena are different from those of $Co_{1-x}Ni_xS_2$, in which ferromagnetism is

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also gradually suppressed with Ni substitution that develops antiferromagnetism, and the end member compound NiS_2 is a Mott-Hubbard antiferrmagnetic insulator.

While, the inverse susceptibility of $Co_3Sn_2S_2$ can be fitted to the Curie-Weiss law above T_C ; from this fit, we obtain $p_{eff} = 0.96$ per Co. Figure 1(c) shows Rhodes-Wolfarth plots that plot T_C and p_c/p_s ($p_c = \sqrt{1 + p_{eff}^2} - 1$) for metallic ferromagnets following Curie-Weiss law. The value of p_c/p_s is 1.9 for $Co_3Sn_2S_2$ and 1.8 for CoS_2 ($p_c/p_s \cong 1$ for localized moment system). According to the Rhodes-Wolfarth scheme, $Co_3Sn_2S_2$ has the same degree of localized moment as CoS_2 . However, from our results, we cannot determine the magnetism of this compound, especially whether it has a localized moment or not.

Finally we would like to comment the NPD data at 10 K, 200 K ($T < T_C$) and 300 K ($T > T_C$) for Co₃Sn₂S₂ as shown in Fig.1(d). Indeed, magnetic peaks originated from magnetic long-range order shows the simple ferromagnetism on 2-D Kagome lattices, indicating the Mielke's prediction [10] that the ground states of Kagome lattices based on the Hubbard model is only one and exhibits the simple ferromagnetism in a finite range of the electron filling factor. The next step will be to reveal differences between the electronic structures of $(Co_{1-x}Ni_x)_3Sn_2S_2$ and $Co_{1-x}Ni_xS_2$ and to reveal the electron filling effect on ferromagnetism on the 2-D Kagome lattices.

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Fig. 1. (a) Magnetic susceptibility and (b) normalized electrical resistivity for $(Co_{1-x}Ni_x)_3Sn_2S_2$. (c) Rhodes-Wohlfarth plot [8, 9]. (d) Neutron powder diffraction data for $Co_3Sn_2S_2$.

Mn-substitution effect on spin correlations in $La_{1.90}Sr_{0.10}CuO_4$

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А recent finding that magnetic fluctuations both in an insulating La_{1.875}Ba_{0.125}CuO₄ (LBCO)[1] and in a superconducting YBa₂Cu₃O_{6.6} (YBCO)[2] have a similar fascinating hour-glass-shape dispersion has attracted much attention in regard to the nature of magnetic fluctuations in high- T_c superconductors: with increasing energy ω , two incommensurate branches disperse inwardly toward (π , π) and finally merge at (π, π) at a so-called resonance energy ω_r =40-50 meV. Upon further increasing energy, the excitations exhibit an outward dispersion, which results in an hourglass-shape excitation. It seems that understanding the origin of the novel spin excitations holds the key to understanding the role of the spin correlations in the high-Tc superconducting mechanism[3, 4].

Quite recently, we have studied the low-energy spin fluctuations in $La_{1.90}Sr_{0.10}CuO_4$ with and without Mn doping into Cu sites[5]. We found that the incommensurate spin fluctuations observed in $La_{1.90}Sr_{0.10}CuO_4$ become commensurate when 3% Mn ions are doped. This results suggests that the dispersion changes into conventional spin-wave like one and a reduction of ω_r by Mn-doping.

To gain further insight into this problem, we performed neutron-scattering measurements on the intermediate Mn doping sample La_{1.90}Sr_{0.10}Cu_{0.99}Mn_{0.01}O₄. Figure 1 shows observed constant-energy spectra for ω =(a) 2 meV, (b) 3 meV, (c) 4 meV and (d) 6 meV at 40 K. The excitations are incommensurate at low energies. However, they emerge into the commensurate (π , π) point as the energy is increases to 3 meV. At energies higher than 3 meV, the excitations again become incommensurate. This feature strikingly resembles the hourglassshape excitations observed in the LBCO and YBCO systems. The substitution of Mn ions with large magnetic moment may strongly affect the spin correlations and reduce the energy scale of the excitations.

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Fig. 1. Low-energy spin fluctuations for the 1% Mn-doped $La_{1.90}Sr_{0.10}CuO_4.$

Magnetism and Superconductivity in RENi₂B₂C

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RENi₂B₂C (RE is a rare earth or Y) exhibits various physical properties such as superconductivity (SC) or magnetic order, by substitution of the rare earth site. In particular, one of them, ErNi₂B₂C, is known to show the microscopic coexistence of the SC and weak ferromagnetism (WFM). Another system, TbNi₂B₂C, does not show the SC, while it has a quite similar crystal structure and magnetic property to ErNi₂B₂C. We have studied the magnetism of this system to understand the coexistence of the SC and WFM by comparison. The system shows a spin density wave (SDW) phase below $T_{\rm N} = 15$ K and the coexistence of this phase and a weak ferromagnetic phase below $T_{WFM} = 8$ K in the absence of the external magnetic field. We have found that many magnetic ordered phases appear in the external field from the magnetization measurement. In the present study, we investigate the magnetic structures for these phases by the neutron scattering measurement, to complete the phase diagram of this system in the magnetic field.

The experiment was carried out at the 4G spectrometer (GPTAS). A set of a ⁴He cryostat and a transverse field magnet was used. The single crystal sample of TbNi₂B₂C was cooled down to 1.6 K. The magnetic field was applied parallel to the *a*-axis, which corresponds to the easy-axis of the system. (*h*0*l*) was selected as the scattering plane. Representative fields where each phase appears, H = 0.9 T, 1.5 T, 2.1 T and 2.8 T were chosen.

The neutron magnetic scattering profiles in the (h01) direction in various magnetic fields at 1.6 K are shown in Fig. 1. The magnetic Bragg peaks corresponding to the SDW phase are observed at $q (=11/20a^*)$, 3q, 5q and 7q. Their positions are not shifted, as the field increases. On the other hand, the magnetization increases step-by-step, suggesting changes in the spin configuration. This fact implies that the spin is flipped as the magnetic field increases, without changing the modulation of the magnetic structure. It is expected that nesting of a Fermi surface is not so sensitive to the magnetic field.



Fig. 1. Neutron magnetic scattering profiles in the (*h*01) direction in the magnetic fields of 0 T, 0.9 T, 2.1 T and 2.8 T at 1.6 K.

1-3-33

Low-energy magnetic excations in a heavy fermion superconducting antiferromagnet CeRhIn₅

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The interplay between magnetism and superconductivity is the interesting and important issue on condensed matter physics. Although it has been considered to be exlusive over quantum critical point, it is now widely accepted that both superconductivity (SC) and antiferromagnetism (AFM) coexist in the vicinity of quantum critical point in the systems of the pressureinduced superconductor CePd₂Si₂, CeIn₃, and CeRhIn₅ [1, 2] and so on after a lot of energetic investigations. Since it, however, is very difficult to establish the coexistence of both two phases under pressure because of the inhomogeneity of the pressure, there is open to argument if the coexistance is intrinsic. Very recently G.G. Chen et al. from Nagoya Univ. [3] reported that high-quality single crystalline CeRhIn₅ display the SC at $T_{SC} \sim 90$ mK even under ambient pressure and its pressuretemperature phase diagram is drastically renewed. These findings indubitably indicate that the identical f electron plays both roles of SC and AFM. Therefore CeRhIn₅ is a very importance material for the investigations on the coexistance of SC and AFM. To elucidate the coexistance mechanism of both SC and AFM, it is very useful to perform inelastic neutron scattering which is a very powerful tool to directly observe the dynamical spin susceptibility of the system. The main goal of our study is to determine the wave vector dependence and its enegy scale of the dynamical susceptibility CeRhIn₅, and to find out the connection between SC and the dynamical susceptibility.

On the other hand, since the Rh and In nuclei are strong neutron absorbers, there has been little information on lowenergy magnetic excitations by inelastic neutron scattering studies. In this work, we prepared a lot of large single crystals of CeRhIn₅ and succeeded in detecting the dynamical spin susceptibility at the ISSP/HER spectrometer in the reserach reactor JRR-3/JAEA. Figure 1 shows inelastic neutron scatteirng spectrum at the antiferromagnetic ordering wave vector Q =(0.5, 0.5, 2.7) at temperatures of T = 1.4 K (below T_N), 10 K and 40 K (above T_N). Accurate temperature-dependence of the dynamical susceptibility have shown that, surprisingly, the low-energy magnetic excitations gradually start developing below 40 K (10 times larger than T_N). We are now continuing to study the overview of the low-energy part of its dynamical susceptibility of both CeRhIn₅.

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Fig. 1. Inelastic neutron scatteirng spectrum at the antiferromagnetic ordering wave vector Q = (0.5, 0.5, 2.7) as a function of temperature.

1-3-34

Crystal structure in a non-centrosymmetric pressure-induced superconductor $$\rm CeRhSi_3$$

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Coexistence between magnetism and superconductivity is the central issue in condensed matter physics. Recently noncentrosymmetric heavy-fermion superconductor CePt₃Si [1] and UIr [2] were reported. From the fundamental point of view of symmetry, the discovery of these materials are very surprising because there are two basic symmetries which are considered indispensable to form Cooper pair: time reversal symmetry and parity. The former is important for Cooper pairing in any case while the latter is mandatory for pairing in the triplet channel. Thus there is no right picture for the non-centrosymmetric superconductivity at present.

Kimura et al. [3] discovered another noncentrosymmetric superconductor CeRhSi₃. Its crystal structure is the BaNiSn₃-type belonging to space group I4mm (No. 107) without an inversion center. [4] CeRhSi₃ exhibits the antiferromagnetic (AFM) ordering below $T_{\rm N}$ = 1.6 K at ambient pressure. By increasing the pressure, T_N shows a maximum around 0.7 GPa, then gradually decreases. Superconductivity appears in a wide pressure range from 1.2 to 2.3 GPa (and more). To determine the magnetic structure of the AFM state, we performed the neutron diffraction measurements using single crystals CeRhSi₃, proving that the longitudinal spin-density wave state with the incommensurate wave vector $Q \sim (0.215, 0, 0.5)$ is realized below $T_{\rm N}$ with a small magnetic moment of 0.16(10) m_B /f.u., which indicates that this material is located in the vicinity of quantum critial point (QCP). [5] On the other hand, as far as we know, there is no information on the lattice parameters and atomic position at low temperature in this material. Therefore there is no band structure calculations suggesting the nesting vector which directly connects with the SDW structure.

To determine the crystal structure in CeRhSi₃ at low temperature, we performed the powder neutron diffraction measurements at the HERMES in JRR-3/JAEA. Figure 1 shows the typical power pattern in CeRhSi₃ at 1.1 K (below T_N). The red solid lines are the obtained data and the blue broken lines are the calculations. Since the magnetic moment is small, no incommensurate magnetic peak is observed. Futhermore we, unexpectedly, found the unknown second phase in the powder. These features are seen in the previous neutron powder diffraction measurments. [6] Then unfortunately we can not determine the crystal structure in CeRhSi3 at low temperature.

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Fig. 1. Neutron power pattern in CeRhSii₃ at 1.1 K (below T_N).

Neutron scattering study of Nd_{0.25}Sr_{1.75}MnO₄

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 $Nd_{1-x}Sr_{1+x}MnO_4$ exhibits complicated magnetic phases due to orbital order. At x=0.75, charge order exists below 250 K, and magnetic order of the antiferromagnetic colinear structure below 150 K.¹

We have performed neutron scattering measurements with the ISSP triple-axis spectrometer GPTAS installed at the 4G experimental port and HQR installed at the T11 experimental port of JRR-3M in JAEA(Tokai).

We prepared the 0.5 cc crystal sample and cooled with a ⁴He gas closed-cycle cryostat.

Figure (a) shows temperature dependence of magnetic Bragg intensity. It indicates that magnetic order appears below 150 K, T_{N1} . There is a hysteresys between 150 K and 75 K, T_{N2} .

Figure (b) shows that temperature dependence of the magnetic fluctuation. It has a peak at 75 K. No hysteresys was observed.

Temperature dependence of the magnetcic fluctuation can be attributed to critical slowing down phenomena. It indicates that T_{N2} is the phase transition temperature. Orbital order may set in.

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Fig. 1. Temperature dependence of the magnetic Bragg intensity (Fig.(a)) and magnetic fluctuation (Fig. (b)).

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Neutron Diffraction Study on the Local Structure around Chloride Ions in Anion Exchange Resins

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Ion exchange resins have wide application in extensive fields of fundamental sciences and industries. In order to obtain structural information on the correlation between the cation and the ion exchanging group [1], and on the hydrogenbonded network among water molecules within the resins [2], neutron diffraction with isotopic substitution method has frequently been adopted.

In the present report, we describe the results of neutron diffraction on hydrated anion exchange resins (AER) containing 35Cl/37Cl isotopically substituted chloride ions to investigate the environmental structure around the chloride ion which is interacting with the anion exchange group, (CH3)3N-.

Anion exchange resins (Amberlite IRA402BL, Cl- form) with different 35Cl/37Cl ratios (equilibrated with D2O), I (AER-35Cl)0.0679(D2O)0.9321, 99.0% 35Cl, and Π (AER-natCl)0.0679(D2O)0.9321, 75.8% 35Cl (natural abundance), were prepared by repeated soaking of the OHform resins by aqueous Na*Cl solutions. Light water molecules within the resins were exchanged to D2O in order to obtain good statistical accuracy of the observed difference function. The resin beads were sealed in a cylindrical quartz cell (12.0 mm in inner diameter and 1.1 mm in thickness).

Neutron diffraction measurements were carried out at 298 K using the ISSP diffractometer 4G (GPTAS) installed at the JRR-3M research reactor with an incident neutron wavelength of 1.092(3) A. Beam collimations used were 40'-80'-80' in going from the reactor to the detector. Scattered neutrons were collected over the angular range of 3 < 2 theta < 118 deg. which corresponds to 0.30 < Q < 9.86 1/A. The pre-

set time was set to 410s. The total number of observed counts was at least 1100000 counts, and regarded as high as 1800000 counts. Measurements were made in advance for an empty cell, a vanadium rod of 10 mm in diameter, and an instrumental background. After corrections for the background, absorption and multiple scattering, the observed count rates were converted to the normalized scattering cross section by use of corrected scattering intensities from the vanadium rod.

The first-order difference function [3], delta Cl(Q), which involves information on the local structure around the chloride ion, was obtained from the numerical difference between scattering cross sections observed for the samples I and II. In the prersent experimental conditions, the observed delta Cl(Q) involves Cl-...D2O and Cl-...(CH3)3N- contributions. The distribution function, GCl(r), (Fig. 1) derived from the Fourier transform of the observed delta Cl(Q) is characterized by a well resolved first peak at around r = 2 A, followed by the second peak appearing at 3 <r < 4 A. These peaks should involve contributions from Cl-...the nearest neighbor D2O molecules as well as Cl-...(CH3)3Ninteractions. The first peak may contain both contributions from Cl-...D(D2O) and Cl-...H(CH3) interactions. The former contributes as a positive peak in the distribution function, while the latter should appear as a negative peak. Structural parameters for the Cl-...D2O and Cl-...(CH3)3Ninteractions were determined by the least squares fitting analysis of the observed delta Cl(Q) function. It has been revealed that the chloride ion is neughboring on a (CH3)3N- group of the ion exchange resin with the nearest neighbor Cl-...N dis-

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tance of 3.10(3) A. The average number of D2O molecules within the first hydration shell of the chloride ion was determined to be 2.4(1) with the nearest neighbor Cl-...D(D2O) distance of 2.25(2) A.

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Fig. 1. Observed distribution function around the chloride ion in the anion exchange resin (solid line). The Fourier transform of the best-fit of the calculated delta Cl(Q) function (thick broken line).

Dynamics of Meso-scale fluctuations in liquid chalcogens near the metal-nonmetal transition

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Liquid Te-Se mixtures exhibit a metalnonmetal (M-NM) transition in a relatively narrow temperature range [1]. This transition is accompanied by anomalies in thermodynamic properties such as the thermal expansion coefficient and compressibility. Recently, sound attenuation measurements for liquid Te-Se mixtures revealed that there occur dynamic anomalies in the M-NM transition region [2]. From the frequency dependence of the sound attenuation coefficient α , their relaxation time is estimated to be of the order of nano-seconds. These anomalies may be related to the relaxation between the metallic and non-metallic states in the liquid, and it is interesting to study the spaceand time-structure of the mesoscale fluctuations. Neutron spin-echo (NSE) is a powerful technique which gives information on the intermediate scattering function I(Q, t). However, to our knowledge, there is no NSE measurement under such high temperature conditions.

In the present work, we developed a new electric furnace which can be used for NSE measurements up to $\sim 600^{\circ}$ C. In order not to disturb the magnetic field around the sample, we used non-inductive resistance heaters. By using this furnace, we measured NSE signals for liquid Te₇Se₃ mixture.

Figure 1 shows the intermediate scattering function I(Q,t)/I(Q,0) observed at 490°C. It is noticed that I(Q,t)/I(Q,0) increases with decreasing the wave vector Q. These data can be expressed by a superposition of two exponential relaxation processes as follows:

$$I(Q,t)/I(Q,0) = A_{\text{fast}} \exp(-t/\tau_{\text{fast}}) + A_{\text{slow}} \exp(-t/\tau_{\text{slow}}).$$

Here A_{fast} and A_{slow} represent the fraction of the fast and slow components, satisfying $A_{\text{fast}} + A_{\text{slow}} = 1$, and τ_{fast} and τ_{slow} are the relaxation times of the fast and slow dynamics, respectively. From a curve fitting analysis, the relaxation times are estimated as $\tau_{\text{fast}} \sim 0.1$ nsec and $\tau_{\text{slow}} \geq 10$ nsec. The slow component becomes dominant in the low-Q region, and this process may lead to the anomalous sound attenuation.

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Fig. 1. Intermediate scattering function I(Q,t)/I(Q,0) for liquid Te7Se3 at 490C. The solid lines indicate the fitting curves expressed as a superposition of two exponential relaxation functions.

QENS Studies of Fast Molecular Reorientations in Isotropic, Cholesteric, Glass and Crystalline Phases of 5*CB

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Chain branching and chirality of molecules affect various physical properties substantially, such as the phase behavior. We have been interested in phase relation and dynamics of some chiral molecules that form a liquid crystalline phase. Here, we report the results obtained from neutron scattering experiments for isopentyl cyanobiphenyl (5*CB).

5*CB has a cholesteric phase, whereas 5CB, which is an enantiomer of 5*CB, has a nematic phase. The calorimetric measurements as well as the dielectric relaxation measurements have already been made [1]-[4]. The isotropic liquid is easily undercooled to form a cholesteric phase, which is metastable and forms a glass on further cooling below 210 K. There exist two crystalline phases (metastable and stable). The dielectric relaxation measurements showed that the molecular reorientational motion along the short axis becomes quite slow near the glass transition temperature of 210 K. The purpose of this experiment was to investigate the molecular reorientational motion along the long axis and the internal molecular motions.

We performed neutron scattering experiments on 5*CB using the AGNES spectrometer at JRR-3M. The measurements were made at 350 K, 325 K, 300K, 275 K, and 250 K for the isotropic liquid and at 225 K for the cholesteric phase with a low-resolution mode (delta E = 120 micro-eV), and also at 350 K and 300 K with a high-resolution mode (delta E = 49 micro-eV). As a reference sample, 5CB was also investigated at 350 K and 325 K for the isotropic-liquid and at 300 K for the nematic phase with a low-resolution mode.

First, we assumed that the spectra obtained were convoluted with a delta func-

tion (an elastic component) and a Lorentz function (a quasielastic component). However, the fitting was not quite. Next, we tried to fit the data with two Lorentz functions, which was actually better. So, we might have observed the diffusional motion as well as the reorientational motion. The high-resolution spectra were also fitted well with two Lorentz functions, and the HWHM was similar to that obtained from the low-resolution spectra. The narrower component can be assigned to the translational diffusion of the molecule and the wider component to the reorientational motion, presumably the reorientational motion around its long axis. The HWHM of the narrow component is plotted against the momentum transfer (Q) to determine the diffusion constant at each temperature. An Arrhenius plot for the diffusion constants gives an activation energy of 15.1 kJ/mol (Fig. 1), indicating that the diffusion constant does not affected by the isotropic-cholesteric phase transition. For the wide component, there still remains the possibility that there is complicated reorientational motions.

The 5CB spectra could also be fitted by two Lorentz functions. The HWHM of the narrow component was significantly broader than that for 5C*B, indicating that the diffusive motion of 5*CB is slower than that of 5CB. The activation energies obtained are very similar for both compounds.

It is also interesting to know the difference in the vibrational DOS among three phases of 5*CB, the glassy cholesteric phase, metastable crystal and the stable crystal. The heat capacity of the metastable crystal at low temperature (below 70 K) was significantly smaller than that of the stable crystal, while the metastable crystal has glass transition at 100 K. The inelastic incoherent neutron scattering revealed that the stable crystal had larger DOS than the metastable crystal at low energies around 1.5 meV, which is consistent to the result obtained by calorimetry [4].

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Fig. 1. An Arrhenius plot of the diffusion constant obtained for $5^{*}CB$ and 5CB

Visualization of Density Fluctuation of Supercritical Carbon Dioxide Using Reverse Monte Carlo Simulation

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It is well known that carbon dioxide (CO₂) molecules aggregate themselves and make clusters around a critical point (31.0 $^{\circ}$ C, 7.38 MPa, 0.468 g/cm³). The aggregate property is considered to be an important key for understanding many characteristic features of supercritical CO₂ as a solvent. Therefore, clarification of the cluster structure in detail is absolutely necessary. Generally, small-angle neutron or X-ray scattering (SANS or SAXS) methods are used for observing the density fluctuation structure of supercritical CO₂. Although, real-space information of the cluster is very important to investigate the structural property of the cluster, it had been difficult or almost impossible to visualize the structure by previous analyzing methods. And so, to accomplish the visualization of the density fluctuation, we have tried to apply a Reverse Monte Carlo (RMC) simulation to a SANS data observing the supercritical CO₂.

The SANS experiment was performed using SANS-U of the Institute for Solid State Physics, the University of Tokyo. For measurement, the supercritical fluid (SCF) system installed at KUR-SANS is used with modification for applying to the SANS-U. In the RMC simulation, the system consists of $50 \times 50 \times 50$ cells which are simple cubic of 5.53^3 Å³. Up to four CO₂ molecules can be entered in each cell. Initially, the molecules are randomly put into the cells and then a scattering intensity is calculated. Next, one of the molecules randomly chosen is moved to another cell and the scattering intensity is also calculated. When the calculated intensity after moving comes closer to the experimental one, this movement is accepted. This procedure is iterated until the calculated intensity reproduces the experimental one.

Figure 1 (a) shows a SANS profile of the supercritical CO_2 at a state of 38 °C, 8.64 MPa, 0.49 g/cm³. A correlation length which can characterize the size of cluster in this state is 16.4 Å. A solid line in the Fig. 1 (a) is the calculated scattering intensity obtained by applying the RMC simulation to the observed one. It can be confirmed that the experimental result is well reproduced by the RMC simulation. The real-space image derived from the RMC result is shown in Fig. 1(b). The structure of the density fluctuation of CO_2 molecules can be well expressed.



Fig. 1. (a) Open circles and a solid line indicate the experimental SANS intensity and the calculated one by the RMC simulation, respectively. (b) Real-space image of the supercritical CO_2 derived from the RMC simulation.

Concentration fluctuations of DMSO-water mixtures

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Amyloid fibril formation is now recognized as a phenomenon common to many proteins and peptides. Amyloid fibrils are associated with fatal diseases such as Alzheimer's, which is caused by misfolding of proteins. Thus, it is important to investigate the underlying mechanism of Amyloid formation for understanding the properties of Amyloid fibrils and preventing the formation of the fibrils. It was reported that fluoroalcohols and dimethylsulfoxide (DMSO) completely dissolved β 2-microglobulin amyloid fibrils although a high concentration [i.e., 80%(v/v)] was required for DMSO [1]. The dissolution mechanism is not known, however. It is very likely that the dissolution of amyloid fibril is related to solvent environment in these mixtures. The small-angle neutron scattering (SANS) in dimethylsulfoxide (DMSO)-D₂O mixtures of DMSO mole fractions (0.3, 0.4, 0.5, 0.6, 0.8) was measured at 298 K. A sample was kept in a quartz cell of 1-mm or 2-mm path length. The distance between the sample and detector was 2 m, corresponding to Q of 0.02 - 0.14 Å⁻¹. Measurements were also made for background, an empty cell, and lupolen used for intensity normalization. For the SANS data, the Ornstein-Zernike plots were made according to I (Q)⁻¹ = I $(0)^{-1}$ (1+ ξ^2 Q²) where ξ is the Ornstein-Zernike (OZ) correlation length, and I(0) is the intensity at $Q = 0 \text{ Å}^{-1}$. The maximum in the correlation length ξ obtained from the analysis of SANS data was found at x_{DMSO} $\simeq 0.5$. As the correlation length ξ is a measure of concentration fluctuation, the SANS data also indicate the structural transition of solvent cluster at this solvent composition. These results are in good agreement with those obtained from X-ray diffraction [2].

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Fig. 1. The OZ correlation length as a function of DMSO mole fraction for DMSO-D2O mixtures at 298 K.

Temperature Dependence of water dynamics in nano-porous material FSM

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In absorption water in the pore of mesoporous silica such as FSM-16 (Folded Sheets Mesoporous Materials), briefly, it can be considered that two kinds of water from which mobility is different exist. One is the absorbed water beside the pore wall (mono-layer water) and another is other absorbed water in the pore. Especially, the mobility of mono-layer water is strictly restricted by the hydrogen bonding to the surface hydroxyl group. The dynamics of mono-layer water.

In order to obtain the activation energy of the absorption water in FSM16 pore, we have investigated the dynamics of monolayer water and full-layer water by using AGNES in the temperature range 150K-318K. On the basis of the result of adsorption isotherm of FSM, the absorption amount of water in the sample was adjusted by steam pressure. The observed spectra of mono-layer sample were analyzed with the model function, given by the convolution of a Gaussian and a Lorentzian function (L1). For the full-layer sample, the spectra were expressed by the convolution function using double Lorentzian function (L1, L2). Here, L1 and L2 are contributions from mono-layer and the other water, respectively. To extract HWHM of L2, two of fitting parameters were fixed. HWHM values of L1 were fixed to values obtained from mono-layer measurements. The ratio of the intensity for L1 and L2 was also fixed in that of the amount of absorption water. As the resolution function, the spectrum of same sample at 150K was used. Fig.1 shows the temperature dependence of HWHM of L2 as a function of the squared scattering vector. This result is well represented by random diffusion model shown as solid lines. Fig.2 shows Arrhenius plot of the

diffusion coefficient of the mono-layer and full-layer sample. Consequently, the values of activation energy of the mono-layer and full-layer sample were 2.5 and 4.7 kcal/mol, respectively. It is interesting to note that the tendency of the temperature dependence of the diffusion coefficient of full-layer water is in good agreement with that of bulk-water [1].

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Fig. 1. (a) Temperature dependence of HWHM of L2. Solid lines represents the random jump dffusion fit. (b) Arrhenius plot of the diffusion coefficient of mono-layer water and the other water in FSM16.

Quesielastic and Inelastic Neutron Scattering Study of Ionic Liquid bmiml

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Room temperature ionic liquids (RTILs) are interesting materials as green solvents owing to their non-volatility, noncombustibility and so on. In previous works, we have carried out neutron scattering measurements on bmimCl (proto-type RTIL), bmimFeCl₄ and nbmimFeCl₄ (single component magnetic liquids) to investigate the dynamics related to the origin of the low melting temperature. In this study, we have measured quiasielastic and inelastic neutron scattering from 1-butyl-3methyl-imidazolium iodide (bmimI), witch has an bigger anion than one of bmimCl and is suitable to watch the size effect on dynamics directly. These measurements were performed on the AGNES spectrometer installed at the cold neutron guide (C3-1-1) of JRR-3M in JAEA (Tokai).

Figure 1 shows the boson peak of bmimI and bmimCl in glass state at 100K. The peak position of bmimI appears obviously at lower energy region than that of bmimCl. This result suggests that the size of anion affects the interaction between molecules in RTILs at glassy state to change the vibrational mode contributing the boson peak. We carried out the temperature scan for the elastic neutron scattering intensity of glassy bmimI. This intensity reflects the mean-square displacement of the vibrational or diffusional motion of bmim. The intensity curve has a bent near a glass transition temperature reflecting the onset of some relaxation phenomenon, e.g. a fast beta relaxation. This behavior is similar to that of bmimCl, bmimFeCl₄, nbmimFeCl₄ and that of molecular and polymer glasses. The quasielastic neutron scattering data for RTILs of bmim group we measured shows the tendency according to the jump diffusion model. The activation energy can

be calculated from the temperature dependences of self-diffusion constants from the analysis of QENS data. The activation energy of bmimI (16.8 \pm 1.2 kJ/mol) is close to that of bmimCl (15.6 \pm 0.7 kJ/mol) and nbmimFeCl₄ (16.4 \pm 0.9 kJ/mol) at observed time scale. On the other hand, the activation energy of bmimFeCl₄ (12.8 \pm 0.6kJ/mol) has obviously lower value than the others. These results show that the activation energy is essentially decreased with an increase of the anion size. We consider that the high activation energy of nbmimFeCl₄ is due to the dipole interaction between nbmim ion with strong polar groups (-CN).



Fig. 1. Comparison of Boson Peaks of bmimCl and bmimI

Quasi-elastic neutron scattering study on diffusion dynamics of water molecules in tert-butyl alcohol-water mixture

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In a previous paper [1], we reported that the characteristic behavior of the excess partial molar volume Ve of 1-propanolwater mixture was interpreted satisfactorily in terms of the hydrophobic hydration of the fractal surface of alcohol clusters. The fraction of the hydrated water molecules on the fractal surface was determined by means of quasi-elastic neutron scattering. Tert-butyl alcohol (TBA)-water mixture is characterized also by the polydisperse mass fractals [2]. Furthermore, the solution shows the same characteristic behavior of Ve as that of the 1-propanol-water mixture. The purpose of this study is to measure the dynamics of water molecules of the TBA-water mixture and examine whether or not the same interpretation of Ve as applied to the 1-propanol-water mixture is valid for the TBA-water mixture.

Diffusion dynamics of water molecules in the TBA-water mixture has been measured at 25, 47 and 70 ° C by using AGNES (C3-1-1) spectrometer, JRR3M at JAEA. In order to observe the dynamics of water molecules, the TBA molecules substituted partially by deuteron (CD3)3COH and the light water molecules H2O were used. The mixtures of TBA content x of 0.0, 0.01, 0.02, 0.04, 0.06, 0.08, 0.10, 0.14 and 0.17 in mole fraction were examined. The dynamical structure factors S(Q,E) in the region of quasi-elastic scattering have been obtained in the range of Qe from 0.376 to 2.504 A^-1.

Detailed analysis on the visualized mesoscale structure of the current solution suggested that the water molecules in the solution were classified into two types at least: one was the bulk-like state and another was the surface-state restricted to the fractal surface of alcohol clusters. Therefore, the S(Q,E)'s from x=0.01 to 0.10 have been analyzed by a linear combination of

the S(Q,E)'s for these two states. The fraction α of water molecules located at the fractal surface and the average number Nws of water molecules in the surface-state per TBA molecule (Fig. 1) have been obtained as a function of x. By extrapolating Nws to x=0, we get the value of 19⁻21 for Nws. This means that about 19⁻21 water molecules are located on the surface of an isolated TBA molecule in water. It is confirmed that the anomalous excess partial molar volume of the TBA-water mixture is explained reasonably well in terms of α in the same way as that for 1-propanol-water mixture [3].

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Fig. 1. Composition dependence of Nws for TBA-water mixture at 25 $^\circ$ C.

Dynamics of Water and Methanol Molecules in Binary Liquid Mixture Confined in Mesopores of MCM-41.

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We had investigated dynamics of water and methanol molecules in pure liquid confined in mesopores of MCM-41 by using quasi-elastic neutron scattering (QENS), and found that both of rotational and translational motions of these molecules in MCM-41 become slower compared with those in bulk liquid around room temperature. In the present study, dynamics of water and methanol molecules in binary liquid mixture confined in MCM-41 was investigated. MCM-41 is one of the most suitable sample to study confined liquids, since it has highly controlled cylindrical nano-space with very narrow pore size distribution.

MCM-41 sample, whose pore diameters were 3.74 nm, were prepared by the method of Beck et al. To observe dynamics of water and methanol molecules separately, we prepared two kinds of partially deuterated binary liquid mixture of water and methanol (molar ratio 1:1), i.e., H2O-CD3OH and D2O-CH3OD. The former gives QENS spectra mainly due to water molecules and the latter those mainly due to methanol ones, especially methyl group in it. For the QENS measurements, we prepared five MCM-41 samples whose pores were filled with different adsorbate: H2O-CD3OH and D2O-CH3OD, H2O, CD3OH, CH3OD. The OENS measurements of these five pore-filled MCM-41 samples, corresponding five bulk-liquid samples, a dried MCM-41 sample and an empty cell were carried out by using time-of-flight type spectrometer AGNES installed at the JRR-3M reactor of Japan Atomic Energy Research Institute. The wavelength of neutron beam was 0.422 nm, the momentum transfer (Q) range 6.4-25.0 nm-1, and the temperature range 200-300 K.

QENS spectra of H2O-CD3OH and D2O-CH3OD confined in MCM-41 as well as corresponding bulk-liquid samples at Q = 18.0 nm-1 and T = 300 K are shown in Figure 1. Here, the displayed spectra are the difference between raw spectra and spectra of the dried sample, and thus contain the contributions only from the confined liquid. All the spectra are normalized ones, in which peak maxima have been coincided with each other to emphasize the change in quasi-elastic wings of the spectra. By comparing line widths of the spectra, it is found that motions of methanol molecules is faster than those of water molecules for both bulk and confined liquid. It is also found that molecular motions in confined liquid are slower than those in bulk liquid for both water and methanol molecules. Detailed analysis is now in progress.



Fig. 1. QENS spectra of confined samples of H2O-CD3OH (bold line) and D2O-CH3OD (open circles) and bulk samples of H2O-CD3OH (fine line) and D2O-CH3OD (closed circles) at Q = 18.0 nm-1 and T = 300 K.

Wide-q Observation of the Self-Assembled Fractal Porous Silica by Ultra-small-angle Neutron Scattering

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The concept of fractal has been well established by the precedent studies and now we recognize that fractal structures are to be included in various natural objects, such as broccolis, branching trees, and so on. Furthermore, sometimes a fractal structure is deeply related with a specific property of the A super water-repellent surface material. made of an alkylketene dimer (AKD), which is a kind of wax, is a typically good example $^{1)}$. When AKD forms a rough surface having a specific surface fractal dimension of $D_s = 2.3$, it shows an extremely large contact angle of 174° for water droplets as compared with the flat surface. Moreover, it is elucidated that the water-repellency largely depends on the surface dimension of D_s . Thus, to control the fractal dimension is of importance to draw favourable properties of the material.

Later on, Mayama et al. have successfully applied the self-assembled AKD particle to the synthesis of porous silica materials, which have well-controlled fractal dimensions²⁾. They utilized flaky AKD particles as a mould and formed a silica matrix by so called sol-gel method. After the solidification of the silica matrix, the original AKD mould was completely burnt away at a high temperature (650 °C) and became pores having a particular fractal dimension. The fractal dimension of the porous silica turned out to be controlled by the compression of the AKD mould at different ratios and that fact was confirmed by the real-space observation with scanning electron microscopy.

In this study, we further investigate this porous silica material by the scattering method, which brings us the following advantages: (i) to facilitate the evaluation of the fractal dimension of the materials, and (ii) to elucidate the hierarchical structure.

Two fractal porous silica specimens, which were prepared by the above sol-gel method and under different compression conditions, were employed for ultra-small-angle neutron scattering(USANS). The measurements were performed on the Bonse-Hart type double crystal diffractometer (at 3G beamport) as well as on the pinhole and focusing SANS spectrometer SANS-J-II at the research reactor JRR-3. From the resultant scattering profiles shown in Fig.1, we can discern that the different mass fractal dimensions were observed in the q-range of $q \leq 1 \times 10^{-2}$ nm⁻¹ between the two specimens whose compression conditions are different.



Figure 1: Wide-q scattering profiles for fractal porous silica materials.

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原子炉:JRR-3 装置:PNO(3G) 分野:中性子散乱(液体・不規則物質)

1. 中性子散乱 5)高分子

1. Neutron Scattering 5) Polymer

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Evaluation of Membrane Lipid Dynamics by Time-Resolved Small-Angle Neutron Scattering

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In biological plasma membranes interbilayer transport and transbilayer movement of phospholipids are controlled by phospholipid transfer proteins and translocase enzymes [1]. Evaluation of these lipid dynamics is, however, limited due to lack of its methodology.

Richter and co-workers [2] have reported that the unimer exchange of polymer micelles in dimethylformamide can be detected by small-angle neutron scattering (SANS) technique using hydrogenated and deuterated polymers. This technique can be applied to phospholipids since the transfer of the lipids is known to be a slow process with a half-life of hours, i.e., detectable timescale by SANS. In this study, large unilamellar vesicles (LUVs) of dimyristoylphosphatidylcholine (DMPC) were prepared and used for timeresolved SANS (TR-SANS) measurements to evaluate the rate of interbilayer and transbilayer transfers of the lipid.

DMPC and d54-DMPC were obtained from Avanti Polar Lipids Inc. (Alabaster, AL). LUVs consisting of d54-DMPC (D-LUV) or DMPC (H-LUV) with a diameter of ca. 100 nm were prepared by extrusion method using Tris-buffered saline containing equivalent volume of D2O and H2O. LUVs consisting of 1:1 mixture of both lipids (D/H-LUV) were also prepared by mixing these lipids before hydration. Phospholipid concentration of each LUV preparation was set to 20 mM. SANS measurements were performed using SANS-U with 7 of incident neutron beam. Sample-todetector distance was set to 4 m.

D-LUV and H-LUV showed almost identical scattering profile, while D/H-LUV exhibited little scattering, suggesting that the scattering length density of D/H-LUV accords with that of solvent, i.e., contrast matching condition.

When equimolar amounts of D-LUV and H-LUV are mixed, scattering intensity should be equal to the average of each LUV preparation if there is no intervesicular lipid exchange. On the other hand, the lipid exchange between D- and H-LUV reduces the difference in the scattering length density of LUVs from solvent (i.e., contrast) with time. In this case, decay of the contrast depends on both the lipid exchange and flip-flop, and can be described by a double-exponential decay function with rate constants of the exchange and flip-flop.

TR-SANS experiments were carried out at four different temperatures. Each measurement was started immediately after mixing equivalent volume of D-LUV and H-LUV. The data were collected every 3 min. Timecourse of the normalized contrast was calculated from the scattering intensity. The contrast decayed more steeply with an increase in temperature. In addition, the normalized contrasts reached below 0.5, suggesting an involvement of flip-flop. The obtained contrast decays were well reproduced by the double-exponential function, which are represented by solid curves in Figure 1. Arrhenius plots of the obtained parameters exhibited good linear relationship, suggesting high accuracy of the data. The half-lives of the lipid exchange and flip-flop at 37 ° C were estimated at about 150 and 510 min, respectively. The results presented here demonstrate that TR-SANS is a powerful method to determine the membrane lipid dynamics.

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Fig. 1. Contrast decays of LUVs after mixing Dand H-LUV at four different temperatures. Solid curves are fitting curves according to the doubleexponential function.
Surface and Interface Structure of (Deuterated Polystyrene with Silsesquioxane End Group/Polystyrene) Blend Thin Films

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Polymer thin films have numerous technological applications which require the presence of a homogeneous film. However, producing stable films is problematic since the polymer thin films tend to dewet from the substrate. Previous study revealed that the addition of polyhedral oligomeric silsesquioxanes (POSS) to the polystyrene (PS) thin films led to an inhibition of dewetting in the films [1]. This inhibition effect can be attributed to the changes of the energetics of the surface and interface of the film by the segregation of POSS. Furthermore, the enhancement of the PS thin films by the addition of POSS-terminated PS (PS-POSS), prepared to improve the affinity of POSS with PS, was also demonstrated [2]. In this study, neutron reflectivity (NR) technique is used to characterize the surface and interfacial structures of the deuterated PS-POSS (dPS-POSS)/PS blend thin film.

dPS-POSS2.9k (Mn = 2900, Mw/Mn = 1.09)/PS44k (Mn = 44000, Mw/Mn = 1.04) (32/68 w/w) blend thin film was spincoated from the toluene solution onto acidcleaned Si wafer. The film was annealed under vacuum at 393 K for 3 hours. NR measurement was carried out using MINE at JRR-3M with 0.88nm of incident neutron beam. Figure 1 shows the NR profile of the dPS-POSS2.9k/PS44k (32/68 w/w) blend thin film. The solid line denotes the fitting curve based on the model scattering length density (b/V) profile, as shown in the inset of Figure 1. Increase in the b/V values was observed at the both of surface and interface of the film, which suggested that dPS-POSS was enriched at the interface as well as the surface. Similar results were also observed in the different deuteration contrast film (PS-POSS2.5k (Mn = 2500, Mw/Mn = 1.11)/deuterated PS38.5k (Mn = 38500, Mw/Mn = 1.07) blend)reported in

our previous study. From these results, it can be concluded that the segregation of POSS moiety was not due to the deuteration effect. The segregation of PS-POSS, which changes the surface and interfacial free energy of the film, can be an important factor in the dewetting inhibition effect.

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Fig. 1. Neutron reflectivity profile of dPS-POSS2.9k/PS44k (32/68 w/w) blend thin film. The inset shows the scattering length density profile of the film.

Structure Analyses of Ultra-Hydrophilic Zwitter-ionic Polymer Brush at Water Interface by Neutron Reflectivity

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Poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC) is a highly hydrophilic polyelectrolyte specially designed for biocompatible medical devices[1]. Neutron reflectivity (NR) of surface-grafted PMPC in an aqueous solution have been studied to analyze the interface structure of swollen polymer brushes, which are fairly extended in a good solvent due to the high osmotic pressure[2]. In this study, the authors investigated the salt effect on the swollen PMPC brush structure by NR.

High-density PMPC brush was prepared by surface-initiated atom transfer polymerization from the quartz immobilized with surface initiator. NR measurements were carried out with the multilayer interferometer for neutrons (MINE), using wavelength of 0.88nm. Neutron beam irradiated from quartz to the interface between heavy water and PMPC brush on quartz glass. A critical angle was clearly observed at q = 0.11 nm-1 in Figure 1 owing to the difference in scattering length density between quartz and heavy water. Scattering length density profiles of PMPC brush in heavy water calculated from the reflectivity curves in Figure 1(b) and (c) indicated that the PMPC chains were stretched up to 50 nm in heavy water forming concentration gradient of heavy water. Interestingly, quite similar reflective curve was observed from the interface of PMPC brush at 0.1 M of NaCl deuterium oxide solution. Generally, isolated polyelectrolyte would shrink in salt solution because the electrostatic repulsion between polymer chains decrease. However, salt ion cannot be diffused into a high-density polymer brush layer due to the high osmotic pressure and high local charge density. Similar results have already been reported by Matsuoka[3], and

Kurihara[4]. In addition, the authors have found that the dimension of free PMPC in water is independent on the ionic strength of salt solution[5]. Therefore, the thickness of PMPC brush in solution was supposed to be hardly changed even in a salt solution.

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Fig. 1. Experimental NR profiles of bare quartz (a), PMPC brush (b) in heavy water, in 0.1 M NaCl solution (c), and corresponding fits. Assumed scattering length density profile for (b) and (c) is shown above.

Structural Formation Process of Polymers under Shear Flow

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Crystallization of polymers under shear flow have been extensively investigated because polymers are exposed to various flows such as elongational, shear and mixed flows during industrial processing. These processes can significantly affect the crystallization kinetics and final morphology. For example, when polymer crystallizes under flows, the so-called shishkebab structure could be observed. The shish-kebab structure consists of long central fiber core (shish) and lamellar crystals (kebab) periodically attached along the shish structure and surrounded by the shish structure. We showed that the small angle neutron scattering (SANS) with deuterium labeling method was very powerful to study the crystallization kinetics of polymers under shear flow.

In the present experiment, we performed the time-resolved SANS measurements on crystallization processes of blends deuterated low molecular weight of and protonated ultra-high molecular weight polyethylene (PE) with the handmade shear cell specialized for observation of polymer crystallization process with/without shear flow [1]. The blend samples were molten at 190 C and then cooled down to a crystallization temperature of 124.5 C at a rate of about 40 C/min. The sample was subjected to pulse shear just after reaching the crystallization temperature. The shear rate and strain are 90 (1/s) and 1000 %, respectively. The molecular weight of low molecular weight deuterated and protonated ultrahigh molecular weight PE (d-PE/h-PE) is 56,500 and 2,000,000, respectively. The time-resolved SANS measurements were carried out on SANS-U spectrometer on JRR-3, JAEA, Tokai, Japan.

Figure 1 shows that the time evolution of 2D SANS profiles for a blend d-PE/h-PE =

3/97 under shear flow. Just after inducing shear flow (0.5 min), the streak-like scattering normal to the shear direction could be observed, and then the strong scattering profiles parallel to the shear direction appeared and became stronger after 2.5 min. The normal streak-like scattering and parallel scattering were assigned to shish and kebab structures, respectively. These results suggest that the shish structure grows before kebab structural formation. Furthermore, the observed shish-structure is in micron ordered and very similar to the shishlike structure observed with time-resolved light scattering measurements. As h-PE concentration decreases the scattering profile became isotropic. This result suggests that the structural formation process depend on the existence of entanglements of high molecular weight components.

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Fig. 1. Figure 1. Time evolution of 2D SANS profiles for deuterated and hydrogenated polyethylene blend.

Structural Formation of Uni-Lamellar Vesicles in a Mixture System of Long- and Short-Chain Lipids

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It has been well known that natural swelling of a dry phospholipid film usually produces large multi-lamellar vesicles [1]. These mimic biomembranes produced from synthetic phospholipid molecules have been extensively studied to understand the actual behavior of real biomembranes. Living cells and their organelle, however, exist as uni-lamellar vesicles (ULVs). Therefore, effective methods to create the ULVs have been studied so far [2].

For a phospholipid mixture system consisting of long- and short-chain lipids, it was reported that bilayered micelles with 10-100 Å diameter, so-called bicelle, are spontaneously formed at low temperature, and they fuse into vesicles at high temperature. Especially, ULVs with 100-1000 Å diameter are formed only when the bilayers are charged [3]. This suggests that the electrostatic interaction is important for the ULV formation in the lipid-mixture system. The mechanism of the ULV formation, however, has not been studied well. Therefore, we have performed small-angle neutron scattering (SANS) experiments on the lipid-mixture system to investigate the effect of the electrostatic interaction on the ULV formation.

In this study, we have performed SANS experiments on a typical lipid mixture system, dimyristoylphosphatidylcholine (DMPC) and dihexanoylphosphatidyl-choline (DHPC) mixture system, at SANS-U, JRR-3M, JAEA, Tokai, Japan [4]. Since multivalent cations adhere onto the hydrophilic part of lipid molecules, the lipid mixture was dissolved in CaCl₂ aqueous solution of 3 mM to obtain charged bilayers. The experiments were performed

for the lipid mixtures with different NaCl concentration, that is, the shielding length of the electrostatic interaction. The obtained results are shown in Fig. 1. The SANS profiles for 0 and 50 mM NaCl are very similar, irrespective of the existence of the salt. It is found from the form factor of a ULV, *i.e.* the profiles in the low-q region, that its diameter for 50 mM (about 1200 Å) is almost the same as that for 0 mM. On the other hand, the low-*q* profile was drastically changed and a new Bragg peak corresponding to a multi-lamellar structure with repeat distance of about 75 Å was observed for 100 mM NaCl. From these results, we concluded that the electrostatic interaction has a little effect on the shape of the ULV, but contributes much to its stability.

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Fig. 1. Dependence of a SANS profile on NaCl concentration.

Surface Segregation in Miscible Polymer Mixtures of Block Copolymer / Homopolymers

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In a miscible blend of two polymers with equivalent degree of polymerization, the lower surface energy component is enriched at the surface to minimize the total free energy of the system. However, it is impossible to strictly control a chain arrangement along the direction normal to the surface. In this study, we evaluated surface segregation phenomena in mixtures of poly(4-trimethylsilylstyrene)(T), polyisoprene(I), and their block copolymer (TI), whose blends are miscible at room temperature, ¹ and compare to what extent of segregation of T homopolymer and that of T block of TI in T/TI/I blend films.

Normal Т (hT), its partially deuterated one (dT), normal I(hI), poly(4-trimethylsilylstyrene-blockpoly(deuterated isoprene) (hTI) and 4-trimethylsilylstyrene-block-isoprene) (dTI) were used in this study. Weight average molecular weights, Mw, for hT, dT, hI, hTI and dTI are 34k, 43k, 24k, 85k and 65k, respectively. Surface free energy of T, being evaluated to be 31.9 mJ/m² based on contact angle measurements, is lower than that of I of 37.4 mJ/m². dT/hTI/hI and hT/dTI/hI blend films were prepared by spin-coating method from toluene solutions onto silicon wafers. Since the volume fractions of T, TI and I were 1:1:1, the ratio of T to I in the whole film is 1:1. Neutron reflectivity (NR) measurements were carried out using MINE-2 reflectometer. Incident neutrons have the wavelength of 0.88 nm and the resolution of 5.1 %. The reflectivity was calculated on the basis of the scattering length density profile along the depth direction by using Parratt 32.

Fig.1(a) shows neutron reflectivity profiles for dT/hTI/hI and hT/dTI/hI blend films. Experimental data sets were represented by circles and squares. Solid lines denote the calculated neutron reflectivities based on the scattering length density, (b/V), profiles shown in the parts (b) and (c) of Fig. 1. The (b/V) values for dT, hT and hI were taken to be 3.63×10^{-4} , 0.57x 10^{-4} and 0.27 x 10^{-4} nm⁻², respectively, using the scattering lengths per monomeric units and the bulk densities of these poly-Since the calculated curves were mers. in good agreement with the experimental data, it can be conceived that the model (b/V) profiles well represent the composition profiles in the blend films normal to the surface. For the dT/hTI/hI blend film, the (b/V) value at the surface is higher than that of the internal bulk region, as shown in Fig.1(b). This means that dT homopolymer is enriched at the surface. On the other hand, for the hT/dTI/hI blend film, dTI was not segregated at the surface. These results indicate that surface segregation power of T component of TI is much lower than that of T homopolymer.

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Fig. 1. (a) Neutron reflectivity profiles for dT/hTI/hI and hT/dTI/hI blend films. Solid lines denote the calculated reflectivities based on scattering length density, (b/V) profiles for (b) dT/hTI/hI and (c) hT/dTI/hI blend films.

Dynamic anisotropy of polymer thin films

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Polymer thin films are very much utilized in industry because their properties are related to many phenomena such as adhesion, wetting, lubricant and so on. Therefore polymer thin films are focused not only from scientific point of views but also from industrial point of view. We have so far studied the dynamics of polymer thin films with inelastic neutron scattering method [1] and found that the decrease of mobility (mean square displacement $\langle u^2 \rangle$) was observed with film thickness for macroscopically isotropic samples. However, polymer chains are spatially confined in the thickness direction. In that sense, polymer thin film is a 2D-confined system. Therefore, we expected that the motional anisotropy would be observed with decreasing film thickness. No other researches concerning the dynamic anisotropy of polymer thin films have not been done yet as far as we know. In the present experiment we studied the dynamics of polymer thin films in parallel and perpendicular directions to polymer surface using triple axis spectrometer (TAS), mainly focusing on the glassy state.

The sample used in this experiment was hydrogenated PS with molecular weight 290K and we prepared thin films 1000Åand 400Åin thickness, which were supported on Al foil and bulk sample as a reference. The measurements were performed on 4G spectrometer and incident energy was 30meV. Fig. 1(a) indicates the Q^2 dependence of elastic intensity for 400Åthin films at 230K for parallel and perpendicular geometries to surface of polymer thin films and the solid lines are results of fit considering the contribution from non-Gaussian parameter [2]. From fit, we can evaluate $\langle u^2 \rangle$ for both geometries and found that $\langle u^2 \rangle$ decreased with decreasing film thickness for both geometries as indicated in Fig. 1(b). However, the evaluated $\langle u^2 \rangle$'s for both geometries almost identical within experimental error, implying that the notable dynamic anisotropy was not observed even for the thinnest film (= 400Å). It can be said that the dynamics for both geometries are correlated. The detailed analysis is now under progress in order to understand this result.

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Fig. 1. (a) Q^2 dependence of elastic intensity of 400Åthin films. (b) Thickness dependence of $< u^2 >$ for parallel and perpendicular geometries at 230K.

Dynamics of diblock polymer in the form of lamellar structure

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Recently, the physical properties of spatially confined glass-forming materials were studied very much and they were focused not only from scientific point of view but also from industrial point of view because their properties were strongly related to nanotechnology. There are so many ways for the spatial confinement of glassforming materials like porous glass, thin film, molecular sieve and so on. One of the biggest objectives in the researches for confined systems is estimation of the characteristic length scale that is responsible for glass transition. However, surface or interface effects could not be ignored with decreasing the size or scale, therefore the characteristic length scale for glass transition could not be evaluated from simple size effect only. Estimation the contribution from surface or interface effect is needed for the full understating of above problem. We have so far studied the dynamics of polymer thin films using inelastic neutron scattering method and found the decrease of mobility with film thickness. We assumed that this result was caused by the existence of low mobility layer that exist between thin film and substrate. It was expected that the interface affected the dynamics very much. In this experiment, we studied the dynamics of diblock copolymer in the form of lamella structure and focused on the motion of polymer chains that were confined in the form of lamellar structure. Compared to polymer thin films, this system is as it were, chemical confinement. We used the deuterated polystyrene (d-PS)/hydrogenated polybutadiene (h-PB) diblock copolymer (SB) with M_w =64k/43K in the former of lamellar and homo h-PB with M_w =43K as a reference sample. We studied the incoherent scattering from h-PB owing to the large scattering cross section from hydrogen compared to other atoms (C, D). The measurements were done with AGNES and the incident energy was set to 4.40 meV. First we focused on the boson peak and Fig.1(a) indicates the dynamic scattering law $S(Q, \omega)$ at 80K. The boson peak was observed at around 2meV for both polymers. Seemingly the intensity and peak position were the same and it was considered that boson peak was not affected by confinement. Next we evaluated mean square displacement $< u^2 >$ for both polymers. In the low temperature region (below the $T_{g} \sim 170 \text{K}$ of PB), the difference was too small to observe. However, above the Tg of PB the difference was observed. The up-turn of $< u^2 >$ was observed for homo h-PB, indicating the onset of relaxation process, on the other hand it was not so clear for SB diblock copolymer. This indicates that the relaxation process was affected by confinement.



Fig. 1. (a)Dynamic scattering laws from SB and PB at 80K. (b) Temperature dependence of $\langle u^2 \rangle$ for both polymers.

Investigation on nanostructure in a block copolymer film having sulfonic acid groups

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Nanostructure in a block copolymer film having sulfonic acid groups, which can be applicable for a proton conducting polymer electrolyte membrane for a fuel cell, was investigated by small angle neutron scattering (SANS).

A cross-linkable block copolymer, poly(styrene-co-4-(1methylsilacyclobutyl)styrene)-b-

poly(neopentyl styrenesulfonate) (poly(Stco-SBS)-b-polySSPen), was precisely synthesized by a nitroxy-mediated living radical polymerization. The degrees of polymerization for poly(St-co-SBS) and polySSPen were estimated to be 136 and 61, respectively. The molar ratio of St/SBS was determined to be 0.9/0.1. A crosslinked film with free sulfonic acid groups, poly(St-co-SBS)-b-polySSH, was obtained by casting a toluene solution of the block copolymer with a platinum catalyst and heating it at 230 degree C.

Neutron scattering experiments on the dry polymer film and wet polymer film in deuterium oxide were performed by SANS-U. Strong neutron scattering was observed in the small angle region in both samples, indicating that some kinds of nanostructure were formed in the block copolymer films. The SANS profile for the dry sample was reproduced well by applying a hard sphere model (Figure A), which suggested that spherical domains (12.5 nm in radius) were randomly distributed in the film. On the other hand, the profile for the wet sample was reproduced by adapting Fournet model (Figure B), which suggested that interaction between neighboring two spherical domains existed. The domain radius and the mean distance between the neighboring domains were evaluated as 14nm and 18nm, respectively. We can reasonably understand these results if we consider that the spherical polySSH domains existed in a matrix composed of poly(St-co-SBS) and that the polySSH domain was swollen by deuterium oxide in the wet sample.

The proton conductivity of the block copolymer film has been already examined and it was found that the film possesses high conductivity that is comparable to a well-known sulfonic acid containing membrane Nafion produced by Dupont.



Fig. 1. Figure (A) SANS experimental and fitting profiles for dry block copolymer film; Figure (B) SANS experimental and fitting profiles for the wet block copolymer film in deuterium oxide.

Structural analysis of a dilatancy solution

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We have found that nanometer-size emulsion and polymer (HEC; Hydroxyethylcellulose) system have shear thickening behaviors, i.e., dilatancy behaviors. Nanometer-size emulsion were made by high pressure emulsification, and their diameter was ca. 30nm [1]. The weight average molecular weight of HEC was ca. 1,300,000 and its concentration was 0.4 wt%.

It is predicted that there are some interactions between emulsion and polymer in this system. In order to analyze such interactions more precisely than in previous experiments, we carried out simultaneous measurements of small-angle neutron scattering (SANS) coupled with rheology, Rheo-SANS. A Rheo-SANS system was installed at SANS-U (C1-2), JRR3M in JAEA (Tokai). Rheological measurements can be carried out on a Physica MCR-501 (Anton Paar) equipped with a double cylinder type shear cell. (Fig. 1)

Simultaneous measurements of rheology and SANS were carried out at several steady shear rates (the range of the shear rate being 0.1 - 100 [1/s]). Typical results of the measurements are shown in Fig. 2 and 3. Fig. 2 shows clear dilatancy (viscosity thickening) at the shear rate of ca. 4 [1/s]. Fig. 3 shows the corresponding SANS profiles observed at the shear rates of 0.1 to 100 [1/s]. At the shear rate above the dilatant point, a steep increase of the scattering intensity was observed in the low-Q region. This result indicates that some semimicrometer-size structure was formed under shear flow at the shear rate above the dilatant point.

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Fig. 1. Photo of the Rheo-SANS system. Fig. 2 Time evolution of the shear viscosity after imposing various rates of stepwise shear. Fig. 3 Changes of SANS profiles observed at the various shear rates corresponding to Fig. 2.

Small-Angle Neutron Scattering Study on Strain-Induced Crystallization and Nonuniformity of Natural Rubber

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It is well known that natural rubber (NR) contains non-rubber components such as proteins, phospholipids and fatty acids, carbohydrates and inorganic substances. However, no reports on the direct morphological evidence of non-rubber components in solid have been published as far as we know. Thus, the microscopic structure of NR was investigated by SANS in this study. It was compared with those of deproteinized NR (DPNR) and isoprene rubber (IR). The results of small-angle Xray scattering (SAXS) and atomic force microscopy (AFM) were also discussed in order to elucidate the structural characteristics of NR. Peroxide-cross-linked NR and IR samples were prepared by milling and heat-pressing. SANS experiments were carried out at SANS-U (C1-2), JRR-3M in JAEA (Tokai). The wavelength was 7.0 Å. The sample-to-detector distances were chosen to be 2.00 and 8.00 m. The scattered intensity were collected with an area detector and then circularly averaged. Dry and swollen samples with deuterated toluene were subjected to SANS.

The following conclusions were obtained. (i) Both SANS and SAXS intensities, $I_{\text{SANS}}(q)$ and $I_{\text{SAXS}}(q)$, of NR have a strong q-dependence as shown in Figure 1, indicating presence of large scale inhomogeneities. Here, q is the magnitude of the scattering vector. This strong q-dependence disappears by deprotenization (DNPR). The inhomogeneities were assigned to protein aggregates, which was supported by AFM. These aggregates were found to be larger in size as well as in volume fraction than those of cross-link inhomogeneities introduced by cross-linking since cross-liking did not produce any significant increase in scattering. (ii) IR does

not show such inhomogeneities. (iii) The microscopic structures of swollen crosslinked NR by deuterated toluene are successfully reproduced by SANS intensity functions consisting of squared-Lorentz and Lorentz functions. The size of protein aggregates was evaluated to be of the order of 200 Å or larger. (iv) Swelling of both cross-linked NR and cross-linked IR introduces gel-like concentration fluctuations whose mesh size is of the order of 20 Å. These results indicate that NR possesses inherent inhomogeneities in bulk and additional thermal concentration fluctuations in swollen state, respectively.[1, 2]

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Fig. 1. SANS (symbols) and SAXS curves (thin lines) of NR rubbers (a) before (NR) and (b) after milling (NR0) without cross-linker. The thick dotted and dashed lines denote the fit with SL-function.

Small-Angle Neutron Scattering Study on the Miscibility and Concentration Fluctuation of Hydrogen Bonding Polymer Blends

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The effects of hydrogen bonding (Hbonding) on the composition fluctuation in miscible polymer blends were examined by utilizing small-angle neutron scattering (SANS) method. Specifically, we used the blends composed of poly(vinyl acetateco-vinyl alcohol) (P(VA-VOH)) with various VOH content (fOH) and deuterated poly(ethylene oxide) (dPEO), since the formation of the H-bond between the hydroxyl group of P(VA-VOH) and the ether oxygen of dPEO is expected. Furthermore, the advantageous point of this system is that the degree of H-bonding can be changed by the variation of fOH. In this study, we prepared P(VA-VOH) samples having different fOH (molar fraction) (= 0, 0.10, 0.18, 0.28, 0.35) by the saponification reaction of PVA. The blend composition of P(VA-VOH):dPEO = 80:20 was mainly examined for the SANS measurements.

For all the blends, the SANS intensities increased with increasing temperature T implying the existence of lower critical solution temperature. For the P(VA-VOH)/dPEO (80/20) blends with fOH <0.28, the scattering profiles S(q) could be well represented by the random phase approximation (RPA) theory. Based on this theory, the interaction parameter X was determined as a function of T. Figure 1 shows the fOH dependence of X at T=343K. As seen in this figure, the X shows a minimum at around fOH=0.15, meaning that the blend at this particular fOH is the most miscible. Furthermore, we found that the random copolymer theory (solid curve in the figure) could quantitatively explain the fOH dependence of X.

For the blend of fOH=0.35, on the other hand, the RPA theory did not fit the S(q) well, especially at the small q re-

gion. The experimental data at the small q were found to be more suppressed than the theoretical prediction. This behavior suggests that the formation of larger number of H-bonds might suppress the composition fluctuation.



Fig. 1. fOH dependence of the interaction parameter X for P(VA-VOH)/dPEO (80/20) blends at T=343K. Solid curve represents the fitted result with the random copolymer theory.

Micellization behavior of non-surface active amphiphilic block copolymer containing fluorine in aqueous solutions

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Introduction

Ionic amphiphilic diblock copolymer consisting of polyelectrolyte and hydrophobic chains shows "non-surface activity" when some physico-chemical and molecular structural parameters are satisfied. Although they are nonsurface active, surprisingly they form micelles in aqueous solutions, which was confirmed by static and dynamic light scattering and other experimental techniques. In this study, the nanostructure of micelles of non-surface active polymer, poly(pentafluorostyrene)-b-poly(styrene sulfonate) ((PFS)m-b-(SSNa)n) was investigated by SANS.

Experimental

Polymers with m:n=30:66, 41:66, and 41:105 were synthesized by living radical polymerization and their heavy water solutions with concentration of 0.1 wt% were measured by SANS-U. The dependencies on m:n and added salt concentration of micelle nanostructure was investigated. The results were summarized in Table 1.

Results and Discussion

Added Salt Concentration Dependence Spherical micelles were observed for polymer with m:n=30:66 under no salt condition. However, at [NaCl]=0.1M NaCl, both of spherical and cylindrical micelles were observed. At higher salt concentration, only rod-like micelles were observed. This behavior can be explained by the change of "effective" area of head group (i.e. ionic hydrophilic block) by the shielding effect of added salt ions for the electrostatic interaction in ionic corona region.

Effect of Hydrophilic Chain Length

The micelles of polymers with m:n=41:66 and 30:105 were spherical with and without added salt. The size of core and the aggregation number evaluated by SANS were larger for m:n=41:66 than for m:n=30:66. In addition, the shell thickness for m:n=41:105 was larger than that for m:n=41:66 although their core size are comparable. These tendencies can be understood by the concept of "Packing Parameter" concept, although they were non-surface active, which is anomalous character for amphiphilic molecules.

| mn | C. 00 | shape | ΦΦ | R: 1) (nm) | 5, b) (nm) | Retail (nm) | Nage |
|--------|-------|--------|-----|------------|--|-------------|------|
| 30:66 | 0 | sphere | 1 | 9.5 | 8.9 | 190 | 567 |
| | 0.1 | sphere | 0.3 | 8.7 | 8.3 | 17.0 | - |
| | | rod | 0.7 | 8.7 | 8.3 | 17.0 | - |
| | 0.5 | rod | 1 | 7.5 | 7.0 | 145 | 280* |
| 41 66 | 0 | sphere | 1 | 11.0 | 9.0 | 20.5 | 520 |
| | 0.2 | sphere | 1 | 11.5 | 8.5 | 20.0 | 723 |
| | 0.5 | sphere | 1 | 11.3 | 10.4 | 217 | 686 |
| 41:105 | 0 | sphere | 1 | 10.0 | 11.0 | 21.0 | 476 |
| | 0.1 | sphere | 1 | 10.4 | 11.6 | 22.0 | 535 |
| | 0.2 | sphere | 1 | 10.3 | 11.7 | 22.0 | 520 |
| | 0.5 | sphere | 1 | 10.6 | 13.0 | 236 | 566 |
| | | - | | | a) racius of the core b) thickness of the shell c) racius of the micelle d) volume fraction of the micelle e) aggregation number | | |

Fig. 1. Micelle nanostructure by SANS

Microstructure Analysis of Weakly-charged Gels Having Different Spatial Distribution of Charged Groups \sim pH Dependence \sim

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Gel microstructure formation according to spatial configuration of charged groups in gel network has been investigated using a two-dimensional SANS spectrometer (SANS-U) of Institute for Solid State Physics, Univ. of Tokyo, located at JRR3M in Japan Atomic Energy Agency (JAEA), Tokai, Japan. Three types of gel consisting of hydrophobic N-isopropylacrylamide (NIPAm) and weakly-charged acrylic acid (AAc) copolymers were prepared with different distributions of AAc monomer units in the network. The first type is NI-PAm/AAc copolymer gel in which NI-PAm and AAc are randomly copolymerized in monomer unit by redox polymerization (code;redox-mono-AAc). The second type is a UV-crosslinked NIPAm/AAc gel in which AAc is copolymerized in units of polymers (code;UV-poly-AAc).^[1] The third type is a NIPAm/poly-AAc polymer gel prepared using redox method in which poly-AAc was not cross-linked but physically entrapped in the NIPAm polymer network (code;redox-poly-AAc). These three types of gel contain the same amount of charged groups (NIPAm/AAc = 668mM/32mM) but different spatial configurations of charged groups.

Fig.1. shows the *T* dependence of SANS profiles, I(q) of each NIPA/AAc copolymer gel at pD=6 or 11. Here, the solid denote theoretical fitting curves. With increasing temperatures, a broad peak appears in I(q)s for redox-mono-AAc and UV-poly-AAc. For a theoretical fitting with this broad peak, we employed Rabin-Panyukov (RP) theory.^[2] RP fittings were quite successful for each experimental result. These results show that UV-poly-AAc undergoes microphase separation with a long-period larger than that of redox-

mono-AAc. Note that these long-period lengths depend on pD for both UV-poly and Redox-mono. The latter results in a higher effective degree of ionization than UV-poly-AAc due to the ion condensation along the poly-AAc chains. On the other hand, in redox-poly-AAc, no pD dependence was observed. In the case of redoxpoly-AAc, non-crosslinked poly-AAc does not affect the gel structure at the microscopic levels. These findings demonstrate that the charge configuration in a weaklycharged polymer gel can be tuned and it plays a significant role in microscopic structures.

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Fig. 1. *T* dependence of SANS profiles, I(q), at pD=6 and 11 for each type of gel network consisting of NIPAm and AAc. Solid lines show theoretical fitting curves.

Analysis of Aggregation States in Ultrathin Polymer Blend Films Confined Between Solid Substrates

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Surface structure in polymer materials has been widely studied, experimentally and theoretically, due to a wide variety of technological applications as well as scientific interests. So far, we have examined surface segregation phenomenon in the miscible blends of polystyrene (PS) and poly (vinyl methyl ether) (PVME).[1] In the case of symmetric blends in terms of degree of polymerization (N), PVME and PS were preferentially segregated at the film surface and the interface with a silicon wafer, respectively, to minimize the free energy of the system. However, there are few reports dealing with segregation phenomenon in ultrathin blend films confined between solid substrates.

A blend film of PVME and perdeuterated PS (dPS) was spin-coated from a toluene solution onto a silicon wafer with a native oxide layer, and then, a silicon layer was evaporated on it. The mixing ratio of the blend was fixed to be 50 wt %. The thickness of the blend film evaluated by ellipsometry was approximately 110 nm. The film was annealed for 150 h at 333 K in vacuo, which was well above the bulk glass transition temperature and below the lower critical solution temperature. The composition profile of the (dPS/PVME) blend film along the direction normal to the surface was studied by the multilayer interferometer for neutrons (C3-1-2-2, MINE) at ISSP, the University of Tokyo. Incident neutrons with the wavelength of 0.88 nm and the resolution of 5.1 % were guided into the specimen, which was vertically set onto a goniometer, from the surface silicon deposition layer. The reflectivity was calculated on the basis of the scattering length density profile using Parratt32, which is a freeware from the Hahn-Meitner Institute

(HMI).

Fig. 1 shows the scattering vector, q, dependence of neutron reflectivity for the (dPS/PVME) blend film confined silicon oxide layers. Although the data fitting analysis has not been perfectly completed yet, we tentatively reach a conclusion that the dPS fraction increased with getting closer to both blend/silicon oxide interfaces. This result would be explained in terms of minimization of the free energy at the substrate interfaces. That is, the higher surface energy component energetically prefers to contact with the hydrophilic silicon oxide. More conclusive study, which discusses interfacial decay length, excess amount and its molecular weight dependence, will be reported in the near future.

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Fig. 1. Neutron reflectivity for the (dPS/PVME) blend film confined silicon oxide layers.

Concentration fluctuation for polymer blend thin film close to critical

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Many interesting phenomena are reported on thin films of polymer blends. We also found in optical microscope and light scattering measurements that spinodal decomposition type dewetting preferentially occurs in the PS and PVME blend thin films for the in-plane structure in a thickness region less than 100 nm in the two phase region. In this study we investigated the density profile perpendicular to the film surface, using neutron reflectivity (NR) before dewetting. We found from the NR results that concentration fluctuations occur normal to the surface before dewetting, which may induce the dewetting. NR measurement was carried out using the MINE neutron reflectometer installed at the cold neutron guide C3-1-2-2 in JRR-3M reactor. We used deutareted PS (dPS, Mw=288,000) and hydrogenated PVME (Mw=90,000) in this study. The fraction of PS dps in the blend was 0.3, which corresponds to the critical composition in the bulk. The polymer blends were prepared by spin-coating onto a silicon wafer. Thicknesses of the polymer blend films were 98nm. All the films were preannealed at 90 ° C in the one phase region for 30 min and then temperature-jumped into the two phase region for phase separation, and annealed for a given duration. The films were rapidly quenched to room temperature for the measurements. Figures 1 show the time evolution of neutron reflectivity profiles (a) and density profiles (b). A typical example of time evolution of NR profiles at 0, 1, 3, 120, 360 min after T-jump from one phase region to two phase region are shown in Figure 1(a). Time evolution of the composition fluctuations along z-axis evaluated from NR profiles is shown in Figure 1(b). In one phase region (t = 0 min)the NR profile is well described by three layer model (PVME/(PVME/PS)/PVME),

and we found that the interface roughness between surface PVME and PS/PVME (or surface roughness) increases with annealing time. The fringed pattern in the profile disappeared once due to dewetting. However, further annealing of 360 minutes show that fringes appear again. It suggests that PVME thin layer segregate on the Si substrate.



Fig. 1. Time evolution of neutron reflectivity in two phase region (a)and Time evolution of composition fluctuations in depth direction in two phase region(b).

Effects of Temperature on the Shear-Induced Structural Transition in the Lamellar Phase of Nonionic Surfactants

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In the past 10 years, much attention has been paid to the effects of shear flow on the structure of a lamellar phase owing to the development of the apparatus which enables us to determine their structures directly under shear flow. In the previous studies, we have measured smallangle neutron scattering (SANS) on the lamellar phases of a nonionic surfactant C16H33(OC2H4)7OH (C16E7) in D2O at 70C under shear flow with shear rate of 0.01 - 10 s-1 which is much lower than those for other studies reported so far. We have found anomalous decrease in the lamellar spacing for the shear rate of 0.1-1 s-1 suggesting local phase separation into concentrated lamellar and water-rich regions [1,2]. In the present study, we have investigated effects of temperature on these structural transition.

Measurements of SANS were carried out at the instrument SANS-U of Institute for Solid State Physics of University of Tokyo in JRR-3M at Tokai with a Couette shear cell [3].

Figure 1 shows temperature dependence of the repeat distance at 0, 1, and 3 s-1 for the velocity-gradient direction for the sample containing 48 wt% of C16E7. The repeat distance at 1 s-1 decreases discontinuously at about 68C. At 3 s-1, on the other hand, the repeat distance takes smaller values than at rest but suddenly increases at about 70C. In our previous SAXS study on the same system at rest, it has been found that the lamellae have water-filled defects in the lower temperature range and that the fraction of these defects decreases with increasing temperature and disappear above about 68C. So the present results suggest that the discontinuous decrease in the repeat distance by shear flow is strongly correlated with the existence of the waterfilled defects.

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Fig. 1. Figure 1. Temperature dependece of the repeat distance at 0, 1, and 3 s-1 for the velocity-gradient direction for the sample containing 48 wt% of C16E7.

Pressure-Induced Phase Separation of Block Copolymers in Aqueous Solution

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Recently, pressure effects on polymer aqueous solutions have attracted attention in the fields of industrial applications. On the other hand, little work was done in basic polymer science, though pressure is an important variable as one of the thermodynamic parameters. Therefore, we focus on the phase behaviors and structural change of polymers in D_2O by varying pressure and temperature.

Block-copolymers, we used, are thermosensitive polymers, showing LCST (Lower Critical Solution Temperature) at about 40° C in D₂O. In the former study[1], phase behaviors at various pressures and temperatures were intensively studied with a concentrated polymer solution (15wt%). However, in that case, complex interactions between micelles prevented detailed and microscopic analyses of the polymers and the hydrated water. Therefore, to understand the pressure effect more quantitatively, dilute polymer solutions (0.5wt%) where the micellar interaction can be ignored was used in this study.

Pressure dependent SANS experiments were conducted with a pressure chamber, PCI-400-SANS, Teramex, Co. Ltd. Kyoto, Japan. The applied pressure was transmitted via a rubber diaphragm connected to the inner cell made of aluminum with quartz and sapphire windows. The outer chamber was filled with D₂O and the pressure was controlled by pressurizing D₂O by a double-cylinder hand pump. The SANS measurements were done at T: 28, 40, 50°C and P: 0.1-400MPa. The SANS experiments were done according to the P-Tphase diagram obtained by dynamic light scattering (DLS) experiments.

Micellization temperatures (MT) were detected by DLS by increasing temperature at fixed pressures. By increasing temperature, a new peak was observed, which is ascribed to the micellar diffusive mode. Obtained *P*-*T* phase diagram was a upwardconvex curve, which behavior is very similar with the former concentrated solution[1].

SANS experiments were done by pressurizing at fixed temperatures. At 28°C below MT, the block copolymers underwent micellization at high pressure. At 40 and 50°C, which were close to and above MT, respectively, the micelles were formed at ambient pressure. By pressurzing, the micelles were destroyed at near 100MPa and the block copolymers were However, further pressurizdispersed. ing induced reentrant micellization at near 200MPa. Fig. 1 shows the schematic pictures of the same core-size-micelles at 50°C at low pressure (left) and high pressure (right) obtained by fitting the scattering curves with the use of Pedersen's micellar model[2]. The water volume fraction in the micellar core was larger at the high pressure than at the low pressure. This result indicates that hydrophobic interacion important to form micelles was weak at high pressures and another competing interaction might be dominant at high pressures.

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Fig. 1. Schematic picture of the same-core-size micelles at 50°C. (left) at low pressure and (right) at high pressure.

Rheo-SANS behavior of Entangled Polymer Chains with Local Label Under Fast Shear Flow

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The shear-thinning of entangled polymer chains has been attributed to significant orientation of the entanglement segments under the shear flow. However, the chain conformation itself has been hardly examined under the shear flow, and no information is available for the orientation distribution along the chain backbone.

For this problem, we have examined the rheo-SANS behavior for polybutadiene (PB) samples dissolved in a deuterated oligomeric butadiene (oB) at the volume fraction of 0.28. The measurement was conducted with the SANS-U spectrometer at the Neutron Scattering Laboratory, Institute for Solid State Physics, University of Tokyo. The incident beam diameter was 0.3 cm, and the sample-to-detector distance was set at 4.0 m.

The PB samples were composed of deuterated and protonated blocks (dPB and hPB) and had almost identical molecular weights of the whole chain (M~120K) and the hPB block (minor block; M[hPB] The location of the hPB block ~ 20K). was different for the samples. The PB1 and PB2 samples had the hPB block at the end and middle of the chain, respectively. The hPB blocks were dilute and not overlapping with each other in the PB/oB systems. The SANS data detected the conformation of these hPB blocks that corresponded to two entanglement segments in the system (M[hPB]/Me[~]2).

The SANS profile was azimuthally symmetric at equilibrium but became a little anisotropic under fast shear flow in the non-Newtonian regime. As an example of such anisotropic profiles, Figure 1 shows double-logarithmic plots of the scattering intensity I(q) for the PB1/oB and PB2/oB systems normalized by the volume fraction and molar volume of the hPB block against the scattering vector q normalized by the radius of gyration Rg of this block at equilibrium. The filled and unfilled circles indicate the intensity sector-averaged over 15 deg in the vorticity and velocity directions, respectively. The solid curves indicate the Debye function that well described the data at equilibrium. For clarity of the figure, the plots and Debye function for the PB2/oB system are shifted downward.

For the data shown in Figure 1, the shear rate normalized by the linear viscoelastic relaxation time was kr = 24 (for PB1/oB) and 29 (for PB2/oB). At these shear rates, the viscosity of the systems was significantly smaller than the zero-shear viscosity (by a factor of ~ 40). Despite this nonlinearity, the I(q) data just moderately deviate from the Debye function (describing the data at equilibrium); cf. Figure 1. The anisotropy is larger for the PB2 chain having the hPB block at the middle than the PB1 chain having the hPB block at the end, but this difference due to the location of the hPB block is not very prominent.

These SANS data allow us to examine the current molecular picture for the entangled chains under fast shear flow. This picture assumes that successive entanglement segments are not orientationally correlated and behave as independent stresssustaining units even under fast flow. Under this assumption, a ratio of the hPB block size in the velocity direction to that in the vorticity direction was estimated from the nonlinear viscoelastic data. This ratio, ~ 1.4, was too large compared to the ratio estimated from the SANS data in Figure 1. Thus, the above assumption fails for the entangled chains under fast flow. The successive entanglement segments appear to have the orientational correlation possibly due to the dynamic tube dilation mechanism.



Fig. 1. Normalized I(q) data of the PB1/oB and PB2/oB systems at 25C in the vorticity and velocity directions (filled and unfilled symbols). The solid curves indicate the Debye function describing the data at equilibrium.

Dynamics of aromatic molecules entrapped in the clathrate phase of syndiotactic polystyrene

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Syndiotactic polystyrene (sPS) is a relatively new commodity polymer. It exhibits a variety of crystalline states depending on crystallization conditions, alpha and beta of TT conformation and gamma, delta and empty-delta of TTGG conformation. The appearance of the delta form is one of the important characteristics of sPS. It is a clathrate crystalline phase with small molecules, such as chloroform, benzene, toluene, xylene and so forth. The guest molecules are included in the cavities between polymer sheets of TTGG helical conformation. In this study we have investigated the dynamical properties of two kinds of stored aromatic compounds, benzene and p-xylene.

In order to reduce the contribution of sPS matrix to quasielastic neutron spectra (QNS), hydrogenated guest molecule were incorporated into the cavities of sPS matrices prepared from fully deuterated styrene. All QNS spectra were measured with AGNES spectrometer of JRR3M (Tokai).

Figure 1 shows QNS spectra of the two sPS clathrates. As for the sPS(benzene) clathrate, the Q dependence of EISF suggests the rotational diffusion of benzene by jump motions among six sites around a circle with a radius of about 2.5A, i.e., the jump motion around the six-fold rotation axis. p-Xylene shows a significant Q dependence of EISF together with a widely spread QNS components in the whole temperature region between 300 and 40 K. The Q dependence of p-xylene is much larger than that of benzene even at 100K, which cannot be attributed only to the rotational diffusion of methyl hydrogen atom by the three-site jump motion, although the methyl hydrogen atoms are the major scattering source in p-xylene. These characteristics of the QNS spectra indicates the existence of fast and large motion of p-xylene molecules as a whole, probably a large librational motion of p-xylene.



Fig. 1. Figure 1. QNS spectra of syndiotactic polystyrene clathrate phase containing benzene at 200K (a) p-xylene at 200K and 100K (b) and (c).

Mobility of Polymer Chain in Clathrate Phase of Syndiotactic Polystyrene

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Syndiotactic polystyrene (sPS) is widely known to show interesting crystalline phases. One of them is characterized by the clathrate formation with various organic molecules, so called delta-form crystal. Recently, we reported that a wide range of compounds can be inserted as a guest molecules by guest exchange phenomenon. It became apparant that relatively large molecules can be easily incoporated into the cavity espesilly with a solution mixed with penetrable solvents. We thought that the plasticizing effects the acceleration of guest exchange. We aimed to produce a new kind of polymer based functional materials and thought it is worth investigating the chain dynamics in amorphous region of sPS delta-phase.

We performed quasielastic scattering measurements on the inelastic neutron spectrometer, AGNES, installed at the JRR-3M reactor. The sPS sample was supplied by Idemitsu Petrochemical Co., Ltd. The delta-phase samples of sPS were obtained by exposing amorphous sPS films, which were previously prepared by quenching the melt in ice-water, to fully deuterated toluene vapor at 300K for 3days. After exposure process, the sPS delta-phase samples were dried in a vacuum for 8h to eliminate excess toluene from amorphous region. The delta-phase samples were processed by treatment with boiling acetone for 8h followed by washing with methanol to prepare the delta_empty-phase sample. The delta-phase samples were inserted into cells in two ways. First, the cell was filled with delta-phase sample and a little amount of dueterated toluene providing saturated toluene vapor as a plasticizer, denoted "wet". Second, the cell was filled with delta-phase films only, denoted "dry". We calculate the mean square displacement $\langle U2 \rangle$ from the momentum transfer Q dependence of the elastic scattering for each measurement. The $\langle U2 \rangle$ s of "wet" is larger than others especially above room temperature. The quasielastic scattering components of "wet" are also larger than others especially above room temperature. On the other hand, at a very low temperature, there are few differnces between $\langle U2 \rangle$ s and/or S(Q,E) spectra of each samples.

We have been trying to analyse the data to obtain details.



Fig. 1. Figure 1. Temperature dependence of S(Q,w) of "wet" sPS delta-phase.

Sol-gel transition of methylated polyrotaxane

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Recently, we prepared successfully a new type of polyrotaxane having hydrophobically modified α -cyclodextrin (CD). Methylated polyrotaxanes, which are substituted the hydroxyl groups on CD with methyl groups, showed thermosensitive sol-gel transition. In this experiment, we carried out small-angle neutron scattering (SANS) measurement in order to investigate the structure change as a function of temperature.

Polyrotaxane prepared was from poly(ethylene glycol) (PEG) and CD. The molecular weight of PEG was 3.5×10^4 . The filling ratio of CD was 27%. The hydroxyl groups on CD molecules were substituted by methyl groups using sodium hydrate and methyl iodide. The degree of methylation was 60% (M60). SANS experiments were carried out at the SANS-U spectrometer. The sample-to-detector distance was 2 and 8m. The temperature was varied from 20 to 80°C. The methylated polyrotaxane was dissolved in D_2O .

Fig. 1 shows temperature dependence of SANS intensity function, I(q), for M60. I(q)s increase with increasing temperature. In particular, I(q) drastically upturns at 60°C, which agreed well with the macroscopic observation of sol-gel transition. The variation of these scattering profiles is similar to a sol-gel transition of block copolymer solution by temperatureinduced microphase separation.

In low temperatures, I(q)s decrease monotonically as a function of q. This means that the polymer solution was homogeneous. We estimated the correlation length, ξ , by using the Ornstein-Zernike function for semi-dilute polymer solutions. The obtained ξ was about 17Å. Above the gelation temperatures, T_{gel} , I(q) shows not only a rapid increase of intensity but also a characteristic shoulder about 0.015\AA^{-1} . The inset in Fig.1 shows the so-called Kratky plot (i.e., $q^2I(q)$ vs q) for $T > T_{\text{gel}}$. In the gel state, the Kratky plots show a single peak. In order to elucidate the gel structure, we evaluated the characteristic size of inhomogeneities in the gel sate using the following equation,

$$I(q) = I(0) \exp(-R_{\rm G}^2 q^2)$$
 (1)

where $R_{\rm G}$ is the radius of gyration, I(0) is zero-scattering intensity. In this case, $R_{\rm G}$ means the size of the hydrophobic domains. The obtained $R_{\rm G}$ was about 160Å.

The following facts were disclosed. CD molecules on PEG are dispersed homogeneously below T_{gel} . On the other hand, with increasing temperature, CD molecules are aggregated each other due to hydrophobic interaction of methyl groups on CD. These aggregations play as a role of physical cross-linking points[1, 2].

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Fig. 1. Temperature dependence of the scattering intensity, I(q) for M60. The inset shows Kratky plots at $T > T_{gel}$.

Neutron spin echo studies on bending modulus of bilayer membrane in DGI/SDS/D2O system

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Dynamics and bending modulus of ndodecylglyceryl itaconate (DGI) bilayer membrane in a DGI/SDS/D2O system were studied. The DGI membrane shows iridescent color from blue to red because of Bragg diffraction when the distance between the DGI membrane reach the order of 200 nanometer by the change in the concentrations of DGI and SDS. However, the reason why the distance is extended so large is still unclear. In order to make clear this, we investigated dynamics and bending modulus of DGI membrane using a neutron spin echo spectrometer and analyzed them along the Zilman and Granek model (Phys. Rev. Lett. 77, 4788 (1996)).

In our experiment, DGI concentration was fixed at 1.6 wt % (44 mmol 1^{-1}) and SDS concentration was changed and temperature was fixed at 56 - 58 °C. At lower concentration of SDS the color is red, however, the color shifts to blue with an increase of SDS concentration. We adopted red sample (No. 1, [SDS] = 4×10^{-4} wt % SDS, 1.1×10^{-2} mmol l^{-1}) and green one (No. 9, [SDS] = 2.7×10^{-3} wt %, 7.43×10^{-2} mmol 1^{-1}), where the interplanar distance *d* was determined to be 240 nm and 220 nm for No. 1 and 9 samples, respectively.

1 and 2 show dependence Figs. intermediate correlation function of I(Q,t)/I(Q,0) on Fourier time t for 1 and 9 samples, respectively. No. The dotted lines are fitting lines by $I(Q,t)/I(Q,0) \propto exp[-(\Gamma_{O}t)^{2/3}]$, which is obtained from Zilman and Granek model, where Γ is coefficient containing some parameters. It is expected that data scattering of No. 9 samples is arising from the beam line condition, not originated from sample.

Figs. 3 and 4 indicate the dependence of Γ_Q on wave number *Q*. According

to the model, $\Gamma_Q \propto AQ^3$, where $A_Q = 0.0025\gamma k_B T^{3/2} \kappa^{-1/2} \eta^{-1}$, γ is almost constant (~ 1), κ is the bending modulus, η is the viscosity of fluid. The solid lines are fitting results on the basis of the model and the obtained indexes are 3.19 and 2.97 for No. 1 and 9 samples, respectively. The values are good agreement with that of the model. Next, from the obtained A, $\gamma = 1$, and $\eta =$ viscosity of bulk water at the absolute temperature T, we obtained $\kappa = 6.7k_BT$ and $34.3k_BT$ for No.1 and 9 samples.

The experimental results can be thus described by the model. Let's discuss the reason why the addition of SDS reduce *d*. The obtained κ rapidly increases from $6.7k_{\rm B}T$ and $34.3k_{\rm B}T$. This may be explained by following scenario. In the solution, dissociated SDS molecules are adsorbed on the surface of bilayer membrane because of hydrophilic interaction and then the charge density on the surface is increased. At lower SDS concentration, the membrane is flexible and can fluctuate. However, with the addition of SDS the membrane becomes stiff and the amplitude of fluctuation becomes small. Thus, the interplanar distance is decreased. In order to understand full scenario, further experiment is required.



Figure 4: Dependence of I₀ on *Q* for N solid line shows the fitting result.

Fig. 1.

Structural study for Thermoplastic Elastomer Consist of Carboxyl-terminated Telechelic Poly(ethylene-butylene) and Stearylamine

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1. Introduction

Carboxyl-terminated telechelic poly(ethyrene-butylene) (CTPEB) and stearylamine (Octadecylamine; ODA) mixtures show a very interesting rheological properties which is quite similar to thermoplastic elastomers as mentioned below. To understand the origin of the rheological properties, it is essential to analyze the structure. Since the main repeating units of CTPEB and ODA are CH2, such study can be performed only by means of SANS measurements using deuterium-labeled samples. Unfortunately, we could not have beam time for this study but preliminary measurements are carried out during IRT work. Here we briefly report the results with rheological properties and other characteristics of the system.

2. Preparation, characterization and rheological properties of the sample

The number averaged molecular weight of CTPEB was 1400. CTPEB and ODA are dissolved in toluene and they are mixed at a condition the moles of carboxyl and amine residues become the same, then the solvent was removed in a vacuum oven. The sample thus prepared had a thermal transition peak in DSC thermogram at around 310 k. IR spectroscopy and WAXD analysis did not show any evidence of formation of large ionic complex but existence of small amount of crystalline of stearylamine at low temperature and its disappearance at elevated temperature.

Dynamic viscoelastic measurements were carried out in a temperature range of 283 ? 343 k. At low temperatures, elastomeric behavior was observed in full range of tested frequency (0.1 ? 100 rad/sec). That is, storage moduli G ' were always higher than loss moduli G " and G' was almost constant at the order of 0.5 MPa. On the other hand, liquid like behavior similar to the behavior of pure telechelic polymer was observed at elevated temperature. Stress-strain curves obtained at 298 k with different shear rates showed that non-linear behavior starts at around 1 % strain and the maximum of stress is observed at around 100 % strain. Thus, dynamic viscoelastic properties of this system in linear region are similar to thermoplastic elastomers; that is, elastic at low temperature and liquid like at elevated temperature. However, it is a very fragile elastomer.

3. SANS measurements

Deutrated CTAB was prepared by adition reaction of deuterium gas to carboxylterminated polybutadiene. The SANS measurements are performed by SANS-U spectrometer at the Neutron Scattering Laboratory of the ISSP, The University of Tokyo, established at C1-2 beam line of JRR3M in JAERI (Tokai), Ibaraki, Japan. The wavelength and beam size of incident neutrons was 0.7 nm and 3 mm?, respectively. The temperature were 298 (elastic state) and to 338 k (liquid-like state).

The data at high q are almost the same irrespective of temperature. The data at low q become higher at the lower temperature, while it dropped to background level at the higher. At the lower temperature, there existed a small shoulder at around q =1.2 (1/nm), which is close to the peak position for aluminum tri-stealyrate/decalin system studied previously. Note that aluminum tri-stealyrate/decalin system show gel-like behaviors and the peak position is very close to that of crystalline of stealyrate derivatives. Thus we speculate that stealyrate residues in CTPRB/ODA still have ordered structure inside the networked structure, though the regularity is much lower than that in the crystals. To clarify the structure, further works are definitely needed.

Thermal transition of viscoelasticity and association structure of small molecule gelator with metal ions

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1. Introduction

It is known that some groups of small molecules associate with each other to form a large size of aggregate in solution state. Such solutions show some specific viscoelasticities such as gelation and large viscosity. Among such small molecules, small molecule galator containing metal ions is one of major interesting groups. We investigated such small molecule gelator and found that some of them showed thermal transition on viscoelstic properties, such as complexes of alkyl triazine and platinum or copper and so on. We preliminary found some of the small molecule gelators with metals showed a heat-set type of thermal gel-transition. In this study, we investigated thermal transition of viscoelsticity and association structure of such small molecule gelators containing metal ions. 2. Rheological properties of the samples

We prepared complexes of alkyl triazine and metals such as platinum and copper with the molar ratio of 3:1 in tetrachlorocarbon, chloroform and dichloromethane. These complexes showed highly viscous property at room temperature. When the solution of platinum complex was heated to 50oC, the viscous solutions changed into gels even when their concentration was below 1wt%. Dynamic viscoelstic measurements on these solutions showed that, at higher temperature, the storage modulus G' was almost independent of angular frequency and almost one order higher than loss moduls G", which confirmed that the sample was gel in this state. On the other hand, at lower temperature regions, G" became higher than G " for low angular frequency regions. Creep and creep recovery measurement confirmed flow property of the samples. The thermal transition was found to occur between 30oC and 50oC.

Furthermore, the transition was found to be reversible.

3. SANS meaturements

SANS measurements were carried out by SANS-U spectrometer at the Neutron Scattering Laboratory of the ISSP, The University of Tokyo, established at C1-2 beam line of JRR3M in JAERI (Tokai), Ibaraki, Japan. The wave length and beam size of incident neutrons was 0.7 nm and 3mm, respectively. The temperature was 25oC. Tetrachloromethane and deutrated chloroform, dichloroethane and decaline were used as solvents.

The atom of chlorine is know to have large absorption property of neutron. The solvents used in this study contained chlorine atoms, so that it needed to spend long time to carry out scattering measurements. For tetrachloromethane solutions, we must have spent more than ten hours on one shot measurements and could not have enough high contrast data to analyze the scattering profile to manifest the structure after substruction of background scattering. As for deutrated dichloroethane, we can meatured scattering profile by several hours measurement for one shot. However, as well known, its boiling point is not high enough to analyze the thermal transition of the gels at high temperature exceeding 50oC. In this study, we found that deuterated chloroform can be used to measure for the thermal transition of association structure when we spend at least several hours on one shot measurement. From the measurement of the deuterated chloroform sample, the gelator formed one dimensional aggregate with diameter around 3nm at room temperature. In this study, we could not measure at the other temperatures. However, it is found that further measurements must manifest details of the

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thermal structural change of the metal containing small molecule gelator.

Structure Analysis of Silicon Nanosheets Synthesized from Layered Compounds

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We have recently synthesized a new material of "silicon nanosheet", which is a monolayer of silicon atoms forming a flexible two-dimensional crystalline structure with a thickness around 1 nm and a lateral size of sub-micrometer.[1] Since silicon is one of the most important elements in the modern technology and the two-dimensional structure induces attractive properties from quantum size effects, the silicon nanosheets are very promising for various applications. Structures of the nanosheets have been studied by transmission electron microscope (TEM) and atomic force microscopy (AFM). Although TEM and AFM are useful for the structure analysis of the nanosheets on grids and substrates, they can not apply for those in dispersions. Thus, measurements of smallangle neutron scattering (SANS) are employed to evaluate the structures of the silicon nanosheets in a dispersion.

SANS was measured for a hexane dispersion of the silicon nanosheets in concentration of 1 wt%. Deuterated hexane is used to reduce the background from incoherent scattering and to enhance the contrast against neutrons. The silicon nanosheets were synthesize by exfoliating layered polysilane (Si₆H₆) by 1-hexene with a catalyst under high temperature, where the hexcyl groups are considered to be grafted onto silicon monolayers. The SANS measurements were performed at SANS-U in JRR-3M (Tokai, Japan). The wavelength was 7 Å and the sample-todetector distances were chosen to be 1, 2 and 8 m.

Figure 1 shows a SANS profile in loglog plot obtained from a dispersion of the silicon nanosheets. The profile presents a straight line in a *q* range of q < 0.2 Å⁻¹. The slope of -1.6 indicates a fractal structure, which is smaller than -1 for thin rods and larger than -2 for thin disks in dimension. At $q \sim 0.2$ Å⁻¹ the line bends down. It is evaluated from this crossover point that the silicon nanosheets have a thickness of about 30 Å (= $2\pi/0.2$ Å⁻¹). The size of the nanosheets can be estimated to be over 600 Å since the straight line hold at least q=0.01 Å⁻¹. The thickness and size are consistent of the results of TEM and AFM, although the fractal property is unexpected.

It would be necessary to confirm this interesting structure of the silicon nanosheets by investigating more samples with various methods. Dispersions prepared in different synthesis condition will be the next target for SANS experiments.

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Fig. 1. SANS profile of silicon nanosheets in *d*-hexane. A straight line with a slope of -1.6 is overlayed.

Mesoscopic structure in near-critical mixtures of D₂O and 3-methylpyridine with salts

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Solvation effects on phase separations associated with critical phenomena have very much interested many researchers not only in the field of chemistry but also of physics. A large number of papers have been devoted on this problem from theoretical and experimental approaches. One of the most well-known system is an alcohol and water mixture. Addition of small amout of salt induces interesting behavior such as the reentrant phase separation phenomenon. By the solvation effects of ions, the clustering of polar molecules occurs and could be the origin of these behaviors.

The 3-methylpyridine (3MP) and water are known to mix uniformly at room temperature and separate into two phases with increasing temperature, and critical phenomena due to the density fluctuation could be observed near the critical point. The addition of salts, such as NaBr, results in the decrease of the critical temperature and the reentrant phase separation behavior. Jacob et al. have already investigated this behavior mainly by DLS [1] and SAXS[2], and showed that clustering of water molecules around ions is induced and the critical crossover behavior from meanfiled to 3D-Ising is observed because the interaction responsible to the phase separation is more long-ranged due to the clustering.

Theoretically, Onuki and Kitamura considered the solvation effects in near-critical binary mixtures. [3] They applied a Ginzburg-Landau theory to the density fluctuation of ciritcal mixtures with salts, and showed that the concentration has a longranged Ornstein-Zernike tail representing strong critical electrostriction with approaching the critical point. As a result, a drastic shift of the critical temperature and the formation of large scale clusters will arise due to strong coupling of the critical density fluctuation and the ions. This theory can give a unified understanding of the effects of salts to the phase separation behavior associated with critical phenomena from the viewpoint of the statistical physics.

In this viwpoint, we have measured the density fluctuation near the critical temperature of the binary and the ternary mixtures of 3MP, deuterated water with and without salts by SANS. The result of the mixture without salt indicates that the critical phenomena belong to the standard universality class for a low-molecular weight binary solution; the SANS profiles are explained by the Ornstein-Zernike function and the critical increases of the osmotic compressibility and the correlation length could be explained with the critical index of $\gamma = 1.26$ and $\nu = 0.63$ (3D-Ising behavior). On the other hand, the SANS profiles from the ternary mixtures could not be explained with the Ornstein- Zernike function. In order to analyze the data, we assumed spherical shape clusters exist even in one phase region. Thus, we tried to apply the scattering function as follows,

$$I(Q) = \frac{I_0}{1 + \xi^2 Q^2} + C \int^{\infty} 0f(R) |F(Q, R)|^2 dR,$$
(1)

where

$$f(R) = \left(\frac{Z+1}{R_m}\right)^{Z+1} R^Z \exp\left[-\left(\frac{Z+1}{R_m}\right)R\right] / \Gamma(Z)$$

where the first term of the first equation corresponds to the density fluctuation which is identical with the Ornstein-Zernike function and the second term comes from the form factor from spherical clusters with Schultz size distribution. *R* is a radius of cluster, *Z* is a width parameter, R_m is a mean radius of cluster, Γ is gamma function, and *C* is a constant.

Figure 1 shows the SANS profile of $3MP/D_2O$ with small amount of KCl. These profiles are well explained with the above function, which means that the mesoscopic size cluster exists in the present system. Temperature dependences of the osmotic compressibility, I_0 , and the correlation length, ξ , follow the 3D-Ising critical behavior.

The estimated cluster size, R_m , becomes larger with approaching the critical point. This evidence indicates that the mesoscopic size cluster is formed near the critical point and their size increases with approaching the critical point. These behaviors were also observed in other ternary mixtures with NaCl and MgSO4 [4]. These are the first evidence that the coupling of the solvation effect and the critical density fluctuation induces mesoscopic scale clusters.

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Fig. 1. The upper figure indicates the SANS profiles near the critical point. These profiles are fitted with a sum of the Ornstein-Zernike function and the scattering from spherical clusters indicated in the lower figure.

The "swollen phase" and the "anomalous swelling" in DPPC aqueous solution with ethanol

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Lipid bilayers are investigated by many researchers in these decades as model biological membranes not only from a viewpoint of biology but also of physics. They exhibit a richness of structures and phase equilibria depending on their environmental conditions such as water content, ionic strength, temperature, pressure, etc. A fluid lamellar phase (liquid-crystalline L_{α} phase) is a basic structure of biological membranes that appears at higher temperature. In this phase, bilayers are regularly stacked and flat on average, forming multilamellar vesicles. With decreasing temperature, several thermotropic phase transitions have been observed; a " main transition" from the liquidcrystalline phase to a gel (P'_{β}) phase and a "pre-transition" from the P'_{β} to another gel (L'_{β}) phase. In these gel phases, the hydrophobic tails of lipid molecules are extended and ordered, whereas the tails are conformationally disordered in the liquidcrystalline phase. In the middle-temperature P'_{β} phase, a twodimensional lattice structure is formed in which the lipid bilayers are distorted by a periodic ripple in the plane of lamellae. Recently, the authors showed the existence of new "swollen phase", in which the thickness of lipid bilayers is almost the same as in the gel phases and only the thickness of the water layer is larger than the other phases, is confirmed between the L_{α} phase and the $L_{\beta I}$ phase. [1] This phase is induced only by increasing pressure (without adding ethanol) and only by adding ethanol (without increasing pressure). The nature of this phase is similar to the anomalous swelling observed between the liquid crystalline phase and the ripple gel phase. [2]

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Fig. 1. The temperature dependence of the decay rate of the intermediate correlation function observed by NSE.

In-situ and Real-time Observation of Simultaneous Living Anionic Copolymerization Process and Polymerization-Induced Self-Assembly by SANS, UV-vis, GPC and NMR

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We proceeded a typical simultaneous living anionic polymerization of isoprene (I) and styrene- d_8 (S) in benzene- d_6 as a solvent, with sec-buthyllithium as an initiator, into a block copolymer polyisoprene- β polystyrene- d_8 .¹⁾ The difference of reactivity between two monomers produced the block copolymer. A specially designed combination of four techniques, including time-resolved small angle neutron scattering (SANS), UVvis spectroscopy, gel permission chromatography (GPC) and nuclear magnetic resonance (NMR) were employed in a single batch, which enabled us to observe the real-time polymerization process and the polymerization-induced self-assembling structures during the reaction. Our results revealed three time regions, as shown in Fig.1. (I) Region 1: On one hand, the intensity of the SANS profiles keeps as a constant and no scattering peak appears, however, the molecular weight keeps increasing, it indicates that mainly homopolymerization is going on. On the other hand, UV absorbance at 450 nm, which is only sensitive to polystyryllithium living end, does not change with time, indicating that polyisoprenyllithium is dominant but that polystyryllithium is not. Therefore, in region 1, mostly polyisoprene blocks are growing. (II) Region 2: UV absorbance at 450 nm increases slowly, revealing that polystyryllithium is generated slowly with time. A broad peak shows up on the SANS profile, and the peak intensity is increasing slowly, which means that some PS segments are formed. In addition, the molecular weight of the polymer is increasing slowly. All the data demonstrates that the living chain ends start to gradually change from isoprenyllithium to styryllithium. Further NMR analysis offers reliable monomer conversions

of both isoprene and styrene. The tapered structures are confirmed. (III) Region 3: All of UV absorbance, peak intensity of SANS profile and molecular weight increase significantly, denoting that PS blocks are growing rapidly. With the volume fraction of a PS block increases, polymerization-induced microphase separation is possibly occurring. Time-resolved SANS enables us to follow the morphology change as shown in Figure 2.



Figure 1: Three time regions defined by SANS, UV-vis and GPC.



Figure 2: SANS profiles in Region 3.

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原子炉:JRR-3 装置:SANS-J(C3-2) 分野:中性子散乱(高分子)

In Situ Observation of the Formation of Actin and Polycation Complexes

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Actin is one of the most abundant cytoskeleton proteins in eucaryotic cell. They play a crucial role in cell motility by polymerizing monomeric globular G-actin into polymeric filamentous actin (F-actin). With actin-binding proteins (ABPs), they form higher order structures such as linear bundles, two-dimensional networks and threedimensional gels. It has been considered that these structures are controlled by ABPs. However, a recent study has shown that the only one kind of artificial cationic polymer can form variety of structures depending its concentration and salt concentration.¹⁾ This system is a good model to elucidate the mechanism of regulation of actin and ABPs complex structure. Based on these backgrounds, we have investigated the effects of salt concentration on the stability and structure of actin-polycation complexes by using a small angle neutron scattering (SANS) technique.

The actin was extracted from the adductor muscle of scallops by the method of Spudich and as a model of ABPs we used an artificial cationic polymer PDMAPAA-Q. In Fig.1 we show SANS profiles from the actin and PDMAPAA-Q complexes for various KCl concentration, where the concentration of actin and polymer are kept constant. At low concentration of KCl, F-actin forms bundle structure as shown by one distinct peak at q = 0.08 $Å^{-1}$. The increase of KCl brings the peak position to lower q and sharpens its peak. By the further addition of KCl, the SANS profiles changed dramatically at KCl = 0.35 M, which means that the bundle structure disassemble to the native filamentous actin. From the first peak we estimated the repeat distance of F-actin inside the bundle d and peak width which is the measure of the orderliness of the actin alignment(Fig.2). Our result shows that the slight fluctuation of salt concentration brings dramatic change of the complex structures, which is important to regulate the motility of cell.



Figure 1: SANS profiles from the actin and PDMAPAA-Q complexes for various KCl concentration.



Figure 2: Repeat distance of actins inside bundles and the width of the first peak as a function of KCl concentration.

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原子炉:JRR-3 装置:SANS-J(C3-2) 分野:中性子散乱(高分子)

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1. 中性子散乱 6)生物

1. Neutron Scattering 6) Biology

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Diversity of protein dynamic structure observed by solution inelasitic neutron scatttering

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Protein expresses biological functions under physiological conditions, generally in aqueous solution. So far, inelastic neutron scattering experiments of biological specimens are performed with the hydrated powder state to avoid the strong scattering from solvent. However, solution inelastic neutron scattering experiments are emerging in the literature recently, which is still challenging. We performed solution scattering experiments with the AGNES using Staphylococcal nuclease (SNase). We measured the scatterings from both native state and heat-denatured state. We also measured the scattering from the truncated mutant. The truncated mutant is SNase without C-terminal 13 residues, which takes a compact denatured structure under a physiological condition. Figure shows the scattering profiles of these three samples. Heatdenatured state as well as the truncated mutant showed larger quasi-elastic scattering intensity than the folded state, while EISF significantly decreases with the heatdenaturation. The appearance of quasielasitc scattering indicates that the protein structure deviates dynamically within the observable time scale of a few tens ps. The difference in EISF suggests that the heatdenatured state can take wider conformational space. These results indicated that the truncated mutant is dynamically different from the heat denatured state, although the truncated mutant takes a denaturedlike structure. The present preliminary data clearly show that the inelastic scattering study with solution sample is promising. The quantitative analysis of solution inelastic neutron scattering will make it possible to characterize the dynamical properties of proteins in natural condition.



Fig. 1. Solution inelastic neutron scattering spectra of SNase in three states, native, heat-denatured and truncated mutant.

Solvent effect on structure and dynamics of beta-lactoglobulin in alcohol-water mixtures

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The effect of alcohol on denaturation of protein is known in biophysics and biochemistry fields. Alcohols have a tendency to increase the content of α -helix structure in proteins. So far, the secondary structure of α -helix forming peptide and protein, Melittin and β -lactoglobulin (BLG), was investigated in aliphatic and fluorinated alcohols-water mixtures [1]. The denaturation effect of these alcohols changes according to the size and nature of the hydrophobic groups of the alcohols. However, an underlying mechanism in alcohol denaturation of proteins is still unclear. The investigation of configurations (size, shape and aggregation of proteins) and diffusive dynamics of proteins in alcohol-water mixture will help us to understand the mechanism of alcohol denaturation of the protein.

In the present study, small-angle neutron scattering (SANS) of BLG in ethanoland trifluoroethanol(TFE)-water mixtures in order to reveal the was measured solvent effect on three-dimensional structure and aggregation state of BLG. Neutron spin echo (NSE) of BLG in water was also measured to reveal the diffusive dynamics of BLG. To minimize the contribution of exchangeable hydrogen atoms of the protein, BLG powder was dissolved in D₂O and then was lyophilized. The dried BLG powder obtained was dissolved in ethanol-D₂O and TFE-D₂O mixtures. The SANS of BLG in both mixtures was measured at 298 K. Concentrations of BLG solutions were 5, 10, and 20 mg ml⁻¹ for each solvent. A sample was kept in a quartz cell of 2-mm path length. The cell was inserted into a temperature-controlled chamber. The distances between the sample and detector were 1 and 4 m, corresponding to Q of 0.007 - 0.3 Å⁻¹. Measurements were also made for background, solvent, and lupolen used

for intensity normalization. The NSE signal for an D₂O solution of BLG of 40 mg ml⁻¹ was measured at 298 K. A sample was kept in a quartz cell of 2-mm path length. The scattering vector Q covered was 0.055 - 0.12 Å⁻¹. The Fourier time was varied from 0.15 to 15 ns. The temperature of sample was controlled within \pm 0.3 °C with circulated water.

Figure 1 shows SANS profile of BLG in ethanol-D₂O mixture at various ethanol volume fractions. The peak corresponding to the correlation between proteins was observed at 0.08 $Å^{-1}$ in ethanol-D₂O mixture of 10 vol% ethanol. With increasing of ethanol fraction, the peak position does not change up to 30 volFor BLG in TFEwater mixtures, the position of the correlation peak between proteins drastically shifted to a small Q region at ~ 20 vol% of TFE. In analogy with the case of ethanolwater mixture, the specific TFE composition of the structural transition of BLG is consistent with that for solvent structure transition from the tetrahedral-like water clusters to the chain-like alcohol ones for TFE-water mixture. The NSE signal of BLG in D₂O could be simulated by the single exponential function. The relaxation time obtained at Q = 0.102 Å^{-1} was 13.1 ns. We will discuss the correlation between diffusion constant and three-dimensional structure of BLG obtained from SANS. The further analysis is in progress. [1] D. Hong, M. Hoshino, R. Kuboi, and Y. Goto, J. Am. Chem. Soc. 121, 8427 (1999). [2] M. Matsumoto, N. Nishi, T. Furusawa, M. Saita, T. Takamuku, M. Yamagami, and T. Yamaguchi, Bull. Chem. Soc. Jpn. 68, 1775 (1995).



Fig. 1. SANS profiles of BLG in ethanol-water mixtures at various ethanol volume fractions.

Small-Angle Neutron Scattering Study on Hydrated Short Lamellar Structure in Mammal's Skin Stratum Corneum

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INTRODUCTION

In mammals, the permeability barrier that restricts excess water loss is maintained by multilamellar structure membranes localized in the intercellular space of the stratum corneum (SC), the outmost layer of the epidermis. The multilamellar structures in SC are classified mainly into long and short lamellar structures with repeat distances of about 13 and about 6 nm, respectively. In certain species, however, the short lamellar structure is not observed by Xray diffraction. The problem whether both long and short lamellar structures exist universally in all mammal's SC remains unsolved. Ohta et al. [1] have proposed that the SC permeability barrier function depends mainly on the short lamellar structures. Thus, from the viewpoints of the barrier function, the universality of short lamellar structure existence is an important problem.

One of advantages of neutron scattering techniques as compared to X-ray techniques is that one can change contrast of samples by using isotope substances. It is believed that there are water layers in the short lamellar structures in SC. Thereby, it is expected that the contrast of SC sample can be enhanced by treating with D2O, and that, even in undetectable cases by X-ray techniques, the short lamellar structures can be clearly detected by using small-angle neutron scattering (SANS) techniques.

EXPERIMENTAL

The SC samples used in this study were prepared from three different animals, i.e., rat, mouse, and pig. According to the method reported in [1], SC was separated from a skin. All samples were dried initially and then soaked in 100% D2O. The water (D2O) contents of the samples were determined by measuring the weight. SANS measurements were performed with the SANS-U spectrometer, (C1-2, JRR3M in ISSP, Tokai, Univ. of Tokyo). The wavelength of the neutron beam was 0.7 nm and two different camera lengths (1m and 4m) were used.

RESULTS AND DISCUSSION

Figure 1 shows SANS profiles from pig SC sample containing 40% water (D2O). A weak but relatively sharp diffraction peak is observed around Q = 1.0 nm-1 from 25 oC to 45oC. Judging from the spacing, the peak corresponds to the short lamellar structure. For other animal samples, such peak was not observed. To get further detailed information on the short lamellar structure, we are planning to perform contrast variation experiments.

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Fig. 1. SANS profiles of pig SC sample.

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Analysis of F-actin dynamics

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Actin, highly ubiquitous protein in eukaryotic cells, plays crucial roles in various aspects of cell motility. The actin monomers (G-actin) polymerize into filamentous form (F-actin). This polymerization, controlled through interactions with various proteins, and flexibility of F-actin have been shown to be the key features in the functions of actin. It is therefore important to understand how the dynamics of actin at various levels, from the internal dynamics of Gactin to fluctuation of F-actin, are related to various functions of actin. Here, as one of the projects towards ultimate understanding of the dynamics of actin at various levels, we carried out neutron spin-echo (NSE) experiments on actin. NSE spectroscopy is a quasielastic neutron scattering technique that can study long range relaxation processes in a macromolecule on nano-sec timescales and nano-meter length scales.

Actin was purified from rabbit skeletal muscles. Actin was polymerized by adding KCl to form F-actin. In the preparation of G-actin, actin labelled by the fluorescent probe tetramethyl-rhodamine-5-maleimide was used to block polymerisation (Otterbein, Graceffa, and Dominguez, 2001). Solutions of G-actin and F-actin were prepared in D2O. The NSE measurements on these solutions were carried out on the NSE spectrometer, iNSE, run by the University of Tokyo instruments, installed at the guide hall of the research reactor, JRR-3M, Ibaraki, Japan. From the set-up of these NSE measurements, information on the dynamics of actin on timescales up to 15 nsec and on length scales from 5 to 15 nm should be obtained. Figure 1 shows the normalized intermediate scattering functions of G-actin and F-actin. The functions at several representative Qvalues were plotted against Fourier time.

Clear differences in the spectra between G-actin and F-actin were observed. While the normalized intermediate functions of G-actin show usual features that the decay of the functions could be fit with single exponentials, the rate of decay of those of F-actin appears very slow. This indicates that there is a large difference in translational diffusion between G-actin and F-actin. To make quantitative comparison of the dynamic behaviours of G-actin and F-actin, detailed analysis of these intermediate functions are currently underway.



Fig. 1. The normalized intermediate scattering functions of G-actin and F-actin.

Structural evolution of human α B-crystallin on UV irradiation

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Alpha-crystallin is a human lens protein which works as a chaperon to prevent from making aggregation of proteins in the lens. This protein is a water-soluble aggregate consisting of two kinds of polypeptides, α A-crystallin and α B-crystallin.

Under environmental stresses, α crystallin makes huge aggregation and then losses its chaperone activity. Therefore, the proteins in the lens also make huge aggregation and finally the lens has become opaque, namely a serious disease, *cataract*, has developed.

The trigger of the abnormal aggregation on α -crystallin is considered to be posttranslational modifications on the polypeptide such as deamidation, racemization and isomerization, truncation, phosphorylation, oxidation, an increase in intramolecular disulfide bonding and glycation. However, the abnormal aggregation process has not been clarified so far. Therefore, we have investigated the abnormal aggregation process of α -crystallin.

In order to reveal the abnormal aggregation process, we developed a UV irradiation system with which *in-situ* SANS observation can be performed. With the system, we observed the structural evolution of human recombinat α B-crystallin under UV irradiation with SANS-U spectrometer. The UV light had wavelength range with 280-360 nm (UV-B) and the SANS intensity was recorded every 30 minutes for 10 hours.

Figure 1 shows the evolution of SANS patterns of α B-crystallin under UV irradiation during 10 hours. The evolution was classified into three stages. In the first two hours (stage I), the SANS pattern was almost unchanged, where the radius of gy-

ration was around 55 Å. Stage I could be an incubation time prior to making the abnormal aggregation. In the next six hours (stage II), the scattering intensity is going to be centering. It means that α B-crystallin is making aggregation in stage II. In the final two hours (stage III), the SANS pattern was almost unchanged again, where the radius of gyration was around 70 Å.

The investigation of the relation between the chaperone activity and the structure in each stage is now in progress.



Fig. 1. Evolution of SANS patterns of α B-crystallin under UV irradiation. (a) Before UV irradiation, (b) after 2 hrs UV irradiation, (c) after 8 hrs UV irradiation and (d)after 10 hrs UV irradiation.

Defect Study of Protein Crystals by Neutron Topography

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In common crystals, the mosaic structure has two structure types that are a Frank network and a fine polygonization wall. Both of the structures are composed of dislocations. However, the mosaic structure of protein crystals has not been identified in terms of dislocation models yet. Thus, the characterization of defects, especially dislocations, in protein crystals is important for the understanding of their quality of crystals. The crystallization originating from dislocations has been investigated using atomic force microscopy (AFM). However, AFM is limited to only local observations of the crystal surface. It is desired that the distribution of dislocations in the whole crystal could be observed. Topographic techniques (X-ray topography and neutron topography) is one of the most powerful tools for characterization of dislocation in the crystal. Therefore, we have performed the application of X-ray topography to protein crystals¹⁾, and consequently, we have succeed in clear observations of the dislocation images in hen egg-white (HEW)lysozyme crystals $^{2)3)}$. On the other hand, the application of neutron topography to protein crystals has not been carried out so far. Especially, effect of water around dislocations can be observed only using neutron topography. Therefore, to obtain the interaction between intracrystalline water and dislocations in protein crystals, we tried to perform the application of neutron topography to lysozyme crystals.

The used orthorhombic HEW lysozyme crystals were grown by a liquid-liquid interfacial precipitation technique. To avoid the high background coming from the incoherent neutron scattering of hydrogen atoms, the crystallization experiments were carried out in D_2O solution. Neutron topography was carried out using LAUE on C2-3-3-4 at JRR- 3. The camera length was 21 cm. Topographs were recorded on a film instead of an imaging plate with exposure times of about 1 week.

Figure. 1 shows Laue topographs which were recorded with the incident beam almost parallel to the [110] crystallographic direction of orthorhombic HEW lysozyme crystal. This is the first photograph of neutron topography applied to protein crystals. It should be noticed that a topographic image corresponds to the shape of crystals of the lysozyme using Xray topography. In addition, this topographic contrast attributes to dislocations observed by X-ray topography. The photo showed the lack of image of the crystal in the lower part of the crystal. This means that the quality of crystals is not sufficient to take a clear image. More detail observation using more high quality crystals should be required to obtain the fine structures.



Figure 1: Topographic image of an orthorhombic HEW lysozyme crystal obtained using neutron topography.

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原子炉:JRR-3 装置:LAUE(T1-4-4,C2-3-3-4) 分野:中性子散乱(その他)

A Neutron Crystallographic Analysis of 2Zn-Insulin

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Insulin is one of most important and wellknown hormones. It is used as one of the main medical treatments for diabetes because it regulates glucose metabolism. A monomer of insulin has a mass of about 5700 Da, which is composed of two peptide chains; an Achain (21 amino acids) and a B-chain (with 30 amino acids). This protein is synthesized and stored in the pancreas as a hexamer with zinc ions and secreted from there in that configuration. A 2Zn insulin crystal used to collect neutron diffraction data was grown by a bach method, and the crystallization conditions are as follows: insulin (5 mg/mL), sodium citrate (50 mM), zinc sulfate (6 mM)and acetone (15 %). The obtained crystal has dimensions of $1.5 \times 1.5 \times 1.0 \text{ mm}^3$ (volume approximately 2.25 mm^3). The crystal was soaked in a supersaturated D_2O solution for one month. The neutron diffraction experiment was carried out at room temperature using the BIX-4 diffractmeter at port 1G-B in the reactor hall, JRR-3, of JAEA. The neutron wavelength used was 2.6 Å. The step scan method (with increments of 0.3°) was used for data collection. The neutron exposure time per frame was 2 hours, and 207 frames and 280 frames were obtained at different rotation axes. The HKL software package, DENZO and SCALEPACK were used for data processing and scaling. A total of 3,734 independent reflections were obtained with an overall R_{merge} of 8.7 % from 11,755 observed reflections. The completeness of the data set was 97.0 % in the 80 - 2.3 Å resolution range and 89.9 % for the outermost (2.3) - 2.38 Å) resolution shell. The structure refinement was carried out using the CNS set of program for reflections collected and graphics program was XtalView. The topology and parameter files for CNS had to be modified for neutron diffraction analysis to include hydrogen and deuterium atoms. The 2Zn insulin structure (PDB ID: 4INS) determined from X-ray data (resolution 1.5 Å) was used as an initial model. It was assumed that the hydrogen atoms bound to carbon atoms were not replaced by deuterium atoms. The hydrogen atoms bound to nitrogen and oxygen atoms were not included in the initial model, and all water molecules were excluded from the model. As the refinement proceeded, the positions of exchangeable hydrogen atoms could be identified using 2|Fo|-|Fc| and |Fo|-|Fc| nuclear density maps, and the current R-factor is 21.8 %, and free R is 30.1 % at resolution of 2.3 Å. The current 2|Fo|-|Fc| positive neutron density map of His10B is shown in Fig.1 Further refinement including water molecules is now under way.



Figure 1: His10B.

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原子炉:JRR-3 装置:BIX-4(1G-B) 分野:中性子散乱(生物)

The State of Cryptobiosis of Larvae of *Polypedilum Vandezplanki* Studied by Incoherent Inelastic Neutron Scattering

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Larvae of an African chironomid, Polypedilum vandezplanki live in temporal rock pools and they can stand complete desiccation in a cryptobiotic (ametabolic) state¹). One of the most characteristic phenomena is a remarkable accumulation of trehalose in the cryptobiotic larva. Slowly-dehydrated larva (slow sample) accumulated sufficient trehalose successfully entered the state of whereas quickly-dehydrated cryptobiosis, one (quick sample) with a small amount of trehalose failed to do. It is suggested that the vitrification of the trehalose is important for cryptobiosis. Generally glassy materials exhibits a boson peak, which is a broad peak found in the low-frequency region of inelastic neutron spectra, and a characteristic fast relaxation process in the quasi-elastic neutron scattering. This study aimed to examine the vitrified state in cryptobiosis by incoherent inelastic neutron scattering using slow and quick samples. The incoherent neutron inelastic scattering experiments were performed with the triple axis spectrometer, TAS-2, in the JRR-3 reactor in Tokai, which has an energy resolution of 0.7 meV. The energy range covered was from -2.0 to 10.0meV. The data were then collected from 100 K to 300 K. Figure 1 shows the inelastic neutron scattering spectrum of the slow and quick samples of Larvae of Polypedilum vandezplanki at 100 K and 300 K. At 100 K significant difference was not observed between the slow and quick samples, although it seems that the slow sample may have a small bump around 2-3 meV, boson peak. But to discuss this further it needs the higher statistic data. At 300 K a broardenings of the elastic peak due to the contribution of quasi-elastic scattering were observed for both samples, indicating the appearance of the relaxation processes. The difference of the neutron spectra at 300 K between the two samples was detectable. The quick sample has stronger quasi-elastic scattering than the slow one. This suggests that the relaxation process of the slow sample is inhibited and / or the timescales of the process is faster than quick one. These observations imply that the importance of the vitrification by the trehalose for the cryptobiosis mechanism of Larvae.



Figure 1: Inelastic neutron scattering spectra of the slow and quick samples of Larvae of *Polypedilum van- dezplanki* at 100 K and 300 K.

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Hydration Water Dynamics at Protein Dynamical Transition by Quasi-Elastic Neutron Scattering

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A protein dynamical transition around 180 ~ 240 K has been observed for the hydrated $protein^{1}$. It was reported for various proteins that their functions are suppressed due to the loss of unharmonic dynamics by dehydration or by cooling down below the transition temperature. It is essential to elucidate the role of water at the protein-water interface to understand protein dynamics and function properly. So far we found that the dynamical transition is observed only above the threshold hydration level: $h \sim 0.2$ (g H₂O/g protein). In this study, the hydration water dynamics were examined by quasi-elastic neutron scattering below and above the hydration level. The scattering from the hydration water on the protein can be selectively estimated by the subtraction of the scattering profile of a D_2O hydrated protein from that of a H₂O-hydrated protein. The neutron inelastic scattering experiments were performed with a triple axis spectrometer, LTAS, in the JRR-3 reactor in Tokai, which has an energy resolution of 100 μeV . The energy range covered was from -0.4 to 1.0 meV. Figure 1 shows the quasi-elastic neutron scattering spectrum of the hydration water and bulk water at 300 K. Bulk water has almost no elastic peak and strong quasielastic scattering, while the hydration water has a non-negligible elastic peak, indicating that the hydration water is confined on the protein surface. But the quiasi-elastic scattering profiles are different between two hydration levels, suggesting that the dynamical properties of the hydration water depend on the hydration level. The stronger quasielastic scattering observed above the threshold hydration level suggests that the hydration water has more diffusive motions than in the case of the lower hydration. It was reported that the relaxation time of the proteinwater hydrogen bond network is 18 ps at 300

 $K^{2)}$.

Therefore, we can conclude that the observed hydration water dynamics involves such a network relaxation. The dynamical coupling between hydration water and protein is essential for the protein dynamical transition.



Figure 1: Quiasi-elastic neutron scattering of protein hydration water at two hydration levels and bulk water. The scattering of Vanadium indicates the resolution function.

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原子炉:JRR-3 装置:LTAS(C2-1) 分野:中性子散乱(生物)

Neutron Diffraction Study of Porcine Pancreatic Elastase with Its Inhibitor

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Porcine pancreatic elastase (PPE) is a serine protease classified in the chymotrypsin family that is possibly the most destructive enzymes having the ability to degrade virtually all of the connective components in the body. Uncontrolled proteolytic degradation by pancreatic elastase (EC 3.4.21.36) causes the fatal disease pancreatitis. Inhibitor for PPE is typical subject of development by structure based drug design (SBDD) because some elastases have similar structures of active sites. Nevertheless, many inhibitors designed by SBDD using X-ray structures still have side effects. A more detailed structure including hydrogen and hydration information is useful to develop highly selective inhibitors. Neutron structure analysis is the only method to determine hydrogen and hydration of protein structures. Last fiscal year, we collected the 2.3 Åneutron data using a crystal with a size of $1.6 \text{ mm}^{3.1}$ Here we report the collection of higher resolution data using a larger crystal of PPE with its inhibitor.

A macro-seeding procedure was repeatedly performed during four months by adding the PPE-inhibitor complex in a deuterated buffer to a seed crystal. Finally, a seed crystal was grown to a size of 3.3 mm^3 . Diffraction data were collected at room temperature using a monochromatic neutron beam (λ = 2.9 Å) and recorded on a neutron imaging plate on BIX-3 diffractometer at JRR-3 in JAEA. Full data set from a rotation about two independent axes was merged to enhance completeness. A total rotation range of 166.8° was covered by 556 oscillation images with an exposure time of 4 h/image by a rotation angle of 0.3° . The data were processed with the programs DENZO and SCALEPACK. Full data set was integrated and scaled to 1.75 Åresolution. The num-

Table 1: Summary of refinment

| R_{cryst} | 0.237 |
|--------------------------------|-----------|
| R_{free} (5 % random) | 0.339 |
| No. of atoms | |
| total | $4,\!372$ |
| H and D | 2,271 |
| mean B value (Å ²) | 12.4 |
| r.m.s. deviations | |
| bond lengths (Å) | 0.012 |
| bond angles (°) | 4.5 |

ber of observed reflections was 69,089, which were merged into 21,103 unique reflections with an R_{merge} of 0.095 and a completeness of 91.9 %. Crystallographic refinement using by the program CNS is now in progress. The present model, including PPE, inhibitor, two ions (calcium and sulfate), and 238 deuterated waters, which were refined to a crystallographic *R*-factor of 23.7 % (free *R*-factor = 33.9 %) to 1.75 Å resolution. Refinement statistics are summarized in Table 1. Protonation of histidine at active site was clearly confirmed on nuclear densities (Fig.1).



Figure 1: Nuclear densities at active sites. light: 2Fo-Fc map $(+1\sigma)$, deep: Fo-Fc map $(+2\sigma)$.

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原子炉:JRR-3 装置:BIX-3(1G-A) 分野:中性子散乱(生物)

Single Crystal Neutron Structure Analysis of a [NiFe]hydrogenase Model Complex

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[NiFe]hydrogenase is a bacterial enzyme that catalyzes the activation of H₂ into two protons (H⁺) and two electrons (e^-). Many synthetic modeling efforts have been devoted to elucidating the core structure of the active form of the [NiFe]hydrogenase. A Ni(μ -S)₂(μ -H)Fe species is one of the candidates for the active form. However, ¹⁰M(μ -S)₂(μ -H)⁸M complexes [where ¹⁰M = group 10 metals (Ni, Pd and Pt) and ⁸M = group 8 metals (Fe, Ru and Os)] as models for the active form of the [NiFe]hydrogenase have not been reported yet.

Here, we report the successful determination of the crystal structure of Ni(μ -H)Ru complex [(Ni^{II}L)(H₂O)(μ -H)Ru^{II}(η^{6} -C₆Me₆)](NO₃) {[2](NO₃)}, where L = N,N'-dimethyl-N,N'-bis(2-mercaptoethyl)-1,3-propanediamine by single crystal neutron diffraction.

We obtained dark-red crystals of $[2](NO_3)$ crystals by the reaction of NiRu aqua complex $[(Ni^{II} L)Ru^{II}(H_2O)(\eta^6-C_6Me_6)](NO_3)_2$ $\{[1](NO_3)_2\}$ with H₂ in water under ambient comditions $(20^{\circ}C \text{ and } 0.1 \text{ MPa})(\text{Fig.1}).$ Since this reaction is similar to the enzymatic reaction of [NiFe] hydrogenase, $[2](NO_3)$ is thought to be a model complex of [NiFe]hydrogenase. A single crystal neutron diffraction measurement of $[2](NO_3)$ was carried out using a $3.0 \times 2.0 \times 0.2 \text{ mm}^3$ crystal with the BIX-3 diffractometer at the JRR-3 reactor in JAEA. The measurement was performed using an incident neutron beam of 1.51 Å wavelength for 8 days at room temperature. Finally, 9451 reflections including 3852 unique reflections were observed. For the structure determination, the positions of hydrogen atoms were determined from a differential Fourier map and those of all atoms except a nitrate ion and a solvent water were refined independently. A nitrate ion and solvent water were refined with a rigid model. As a result of the structure analysis, we successfully the observed a negative peak which indicates existance of H between Ni and Ru (Fig. 2). This result clearly shows that [2](NO₃) has a Ni(μ -H)Ru structure, and strongly suggests that the active form of the [NiFe]hydrogenase has a Ni(μ -H)Fe core structure. A paper including this result has recently been published.¹)



Figure 1: Formation of a Ni(μ -H)Ru complex from the reaction of a NiRu aqua complex with H₂.



Figure 2: Fo-Fc map around the core structure of $[2](NO_3)$. The mesh between Ni1 and Ru1 indicates the existance of H.

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原子炉:JRR-3 装置:BIX-3(1G-A) 分野:中性子散乱(生物)

Contrast Variation Measurements of Hen Egg White Lysozyme Amyloid Protofilaments

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Amyloid fibrils are filamentous protein aggregates found in a wide variety of proteins including disease-related proteins. An understanding the mechanism of the amyloid fibril formation is not only important for the development of therapeutic strategies against amyloid diseases but also of considerable help to gain an insight into the generic properties of proteins related to the mechanisms of folding and stability. It was found recently that hen egg white lysozyme (HEWL) forms the amyloid fibrils in a highly concentrated ethanol solution¹⁾. The HEWL-waterethanol system is suitable to study the general mechanism of the amyloid fibril formation. From small-angle X-ray and neutron scattering (SAXS and SANS) measurements, we showed that a pathway of the amyloid fibril formation of HEWL consists of three stages; the formation of the dimers, the formation of the protofilaments, and the formation of the amyloid fibrils via a lateral association of the $protofilaments^{2,3}$.

In order to understand more in detail the mechanism by which the amyloid fibril formation occurs, it is important to obtain more detailed information on the structures of the dimers, the protofilaments, and the amyloid fibrils. In this study, as a first step towards this goal, we performed SANS experiments of the protofilaments of HEWL using the contrast variation technique. HEWL solutions, the concentration of HEWL in which was 2 mg/ml, were prepared in 90% ethanol, the condition under which the protofilaments were formed, in various fractions of the deuterated solvent. SANS curves of these solutions of HEWL were measured with SANS-J at the guide hall of the reactor JRR-3 in JAEA. The cross-sectional Guinier analysis of the curves obtained was done to estimate the cross-sectional radius of gyration at each con $\operatorname{trast.}$

The dependence of the cross-sectional radius of gyration on the contrast was analyzed by the Stuhrmann $\text{plot}^{4)}$, i.e., the plot of the square of the cross-sectional radius of gyration against a reciprocal of the contrast. Figure 1 shows the Stuhrmann plot of the protofilaments of HEWL. A negative slope of a linear fit to the data implies that a region of high density is located near the center of the filament.

Detailed analysis with aid of model calculation is currectly underway.



Figure 1: The Stuhrmann plot of the cross-section of the amyloid protofilament of HEWL.

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原子炉:JRR-3 装置:SANS-J(C3-2) 分野:中性子散乱(生物)

Hierarchical Structure for Red Blood Cells Observed by Small-Angle Neutron Scattering with Solvent Contrast Variation

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Red blood cells (RBCs) have a disk shape with an average thickness of 3 μ m and an average diameter of 10 μ m and are composed of hemoglobin, cell membranes, cytoskeletons, and glycocalyx. Except mammals, the RBC has a nucleus. The length scale of the above constituent elements widely.

Ranges from 1 nm to 10 μ m. It is well-known that the hierarchical structure of RBCs has a close relation with biological functions and diseases. To reveal the correlation between the hierarchical structure and biological functions, we have investigated the hierarchical structure of the RBCs by using combined three small-angle neutron scattering (SANS) techniques; conventional pinhole SANS, focusing ultra small-angle neutron scattering (USANS) and double-crystal USANS.

In this study, we presented the results of SANS and USANS with solvent contrast variation. The solvent contrast variation method is applied in order to selectively extract the structural information of mainly components of RBC.

Chicken bloods were purchased from Nippon Biotest Laboratories Inc. The RBCs were isolated by centrifugation at 100 G for 20 min at 4 °C and washed by resuspending in 20 mM phosphate buffer containing 9 mg/ml NaCl (pH 7.2) and by centrifuging for five times at 2000 G for 10 min at 4 °C.

SANS measurements were performed on focusing USANS spectrometer SANS-J-II and on double crystal USANS on PNO at JRR-3 reactor of Japan Atomic Energy Agency, Tokai, Japan. The covered Q range is 3×10^{-5} - 3×10^{-1} Å⁻¹. SANS and USANS measurements were performed at room temperature.

Figure 1 shows scattering profiles for chicken RBC suspension in four different



Figure 1: Scattering profiles for chicken red blood cells in 20 mM Phosphate buffer containg 9 mg/ml NaCl at pH 7.2 ($D_2O/H_2O[v/v] = 100/0, 60/40, 45/55, 0/100$, respectively).

 $D_{2}O/H_{2}O$ fractions ($D_{2}O/H_{2}O[v/v] = 100/0$, 60/40, 45/55 and 0/100, respectively). The scattering profiles of $D_2O/H_2O = 100/0$, 60/40 and 0/100 showed Q^{-4} behavior in the Q range from 2 \times 10⁻⁴ to 1 \times 10⁻² Å⁻¹, which is due to interface scattering between the RBCs and solvents. The scattering profile of $D_2O/H_2O = 45/55$, on the other hand, has an evidently different future in comparison with these for other D₂O/H₂O fractions. The scattering profiles showed Q^{-2} behavior in the Q range from 3 \times 10^{-4} to 8 \times 10^{-2} $Å^{-1}$ and obeys the power law of Q^{-4} above $Q = 8 \times 10^{-2} \text{ Å}^{-1}$. This becomes same as that of the unilamellar vesicles of lipids, because $D_{2O}/H_{2O} = 45/55$ is a contrast matching point of hemoglobin. All the scattering profiles were analyzed by fitting with a tripleshell disk model coupled with results obtained by optical microscopy. We were able to quantitatively determine the size of a nucleus in cytoplasm, the thickness of a cell membrane and the ratio of volume fraction between the hemoglobin and the water in the cytoplasm.

原子炉:JRR-3 装置:SANS-J(C3-2) 分野:中性子散乱(生物)

The Structure of 4-Repeat Tau and 3-Repeat Tau Monomer and their Self-Assembled Clusters

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Tau is one of the microtubule-associated proteins. Mainly, 4-repeat tau (4Rtau) containing two cysteine residues and 3-repeat tau (3Rtau) lacking one repetition domain containing one cysteine residue are expressed in normal brain (Fig.1). The abnormal aggregation of tau often observed in Alzheimer's disease brain causes cellular degeneration and death.



Figure 1: Diagram of 4-repeat tau and 3-repeat tau.

We prepared a tau aqueous solution suggesting the monomeric dispersion¹⁾ by DLS and confirmed that the conformation was unchanged if reductive atmosphere was maintained. The 4Rtau monomer and the 3Rtau one are not stable and immediately selfassemble to form huge clusters comprising several thousands of molecules. Under an oxidative environment, the cluster size of 3Rtau increased by the formation of intermolecular cystein crosslinkages.²⁾ The size and shape of 4Rtau monomer and 3Rtau one are estimated from the R_h values obtained by a dynamic light scattering analysis (Table 1).

4Rtau presented a intermediary structure between globular form and random coil. 3Rtau presented almost random coil. The size and shape of 4Rtau and 3Rtau clusters are determined by SANS-J [wavelength ($\lambda = 1.14$ nm), sample distance (L = 10 m)] and by SWAN at KEK.

| Table 1: | The | size | and | shape | \mathbf{of} | 4Rtau | and | 3Rtau | monome | r |
|----------|-----|------|-----|-------|---------------|-------|-----|-------|--------|---|
|----------|-----|------|-----|-------|---------------|-------|-----|-------|--------|---|

| | | | | Glebu | Random | | |
|---------------------------------------|--------------------------|---------------------|---------------------|-----------------------------------|-------------------------|--|--|
| Tau am | Number of ino acid (a.a) | Molecular weight | R#() determined | Rg() estimated from s. a. number | Rb() estimated from Rg | Rb() estimated from molecular weight | |
| R monomer 448 46,33 | | 46,332 | 38 | 22.2 14.7 | | 63.8 | |
| 4R cluster R monomer 2D cluster | 417 | 43,015 | 606 57 | 21.7 | 14.3 | 61.3 | |
| 3R cluster | | | 637 | | | | |
| n an | nino ac | ids, i | R_q, R_q | $= 2.9^{\circ} n^{(1)}$ | 1/3 3) | prising of | |
| b)Rela | tion be | tweer | R_g ar | nd R_h (hy | drodynan | nic radius), | |
| $R_q =$ | = 1.51* | $R_h^{(4)}$ |) | | | | |
| -) 0 . | - f 1 | 1 | | M 1(| | 22*1(M) | |

c) $\tilde{R_h}$ of molecular weight , M, $\log(R_h) = 0.533^* \log(M)$ - 0.682 ⁵)

4Rtau may form a rod-like rotating ellipsoid ($R_g = 850$ Å, long axis, a = 1895 Å and short axis, b = c = 105.3 Å). 3Rtau may form random coil (*slope* = -2) and the R_g was estimated to be 962 Å.



Figure 2: SANS profiles of 4Rtau and 3Rtau. Figure 2 shows the SANS profiles of 4Rtau and 3Rtau below a concentration of C^* .

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原子炉:JRR-3 装置:SANS-J(C3-2) 分野:中性子散乱(生物)

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Development of beam splitting etalons for pulsed neutrons

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A large dimensional interferometer for long wavelength neutrons has the advantage to increase the sensitivity to small interactions. Multilayer mirror is suitable for Bragg reflection of cold neutrons. We demonstrated Jamin-type interferometer for cold neutrons using 'beam splitting etalons (BSEs), 'which enables us to align the four independent multilayer mirrors in the interferometer within required precision [1]. We are preparing for high-resolution measurement of Aharonov-Casher effect [2,3] by using this type of interferometer.

The interferometer for pulsed neutrons can increases neutron counts available for AC measurement because the phase shift is independent from the velocity of incident neutrons. Neutron interferometer with multilayer mirrors can be applied to pulsed neutrons. Neutron supermirror [4], which is a variety of multilayer mirror with continuous lattice constants, can reflect neutrons with wide range of wavelength at a proper incident angle. In the case of neutron spin interferometer of Jamin type, a magnetic supermirror on the one plane of the BSE reflects only up-spin component of the neutrons and a non-magnetic supermirror on the other plane reflects transmitted down-spin component. The second BSE with supermirrors recombines the two components. High polarization of both of reflected and transmitted beam for the magnetic supermirror is required in order to split the beam into two paths according to the spin states. We deposited magnetic supermirrors on silicon wafers by using ion beam sputtering instrument at KURRI for test of BSE. Figure 1 shows measured reflectivity of the magnetic supermirror by scanning of incident angle instead of neutron wavelength. Test experiment was performed using the cold neutron beam line MINE2 at the JRR-3M reactor in JAEA. The beam had a wavelength of 0.88 nm and a bandwidth of 2.7% in FWHM. We found that the magnetic supermirror can be used as one mirror in BSE for neutrons with the wavelength from 0.52 nm to 0.88 nm at the incident angle of 1.0 degree. External magnetic field of 17mT was required for magnetic saturation of the mirror. Strong magnetic field in neutron spin interferometer would decrease the visibility of interferogram due to depolarization. Magnetic supermirror for lower external field is quite important. The interferometer for the AC measurements must have perfectly separated two paths enclosing an electrode. We are also continuing on the constructing of interferometer using BSEs with large gaps.

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Fig. 1. Reflectivity of magnetic supermirror for BSE for pulsed neutrons.

Activity Report on Neutron Scattering Research: Experimental Reports 14 (2007) Report Number: 35

1-7-2

Preliminary masurement of hydrogen content absorbed in Pd using neutron composite mirror

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Preliminary experiments on the measurement of hydrogen content in Pd using composite mirrors was performed. The composite mirror consists of neutron a halfmirror, a gap layer, and a second halfmirror. The gap layer is made of target material Pd. The half-mirrors are Ni/Ti multilayer with the refelctivity of about 50%, Neutrons which enters the composite mirror, is partly reflected by the first halfmirror and the remaining neutron goes through the gap layer and is reflected by the second half-mirror.

Between these two reflected neutrons, phase difference ϕ is introduced by the gap layer. $\phi = 2nD\sin\theta/\lambda$, where *n*, *D* are the neutron refractive index and the thickness of the gap layer, and *theta*, λ are neutron incident glancing angle and neutron wavelength, respectively.

In the reflectivity curve of the composite mirror interference fringes due to the phase difference is observed. When D or nchanges, the interference fringe is shifted. In our experiment, from the shift of the interference fringes we detect the change in nand D of the gap layer material Pd due to hydrogen absorption.

In the present experiments, two composite mirrors are arranged in (+-) configuration, in order to increase the contrast of the interference fringes.

The composite mirrors were fabricated with vacuum evaporation method at KURRI. The number and mean thickness of Ni and Ti layers in a half mirror are 6 and 10nm, respectively. The thickness of the gap layer is 100nm. During the evaporation of top half-mirror, a mesh mask is placed over the composite mirror in order to expose partially the bare Pd gap layer.

Neutron reflectivity measurements were

performed at C3-1-2-2 (MINE) beam hole of JRR-3M reactor in JAEA. Neutron wavelength and the wavelength resolution is 0.88nm and 2.7%.

The neutron reflectivity result is shown in Fig.1. Horizontal and vertical axis represent neutron incident angle to the second composite mirror and the reflectivity, respectively. The broad peak from 0.9deg to 1.5deg is due to the half-mirror, and small interference fringes over the broad peak are caused by the gap layer. The measured result is well reproduced by the calculated result.

In the present experiment, hydrogen absorption was not done because of technical reason. Experiments using hydrogen is planned in the beginning of the next budget year.



Fig. 1. Neutron reflectivity of the composite mirrors in (+-) configuration.

1-7-3

Observation of roughness at iron-surface by neutron reflectometry

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A new method of observation of the surface roughness of metallic iron has been developed. Various types of surface roughness of iron materials in air and at solid-solid interface were investigated using a neutron reflectometer, MINE-2. Wave length of the beam was adjusted to 0.88 nm. At first, the iron with surface roughness shown in Fig.1 (a) was used, where the roughness was measured by a contact-type roughness gauge and by a two-dimensional optical roughness gauge. To make the interface, the iron surface was covered with Si-block and with Al-block. The surface of the Siblock was optically flat and the surface of Al-block was polished to have roughness of Rmax=0.07 μ m. Incident angle of the beam to the iron surface was 0.6 $^{\circ}$, which is sufficiently smaller than the critical angle of iron, 0.805°. The direction of the incident beam was perpendicular to the stripe of abrasive trace. Off-specular distribution of the reflected beam was observed by an IP (imaging plate), which was placed on the arm at 1.2° from the direct beam. 1 pixel of the IP was 50 μ m \times 50 μ m. Distance from the sample to the IP was 620 mm. We were able to obtain the two-dimensional image of the reflected beam. Measured distributions of reflected beam for three cases are shown in Fig.1 (b). Assuming Gaussian distribution, the obtained half-widths were 69.3 pixels in air, 72.2 pixels with Si-block and 76.0 pixels with Al-block. In the cases of interface, the width is slightly wider than that of surface in air.

Next, grating on the iron surface was prepared using a diamond bit as shown in Fig. 1 (c). The period of the grating was 50 μ m and the depth of the grating was nearly 10 μ m, although the grating is not perfect as shown in the photograph on the left-hand side. Measurement was made in air. Incident angle of the beam to the surface was 0.4° and the beam was perpendicular to the stripe. The reflected neutron was detected by a He-3 counter moving against the incident beam. The result is shown in Fig. 1 (d). We see a broad distribution due to incomplete grating and small diffraction peaks on it corresponding to the period of the grating.



Fig. 1. (a) The roughness on the iron surface, (b) distribution of the reflected beam for three different cases of the surface, (c) grating engraved on the iron surface and (d) distribution of the reflected beam from the grating.

Development of a neutron focusing device with an ellipsoidal supermirror

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We are developing an ellipsoidal focusing mirror. An ellipsoidal surface mirror can guide neutrons those leave a small area to another small area. That kind of mirrors works as a neutron focusing device and makes it possible to build an experimental setup of high-resolution focusing small-angle neutron scattering (focusing-SANS). When higher Qc supermirror will be deposited on the ellipsoidal surface of the mirror, the two of small area where neutrons leave or arrive at approach nearer without reducing the amount of neutrons to be focused. That means the focusing-SANS system becomes compact by high-Qc supermirrors.

The original ellipsoid of the curved surface shaped on the substrate had the distance of 4000mm between two focal points on the major-axis and the semi-minor axis was 20mm. Some part of the original ellipsoid was ground on the borosilicate glass of 900mm \times 50mm \times 9mm by the Electrolytic In-process Dressing (ELID) method. Here, the length of 900mm was achieved by three pieces of 300mm substrates.

Figure 1 (top) shows three pieces of an ellipsoidal focusing mirror coated by Ni monolayer. The Ni monolayer of 2000Å in thickness was successfully deposited on the ellipsoidal surface, while 2Qc Ni/Ti supermirror of 13400Å was peeled off the curved surface. The reason of the peeling off seems to be due to using the detergent and scouring powder and insufficient washing by water and alcohol. The 2Qc supermirror was successfully deposited on the flat surface of the borosilicate glass cleaned by one-hour supersonic washing in the hot water. This cleaning method will be applied to the substrate with the curved surface ground by ELID method. We are also trying to uniform the layer thickness of

supermirror all over the curved surface, because an excess of layer thickness increases the stress in the layers and results in peeling the layer off the substrate.

Figure 1 (bottom) shows the reflectivity of 2Qc supermirror deposited on Si substrate with the flat surface. The same amount of reflectivity will be realized on the 2Qc supermirror successfully deposited on the curved surface.



Fig. 1. An ellipsoidal focusing mirror coated by Ni monolayer (top), the reflectivity of 2Qc supermirror deposited on Si substrate with the flat surface (bottom).

A Development of the Neutron Beta Decay Experiment with Superconducting Tunnel Junction (STJ)s

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Neutron beta decay is the best reaction to determine the coupling constant of a weak interaction, because the decay is independent of any nuclear structure and is then the simplest and only semileptonic reaction through the weak interaction. From the decay parameters such as lifetime or energy spectra of decay products, we can obtain V_{ud} , a matrix element of Cabbibo-Kobayashi-Maskawa (CKM) matrix, which describes the mixing between quark mass eigenstates and weak eigenstates. A CKM matrix obeys unitarity in the standard model of particle $physics^{1}$. Our research goal is to determine V_{ud} by a precise spectroscopy of recoil proton and electron from neutron beta decay.

However, the spectroscopy of a recoil proton is difficult because its kinetic energy is very small, whose maximum energy is 752 eV, so that it is hardly detected by semiconductive detectors like SSD. Thus, we are trying to apply a superconducting detector for the spectroscopy of the recoil proton. We apply superconducting tunnel junction²⁾ (STJ) for proton spectroscopy. Generally, STJs are working at 300 - 400 mK, and have an energy resolution of less than a hundred eV. These STJs are working without a dead layer so that the recoil proton deposits full kinetic energy on the detector. For this purpose, we made STJ array with a large area (500 $\mu m \times 500$ μ m) at RIKEN in order to cover a large detection area. Eight STJs from 3×3 array provide reasonable uniformity.

We installed an apparatus for the neutron beta decay measurement with STJs at LCE (T1-4-1A). Note that we have already succeeded in measuring the neutron beta decay with conventional detectors consist of CEM and PMTs with plastic scintillators for the recoil proton and electron detection, respectively³⁾. The new apparatus is analogous with the conventional one, though it consists of STJs in the cryostat instead of CEM and a PMT. For the STJ experiment, a cryogen-free refrigerator was introduced to realize a long measurement time. The refrigerator was working about 20 hours continuously.

The pulseheight spectra of a STJ are shown in Fig.1. Because of a large background caused by neutrons, the beta decay event could not be identified. The resolution of STJ was worse due to electrical noise. By reducing the background rate and electrical noise, we will establish an experimental environment for low-energy proton detection.



Figure 1: The pulseheight spectrum of a STJ. The solid and dashed lines are the spectrum of neutron beam and that without coincidense event. The dotted line is the spectrum by a checking source of 55 Fe.

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原子炉:JRR-3 装置:LCE(T1-4-1A) 分野:中性子散乱(基礎物理)

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1. 中性子散乱 8)装 置

1. Neutron Scattering 8) Instrument

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Development of a Neutron Focusing Guide for High Q-Resolution Triple-Axis Spectrometer HQR (T1-1)

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For upgrading on inelastic neutron scattering in High Q-Resolution triple-axis spectrometer (HQR) at T1-1 port, a neutron focusing guide was designed to increase the neutron flux at sample position and it's focusing effect was investigated. The shape and geometrical configuration of the focusing guide were optimized to increase the neutron intensity at the sample position by using the Monte Carlo program Mc-Stas, and the focusing guide was then determined to be a parabolic focusing mirror guide with vertical and horizontal reflection surfaces with the total length of 1000 mm. The focusing guide is composed of supermirrors with m=3 and reflectivity over 85%. The neutron focusing effect was investigated by using a two dimensional position sensitive detector composed of ZnS(Ag)/6LiF scintillator and a CCD camera. The tilting and focusing angle of PG monochrometer and the positioning and tilting angle of the focusing guide were optimized to increase the neutron intensity at the sample position. As the result, the neutron intensity increased 4 times at the peak position and 3.3 times at the area of 5x5 mm2 in comparison with the case without the focusing guide. The quality of the design was confirmed by the fact that the obtained intensity gain was consistent with the values obtained by the simulation. Furthermore, in an inelastic neutron scattering experiment, we observed a gain of 2.7~2.8 in the scattering intensity by the focusing effect as shown in Fig.1. In conclusion, a neutron focusing guide was a very powerful tool for upgrading the inelastic neutron scattering experiments.



Fig. 1. The measured results of vanadium standard sample in inelastic neutron-scattering configuration with and without the neutron focusing guide.

Activity Report on Neutron Scattering Research: Experimental Reports 14 (2007) Report Number: 26 1-8-2

Development of resonance spin flipper with high frequency

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(A)KURRI, (B)Kyoto Univ., (C)JAEA

Neutron spin echo (NSE) is one of the spectrometers with the highest energy resolution for measurement of quasi-elastic scattering [1]. In neutron resonance spin echo (NRSE), the two separated neutron resonance spin flippers (RSFs) replace a homogeneous static magnetic field for spin precession in the conventional NSE [2]. The fourier time of the NRSE spectrometer is proportional to the frequency of the oscillating magnetic field in the RSFs. RSFs with high frequency magnetic field are required for high resolution NRSE spectrometer. RSF with pure aluminum had been developed in order to reduce the scattering from the surfaces [3]. The MIEZE signal with the effective frequency of 1MHz was observed by using the RSFs in cold neutron beam line MINE1 in JRR-3M in JAEA [4]. The wavelength of the neutrons was 0.81 nm and the bandwidth was 10%. The visibility of the echo signal according to the phase of the RSFs was 0.4.

For practical uses of the MIEZE spectrometer, the RSFs has been upgraded (fig. 1). The static field coil had gaps between the pure aluminum wires due to the way of fabrication. The wires were cut out from the pure aluminum plate bonded on the cooling base. Leak of magnetic flux from the gaps made the depolarization of neutrons. The decrease of the visibility of MIEZE signals was observed when neutrons passed through the gaps. The new static field coil has wider wires with the width of 20 mm to make more flat surface of the magnetic field. The frequency of 300 kHz of oscillating field can be satisfied resonance condition with the static field made by the current of 120A. Cooling base has been optimized to maximize water flow. The temperature is kept lower than 30 degree. The RF power supply, which is made by Meisho

Kiko co. and Noda RF Technology co., can provide a maximum of 500W to the RF coils. We have also made LCR resonance circuits for the coils, which selects capacitance to enable us to find the resonance condition of the electric circuit in the frequency range of the frequency from 55 kHz to 300 kHz. We have develop MIEZE spectrometer with the effective frequency which can be change from 110 kHz to 600 kHz by using these RSFs. Remote control system with temperature sensors for RSFs have enabled us to perform stable operation of measurements. Some sample environments is also preparing now. We are continuing on developing RSF with much higher frequency for NRSE spectrometer with high resolution at J-Parc.

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Fig. 1. Resonance spin flipper (left) and MIEZE signal with effective frequency of 400 kHz using the RSFs (right). Bottom shows MIEZE setup at MINE1.

Development of fine-pixel detector for UCN

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We are developing a fine-pixel detector for detecting UCN's.

We selected CCD sensors as fine-pixel detectors, because we can know the position and timing precisely. The selected CCD sensor has 512 x 512 pixels, and each pixel has an active area of 24 x 24 microns². Since CCD's cannot detect neutrons by itself, a thin converter for neutrons, such as Li-6 or B-10, was evaporated on to a CCD surface at KUR. The thickness of the converter was 200 nm. The CCD sensors with the neutron converter were exposed to the neutron beam at the C3-1-2-2 beam line.

We've just started our analysis. Our veryquick analysis shows neutrons were successfully observed with our CCD-based detector.

Our analysis is still on the way. We will study a detection efficiency and a spatial resolution for neutrons.



Fig. 1. An examples of the observed image of neutrons. The "height" of each bar shows total charge deposited in the CCD.

1-8-4

A new layer structure for large-m polarizing neutron supermirror

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Magnetic multilayer mirror consisting of ferromagnetic layers and nonmagnetic layers is useful to polarize neutron beam. Polarizing supermirror is a stack of magnetic multilayer with gradually increasing value of the d-spacing. Several kinds of magnetic supermirror have been developed as neutron polarizeing device.

There was no m>4 polarizing supermirror except for our previous report[1]. Some of authors have succeeded in fabricating m>5 Ni(C)/Ti supermirrors and small d-spacing multilayer monochromator

with high reflectivity by using ion beam sputter (IBS) technique [1,2].It is possible to fabricate smmoth and small d-spacing layer structure but it is nessesary for strong external magnetic field.

In the report, we succeeded in fabricating m=5 Fe/Ge polarizing supermirror by using improved magnetic sputter target[3]. The target is well deoxidized iron target by heating it in hydrogen atmosphere.

The reflectivity and polarization efficiency under an external magnetic field of 45 mT were above 0.67 and 0.90, respectively.

The reflectivity is very high but the polarizaition is not so high.

The durability of the sputter target was not long enough for production. Thus we tried improve magnetic property of the supermirror without the deoxidized iron target. Here we noted the different magnetic property between Fe/Ge and Fe/Si multilayers. By inserting thin Si layer in which thickness 0.5 nm between Fe and Ge layer, the magnetic property of Fe/Ge(Si:0.5nm) multilayer is better than Fe/Ge and Fe/Si ones. We have fabricated m=4.9 Fe/Ge(Si:0.5nm) supermirror using IBS technique and tested the performance as a polarzing divice.

The measurement was carried out at C3-1-

2-3 port (MINE2) at JRR-3M at JAEA. The average wavelength of incident neutron is 0.88 nm and the resolution is 2.7 % in full width half maximum. The divergent angle of neutron beam was smaller than 1 mrad. The strength of external magnetic field is 45 mT. The reflectivity and polarization efficiency is estimated to be above 0.7 and 0.94, respectively.

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Fig. 1. Measured reflectivities of up (red) and down (blue) spin neutron for m=4.9 Fe/SiGe3(Si:0.5nm) supermirror. The green line indicates flipping ratio that reflectivity of up spin neutron devided by that of down spin one.

A test of MIEZE-Reflectometer for study of surface and interface

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Neutron Spin Echo(NSE) method is very powerful spectroscopy to investigate slow dynamics for condensed matter[1]. Neutron Resonance Spin Echo(NRSE)[2] is a variant of the NSE technique that replaces Larmor precession field by two neutron resonance spin flippers (RSFs). We installed MIEZE spectrometer to C3-1-2-2(MINE1) port at JRR-3M in JAEA[4]. MIEZE spectrometer is one of NRSE and there is no optical component between sample and detector. It is well suited to small angle neutron scattering method[3] and reflectometry[5]. By combining of neutron reflectometry and the MIEZE, it is possible to detect in- and quasi- elastic scattering on surface and interface. We installed MIEZE spectrometer to C3-1-2-2(MINE1) port at JRR-3M in JAEA. In this report, we show present status of MIEZE spectrometer and the feasibility of MIEZE reflectometer(Fig.1(a)). Three RSFs are used on the MIEZE spectrometer. These RSFs are set on bootstrap arrangement. There are two kinds of detector. The He-3 point detector is used to adjust the beam line and measure reflectivity by the sample. 2D-PSD is used for the MIEZE .The two dimensional position sensitive detector (2D-PSD) is to measure off-specular scattering since inelastic scattering component is in it. The 2D-PSD consists of ⁶Li enriched glass scintillator and a position sensitive photomultiplier in five inch diameter, in which position resolution is 1 mm. Magnetic guide field coil is set from the first DC-flipper to the analyzer to avoid depolarization of neutron

spin. The length between RSF3 and 2D-PSD is 0.5 m. The frequency of RSFs is 600 kHz. Fourier time is estimated to be 1 ns (\sim 0.6 μ eV). Fig.1(b) show measured P_{NSE} of specular reflection from m=7 NiC/Ti supermirror as a function of incident angle. There is no decay of P_{NSE}, we have succeeded in measuring standard elastic samples for MIEZE reflectometer in which Q is up to 0.135 nm⁻¹.

in which frequency.

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Fig. 1. (a) Photograph and schematic layout of MIEZE installed at MINE1. (b) Measured PNSE of specular reflection from m=7 NiC/Ti supermirror as a function of incident angle.

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Development of miniaturized McWhan type high pressure cell for elastic and inelastic neutron scattering experiments

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Over the past few decades, a considerable number of studies have been devoted the physical properties of Ce-, Yb- and Ubased intermetallics, the so-called strongly correlated electron systems. In these systems, an external pressure is often a key to bring about a new type of ground state accompanied with exotic physical phenomena, such as a heavy fermion superconductivity or valence transition and so on. Accordingly, nowadays the concern with an application of high pressure generation techniques to various sorts of experimental measurements has been growing remarkably. So far, most of neutron scattering experiments, especially inelastic neutron scattering experiments, of strongly correlated electron electrons systems or magnetic materials have been being performed using so-called McWhan type high pressure cell developed by Onodera et al.¹ This apparatus, however, is in Japan. not adequate to the experiments below 1K as a cell volume is considerably large (100 mm $\phi \times$ 140 mm height). Therefore, there is an urgent need to develop a better suited pressure cell for the elastic and inelastic neutron scattering experiments at such extremely low temperature to study physical phenomena near a quantum critical point. In this work, we have newly designed the McWhan type pressure cell with smaller heat capacity. Cylinder was made of an aluminum-based new hardened material, Mesoalite. An ultimate tensile strength of this material is almost twice as high as that of conventional duralumin (A7075). Support cylinder was made of ZrO₂ whose neutron transmittance is 50% larger than that of Al₂O₃. Consequently, we succeeded in reducing the cell volume to one-third (66 mm $\phi \times$ 92 mm height) and

improving the neutron transmittance up to about twice comparison with those of the McWhan type pressure cell designed by Onodera et al.¹. A cross-section diagram of newly designed McWhan type pressure cell for neutron scattering experiments below 1K is drawn in figure. Pressurization examination was performed at room temperature. Glycerin and a single crystal of NaCl were used as a pressure transmitting medium and a manometer, respectively. Generated pressures were determined based on a compressibility of NaCl by estimating a lattice constant from its (200) reflections at various external loads. At present, we succeed in generating pressure above 2.3 GPa by this pressure cell. With a suitable change to the specification, it is possible to improve the highest pressure.

¹ A. Onodera et al., Jpn. J. Appl. Phys., 26 (1987) 152.



Fig. 1. A cross-section diagram of miniaturized McWhan type pressure cell for elastic and inelastic neutron scattering experimetns.

Activity Report on Neutron Scattering Research: Experimental Reports 14 (2007) Report Number: 213

Bent Perfect Silicon Crystal Monochromator for Cold Neutrons

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Usually, SANS (small-angle neutron scattering) instruments are installed at an endguide position because they require rather large space for detection system, very low background and a wide wavelength band of about $\Delta \lambda / \lambda ~ 10\%$. The last condition is not easy fulfilled by using a conventional crystal monochromator and therefore, at present a velocity selector is usually used for such purposes. We are now developing a compact ellipsoidal-mirror focusing small-angle neutron scattering instrument (mfSANS) employing a wide-wavelength band monochromator, and have a plan to install several such SANS instruments along the guide tubes at JRR-3 reactor of Japan Atomic Energy Agency or at many other research reactors. In order to realize such project, we have to develop a widewavelength band monochromator for cold neutrons having $\Delta \lambda / \lambda$ of several percents, preferably 10%.

In the case of the mfSANS instrument, we will use a beam entrance collimator of about 1 mm to 5 mm in diameter. When Pyrolitic Graphite (PG) monochromator is used in such a geometry, the $\Delta \lambda / \lambda$ of the monochromator becomes too small, of the order of a few-tenth of percent, irrespective of the mosaic spread of the crystal. Bent perfect crystal (BPC) of Si in the fully-asymmetric diffraction geometry represents a good alternative for realization of such a monochromator with required parameters. However, there are no corresponding data available in the cold neutron region and as far as we know, even for the bent crystal in the symmetric diffraction geometry.

Therefore, we studied neutron optical characteristics of the BPC silicon slabs in the cold neutron region. Unfortunately, we did not have access to a white-neutron beamport, we used the ULS instrument at the C1-3 port of the cold neutron guide C1 of JRR-3. The instrument has a PG(002) monochromator, which provided us neutrons of about the wavelength of 0.47 nm. First we measured the beam-characteristics from the PG-monochromator using a 5-inch diameter scintillation-counter based on a resistive-wire type photo-multiplier tube. With its very-high positional resolution combined with a fine slit, we could measure the phase-space intensity of the beam, namely, not only the position dependent flux, but also the angular divergences of them.

Knowing the beam parameters from the PG-monochromator, then we put BPC- and in Si(111) slabs on the second axis of the diffractometer for diffraction in symmetric reflection geometry ((111)-crystal planes were parallel to the main face of the crystal slab) and in the non-dispersive setting with respect to the PG(002) monochromator. We made rocking curve measurements with various bending radii in the range of R>2 m. First, one BPC Si slab was used, then we repeated the measurements with two and three BPC Si slabs stacked together as a sandwich. We successfully measured 2-dimensional images of reflected neutrons with the position sensitive detector.

At first, with changing the bending radius R from almost infinity to several meters, reflected beam intensity increased without broadening of the rocking curve, which means that the total angular change brought about by bending is smaller than the mosaicity of the PG-monochromator. However, by bending the Si-crystals furthermore, the situation distinctly changed, the peak reflectivity was saturated and broadening of the rocking curve was observed. We also observed reflected intensity enhancements when one or two crystals were added to the sandwich.

In order to check whether we could enhance the wavelength-bandwidth further more, we conducted another type of experiment using the pulsed neutron source of Hokkaido University based on a 45-MeV electron-linac. In the experiment, white cold-neutron beam was incident into several-different positions of the BPC with slightly different angles and the wavelength-shifts were measured using a time-of-flight technique.

Detailed analysis of both experiments is underway.
Development of High Performance Neutron Supermirrors with Ion Beam Sputtering Technique

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less than 4%³⁾.

Neutron scattering is a useful source of information about the positions, motions, and magnetic properties of condensed matter. Neutron scattering is important because it provides valuable information that can not be obtained using other techniques such as Xray scattering. In order to study a wide range of problems in material and life science with a much higher neutron intensity, a new spallation neutron source (Japan Proton Accelerator Research Complex, J-PARC) is now under construction. The development of neutron supermirrors with high reflectivity and large m, the ratio of the critical angle of the supermirror to that of natural nickel, is important for the J-PARC project since it greatly increases the available neutron intensity. For example, a *m*-supermirror guide would bring about a gain factor of m^2 in the neutron flux at the end of the guide when it is used instead of the Ni guide. Neutron supermirrors consist of alternating layers of two materials with different refractive indices for neutrons.

We have developed neutron supermirrors by employing the ion beam sputtering (IBS) technique because it enables the production of layers with a high density and small grain size. We have also demonstrated the efficiency of the ion beam polishing technique combined with the IBS deposition to suppress the interface roughness, which is an important problem in the fabrication of supermirrors with large $m^{1,2}$. Although the IBS technique produces high quality layers, its disadvantage is that the deposition area and rate are relatively small. Based on the results of our development, a new IBS system with a large deposition area of 0.2 m^2 (diameter of 500 mm) has been designed and installed in JAEA. The difference in the deposition rate over the entire deposition area has been confirmed to be Ni/Ti supermirrors with m = 3 and 4, for use as neutron guides in the J-PARC project, have been fabricated using the IBS system. The total number of layers is 403 and 1201, respectively. The neutron reflectivities of mirrors with m = 3 and 4 at their critical angles are 82 and 66%, respectively. Ni/Ti supermir-



Figure 1: Reflectivity profiles of Ni/Ti supermirrors with m = 3, 4, and 6.7.

ror with m = 6.7, which is a record breaking critical angle, has also been fabricated. The total number of the layers is 8000. The neutron reflectivity at the critical angle is 23% ⁴⁾. Thus, we can contribute to the J-PARC project in which the production of neutron guides, benders and other devices using supermirrors is planned.

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原子炉:JRR-3 装置:SUIREN(C2-2) 分野:中性子散乱(装置)

Feasibility Tests on the Pressure-transmitting Media for Single-crystal Magnetic Neutron Diffraction Experiments

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Pressure transmitting-mediums have extremely important roles in single-crystal diffraction experiments. Low hydrostaticity of the mediums under pressure highly depraves the crystallinity of the sample. As a result, the diffraction intensity lowers further. In order to investigate the hydrostaticity of the mediums, we measured the mosaic spread of NaCl single-crystal under pressure at room temperature. The investigated mediums are graphite powder, a (1:1) mixture of Fluorinert FC77 and FC70 (Sumitomo 3M, Inc.), Fomblin oil (Y140/13, Solvay Solexis Inc.), Si oil (KF96-50CS, Shin-Etsu Chemical Co., Ltd.), Daphne7373 oil (Idemitsu Co., Ltd.) $^{1)}$ and glycerin. The measurements were performed using TAS-1 spectrometer. The pressure was applied by using an anvil-type high-pressure device and monitored by a standard ruby-fluorescence method.



Figure 1: Rocking curves of the (200) reflections of the NaCl crystal at the selected pressures for the mediums of (a) Fluorinert and (b) glycerin.

Fig. 1(a) and (b) show the rocking curves of the (200) Bragg reflections of the NaCl single-crystal under pressure with the mediums of Fluorinert mixture and glycerin. In Fluorinert mixture, the clear peaks are observed at ambient pressure, 0.4 GPa and 0.9 GPa. At 1.4 GPa, the peak suddenly extends over more than 10 degree and the peak intensity goes down further. This indicates that Fluorinert mixture solidifies at around 1 GPa. On the other hand, in glycerin, the width of the diffraction peak increases very gently with increasing pressure and is only 1.1 times at 3 GPa and 1.5 times even at about 7 GPa. This shows that the glycerin medium transmits nearly hydrostatic pressure at least up to 7 GPa. Fig. 2 summarizes the experimental results on the hydrostaticity of the mediums. Upper limitations of the available pressures of the mediums in the diffraction experiments are also summarized in the figure.



Figure 2: Pressure dependence of the (200) peak width of NaCl crystal. Each value of the width is normalized by that at ambient pressure.

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Performance Test of Neutron Detector for Engineering Diffractometer in J-PARC

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A prototype linear scintillation neutron detector originally developed in RAL was fabricated for the engineering diffractometer in J-PARC. In this paper, some results of the performance test of the detector are described.

The fabricated detector was designed to have a small detection pixel with a spatial resolution of 3 mm. The detector had 120 pixels to establish a large neutron sensitive area. Scattered neutrons were detected based on the nuclear reaction of ${}^{6}\text{Li}(n,\alpha)$ in ZnS/LiF scintillators in the pixel. Incident neutron position was determined by a $_2C_n$ coding method. The applied voltages of PMTs are individually set to have a gain of 3×10^7 . The PG monochromator was used for the experiments. A collimated neutron beam was irradiated to the detector for the measurement of a spatial response. Neutron count linearity was also measured by changing the neutron intensity with a disperser.

Fig.1 shows the results of the measurement of the spatial response. The beam size of an incident neutron was $2 \times 1 \text{ mm}^2$. Since a scintillator in a detector pixel was optically isolated from the other pixels, the spatial resolution is the pixel width of 3 mm, in principle. One can recognize that an intense signal was generated from only one pixel. It can be confirmed that the detector had a spatial resolution of about 3 mm and that there was no coding misses and no remarkable crosstalk between the pixels.

Fig.2 shows the results of the linearity measurement. Neutron counts were calibrated with a ³He gas neutron detector. As can be seen in the figure, neutron counts of both the fabricated detector and the ³He detector were almost the same up to 3×10^3 cps.

In summary, the fundamental performance of spatial resolution and the neutron count linearity of the fabricated detector were confirmed. Other performance such as neutron detection efficiency and uniformity are under investigation.



Figure 1: Results of spatial response.



Figure 2: Linearity of neutron counts.

原子炉:JRR-3 装置:MUSASI(T2-3) 分野:中性子散乱(装置)

Measurement of Energy Spectrum of Neutron Beam at MUSASI Port

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The high-angle MUSASI beam port provides a neutron beam with a scattering angle of 82 degrees. When PG is used as a monochromator, however, neutrons with higher harmonic ones will be generated because of the intrinsic characteristics of PG. To provide neutron energy information to users who adopt PG as a monochromator, neutron energy spectrum was measured by a TOF method.

The experimental setup is schematically shown in Fig. 1. An neutron beam was chopped by a chopper and the chopped neutrons were detected by a ³He detector with a flight path of 1.27 m. Logical pulses generated by a discriminator were measured by a multi-channel scalar with a dwell time of 2 μ s.

The measured neutron spectrum is shown in Fig. 2. The TOF time was converted to neutron wavelength according to the relationship between TOF time and the flight path. One can observe four peaks corresponding to neutron wavelengths of 4.48 Å, 2.24 Å, 1.49 Å and 1.12 Å, respectively. No noticeable peaks was observed above 5 Å. Table 1 lists the peak ratios calculated by fitting each peak with a Gaussian function. The most intense component was 2.24 Å-neutrons that made up 53 % of the total beam. Note that the data were not corrected by the neutron detection efficiency of the ³He counter.

Table 1: The intensity ratios of detected peaks

| $\lambda(\text{\AA})$ | 1.12 | 1.49 | 2.24 | 4.48 |
|-----------------------|-------|-------|-------|-------|
| ratios | 0.028 | 0.190 | 0.534 | 0.248 |



Figure 1: Experimental setup.



Figure 2: Neutron energy spectrum.

原子炉:JRR-3 装置:MUSASI(T2-3) 分野:中性子散乱(装置)

Development of High Quality Neutron Mirrors with Upgrading Cold Neutron Bender System

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A cold neutron bender system has been installed in the JRR-3 beam hall to increase the number of beam ports. In 2006, the neutron beam transportation ability of the system was upgraded by using high quality neutron mirrors. These mirrors have high quality Ni/Ti multilayers with m = 3 on both side of silicon substrate and Boron float glass substrate. The ion beam sputtering (IBS) technique enables the production of layers with a high quality and density. A large silicon substrate, which is 40 mm in width, 105 mm in length and 0.2 mm in thickness, was selected in order to improve the installation accuracy. Neutron mirrors on silicon substrates were installed as curved neutron guides. Neutron mirrors on glass substrates were installed as straight neutron guides in the cold neutron bender system. In this report, we report the neutron reflectivity of mirrors with silicon substrates and with glass substrates using the cold neutron bender system.

The measurements of neutron reflectivity of a newly producted neutron mirror were carried out at SUIREN in the JRR-3 beam hall. The incident neutron wavelength is 3.83A.

Neutron reflectivity of a Ni/Ti supermirror on both sides of silicon substrate are shown in Fig.1 and Fig.2, respectively. Figure 1 shows the neutron reflectivity of a Ni/Ti supermirror on one side of the silicon substrate and Fig.2 shows the neutron reflectivity on the back side of it. The reflectivities at the effective critical momentum transfer were 0.9 and 0.9 respectively. It was found that the features of the reflectivities of mirrors on one side of substrate are almost the same as that of the other side. It was also found that the reflectivity at the effective critical momentum transfer of the glass substrate was 0.8. We succeeded in manufacturing of a high reflectivity (90%) Ni/Ti supermirror with m = 3 on the silicon substrate.



Figure 1: Neutron reflectivity on the front side of a Ni/Ti multilayer supermirror carried out at SUIREN.



Figure 2: Neutron reflectivity on the back side of a Ni/Ti multilayer supermirror carried out at SUIREN.

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原子炉:JRR-3 装置:SUIREN(C2-2) 分野:中性子散乱(装置)

1-8-13

Upgrading Cold Neutron Bender System

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In order to effectively utilize neutron beam, we plan to increase the numbers of cold neutron beam ports that are able to install neutron beam instruments. A cold neutron bender system has been installed in the JRR-3 beam hall. The cold neutron bender system divides a cold neutron beam line into three beam lines. One is a straight beam line called C2-3-1, and the other two beam lines, C2-3-2 and C2-3-3, are bend from the straight beam line. C2-3-2 beam line bend 10 degree from the straight beam line and C2-3-3 beam line bend 20 degree from the straight.

However, the intensity of neutron beams at the ends of divided neutron guides was much lower than calculated one. Therefore, the neutron beam transportation ability of the cold neutron bender system have been upgraded using newly developed neutron mirrors.

In this paper, we report the measured spectrum at the end of C2-3-3 beam line using a chopper spectrometer because Ni monolayer mirrors were replaced with Ni/Ti multilayer supermirrors of the straight neutron guide section in the bender system.

Neutron spectrum was measured at the end of the C2-3-3 beam line by the time-of-flight method. The neutron chopper has a slit of 10 mm, a disk diameter of 1400 mm and rotation speed of 5000 rev/min. The flight path length between the end of C2-3-3 beam line and the chopper was 1.7 m, and the length between the chopper and detector was 1.3 m.

The conversion factor from the time channel to the wavelength was calibrated on a dip formed by a monochromator in the spectrum.

Figure 1 shows the neutron spectrum measured by the chopper spectrometer. The characteristic wavelength of the C2-3-3 beam line is 5.4 A for improvement.



Figure 1: Neutron spectrum measured at C2-3-3 beam line by the time-of-flight method.

measured at depths of 2.5, 4.5, 8.5 and 12.5mm are shown in Fig.2, in which the profiles were obtained from poled, unpoled, poled and unpoled specimen, respectively. The peak intensities of (002) reflection in the poled specimens are larger than those in the unpoled specimens, showing that the spontaneous polarization direction is parallel to the [002] direction. Therefore, the domain switching properties can be estimated from the difference between the diffraction profile of a poled specimen and that of an unpoled one. The (002) and (200) diffraction intensity distribution with respect to scattering angle and penetration depth is plotted in Fig.3. The lowest intensity (zero) is shown by black (dark) color, and the color becomes brighter with increasing the intensity. As shown, the first two layers are profiles from the poled specimen, the next four layers are those from the unpoled one followed by four layers from the poled one, and the last three layers are those from the unpoled one. The profiles were fitted by a convolution of Gauss and Lorenzt functions and integrated peak intensities of both reflections were evaluated. Domain switching properties can be estimated from the integrated peak intensity ratio between (002)and (200) reflections, i.e., I_{002}/I_{200} . Figure 4 shows the I_{002}/I_{200} value in a function of penetration depth. The I_{002}/I_{200} values are higher than 1 for the poled specimen, and approximately 0.5 for the unpoled specimen. The I_{002}/I_{200} value of the unpoled specimen is in a good agreement with the theoretical I_{002}/I_{200} value, demonstrating that the neutron diffraction results have good reliability. The I_{002}/I_{200} values are almost constant for different penetration depths. This is due to the fact that there was no treatment applied to the specimen, and then the degree of polarization in a whole specimen is almost uniform. On the contrary, the I_{002}/I_{200} values have fluctuations that may show the inhomogeneities of polarization in the specimen, induced during the polarization treatments. The results described above are difficult to measure by the means of XRD that only measure surface part. A combination of neutrons

having high penetration ability and a fine radial collimator can realize this kind of measurement.



Figure 3: (002) and (200) diffraction intensity distribution with respect to scattering angle and penetration depth.



Figure 4: Integrated peak intensity ratio (I_{002}/I_{200}) value) as a function of penetration depth.

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Test of Prototype ³He PSDs and Related Electronics for New Spectrometers at J-PARC

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At MUSASI port, we have tested prototypes of detectors and related electronics, which will be employed by spectrometers for J-PARC. For neutron scattering instruments planned for the new spallation neutron source at Materials and Life science experimental Facility (MLF) at J-PARC, various novel types of ³He position sensitive detectors (PSDs) are considered to be used. Since the detector is one of the most important key components, it is indispensable to evaluate the feasibility and the performance of these new detectors and related electronics prior to actual construction of the instruments.

One of the new types of the PSD is a long tube PSD for 2 chopper spectrometers, AMATERAS and 4SEASONS. The length of these detectors are l = 3 m and 2.5 m to minimize gaps between detectors (see Fig. 1). They will be accommodated in the scattering chamber under the high vacuum condition ($\sim 10^{-6}$ Torr) to reduce the background. Therefore, new long PSDs are equipped with newly designed vacuum couplings with SHV connectors at the ends. A number of long PSDs, which are deferent in lengths (l), diameters (ϕ) , gas pressures (p), have been prepared by two different detector venders. The detectors were set on the testing stand, and we have examined them using neutron beam.

A typical result of performance tests is shown in Fig. 2. The linearity of the position sensitivity is confirmed within the error of 3 mm for all tested detectors. The resolution is less than 19 mm in FWHM. These performances are almost equivalent to those of conventional short PSDs commonly used at KENS. We have found slight differences in the performance between the detectors provided by different venders, which are, however, completely acceptable to us.

According to the present results, we have fixed the final specifications of detectors for 2 chopper spectrometers, that is, l = 3 m, $\phi = 1$ inch, p = 10 atm PSDs for AMATERAS and l = 2.5 m, $\phi = 3/4$ inch, p = 20 atm PSDs for 4SEASONS.



Figure 1: A 3 m length $^3\mathrm{He}$ PSD on the testing stand at MUSASI.



Figure 2: Position dependence of output position (position channel) and peak width of 2.5 m length, ³He PSDs ($\phi = 2/3$ inch, p = 10 atm) provided by different vendors.

原子炉:JRR-3 装置:MUSASI(T2-3) 分野:中性子散乱(装置)

1-8-15

Development of a Neutron Polarizing Device Based on a Quadrupole Magnet and Evaluation of Its Polarizing Power

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So far, we have developed a Halbach-type permanent quadrupole magnet (HQM) composed of a strong permanent magnet NdFeB with an effective aperture size of 3.5 mm in diameter and a length of 600 mm as a neutron polarizing device¹). As a result of the cold neutron beam polarization experiment, a very high neutron polarization degree of $P = 0.9993 \pm 0.0025$ was obtained¹⁾. The polarizing device based on the HQM is considered to be a suitable polarizer for a focusing geometry small-angle polarized neutron scattering instrument using a magnetic neutron lens because of its high polarization efficiency and high polarized neutron $transmission^{2}$. However, for the practical application to the neutron scattering experiments, an HQM with a larger aperture size is demanded. Therefore, we have developed the HQM with a larger aperture of 7 mm in diameter and length of the 700 mm (Fig.1). According to the magnetic field measurement, the magnetic field gradient was obtained to be $\partial |\mathbf{B}| / \partial r = 515.8 \pm 1.4 \text{ T/m}$ inside the HQM aperture. Neutron-absorbing cadmium (Cd) slits with an inner diameter of 5 mm were inserted between the HQM units in every 100 mm interval along the magnet length to prevent neutrons from hitting the inner surface of the HQM. Therefore, the effective aperture of the HQM is 5 mm in diameter.

We have performed a cold neutron polarization experiment using the HQM at the beamline of C3-1-2-1(NOP) of JRR-3 in Japan Atomic Energy Agency. The experimental setup is shown in Fig.2. The neutron wavelength was $\lambda = 8.07$ Å. The neutrons, which passed through the HQM, were focused and defocused by the magnetic neutron lens depending on their spin polarity^{3,4)}, and were detected by the 2d-detector. Figures 3 (a)



Figure 1: The Halbach-type permanent quadrupole magnet.

and (b) show the two-dimensional intensity distributions on the detector, when the spin flipper (SF) is off and on. The radial averages of the intensity distributions are shown in Fig.⁴.*Thepeaksappearinginthebothcasesareproducedbythepc* Thus, the peak height ratio $\Delta I_{\rm SF}$ off/ $\Delta I_{\rm SF}$ on corresponds to the so-called flipping ratio R. Therefore, we get the relation⁵⁾

$$R = \frac{\Delta I_{\rm SF off}}{\Delta I_{\rm SF on}}$$

=
$$\frac{1 + P_i P_a (1 - D)}{1 + P_i P_a (1 - D) (1 - 2f)},$$
 (1)

where P_i and P_a are the polarization efficiencies of the polarizer and analyzer, respectively. In this study, the magnetic neutron lens corresponds to the analyzer. f is the flipping efficiency of the SF, D is the depolarization factor. By assuming $P_a = 1$, f = 1and D = 0, we obtain

$$P_i = \frac{(\Delta I_{\rm SF off} - 1)}{(\Delta I_{\rm SF off} + 1)}.$$
 (2)

Based on Eq.(2), we calculated the neutron polarization P_i of the neutrons which passed

原子炉:JRR-3 装置:NOP(C3-1-2-1) 分野:中性子散乱(装置)



Figure 2: The experimental setup.

through the HQM, and obtained $P_i \sim 0.999$.

In conclusion, we have developed the HQM with an aperture of 7 mm in diameter and a length of 700 mm, and performed the cold neutron beam polarization experiment. As the result, we obtained the highly polarized neutron beam with a polarization degree of $P_i \sim 0.999$.



Figure 3: Two-dimensional intensity distributions. (a) SF is off, (b) SF is on.



Figure 4: The radial averages of the intensity distribution, when the spin flipper is on and off.

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Profile of a Neutron Reflectometer SUIREN at C2-2, JRR-3

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A new neutron reflectometer "SUIREN" has been in operation at the C2-2 port of the JRR-3 of JAEA since 2006. JAEA accepts proposals from academic and industrial researchers. JAEA hase already provided 26 days for outside researchers in 2006 and will provide about 60 days in 2007. This instrument has vertical-sample geometry and is going to be used for studies on supermirrors¹⁾, polymers, magnetic thin films and other materials with solid surfaces.

Specifications of the SUIREN reflectometer are collectively shown in Table 1. The intensity (* in the table) depends on the status of the LTAS instrument operating at the C2-1 port, but can be normalized by monitoring incident neutron counts. The back-ground level $(4.5 \times 10^{-3} \text{ n/s})$ was measured when the local beam shutter was closed and the detector window was covered with a B₄C rubber sheet.

Test measurements were performed before starting operation for users. Fig. 1 shows a specular reflectivity of a silicon wafer (3 inches in diameter) with a fit curve for a Si wafer with surface oxidization of 5 Å. It was found that reflectivity down to 10^{-6} ($Q_z \leq 0.22$ Å⁻¹) can be measured unless sample itself causes significant background. The measuring time was about 32 hours. The reflectivity of a Ni/Ti multilayer was also measured down to $10^{-6} (\leq 0.42$ Å⁻¹), and Bragg peaks up to the sixth one were identified. It took 59 hours for the measurement.

In conclusion, the neutron reflectometer SUIREN showed a high performance in test measurements and has been used by industrial and academic researchers. As for future plans, polarization analysis will be available in 2007. Fe/Ge multilayer monochromators²⁾

Table 1: Specifications of the SUIREN reflectometer. The intensity(*) is not fixed as described in the text.

| Wavelength λ | 3.8 Å | |
|---|------------------------------------|--|
| $\Delta\lambda$ / λ | $1.3 \ \%$ | |
| Maximum Beam Size | $80^H \times 20^W \text{ mm}^2$ | |
| Slit1-Slit2 Distance | $1450 \mathrm{~mm}$ | |
| Sample-Detector Distance | $1100~\mathrm{mm}$ | |
| Incident Angle Resolution | $\geq 0.004~{\rm deg}$ | |
| Scattered Angle Resolution | $\geq 0.015~{\rm deg}$ | |
| Intensity*($\Delta \theta_{in} = \pm 0.04 \text{ deg}$) | $2.3 \times 10^4 \text{ n/s/cm}^2$ | |
| Back Ground | $4.5\times10^{-3}~{\rm n/s}$ | |
| Measurable Reflectivity | $\gtrsim 10^{-6}$ | |

(coated at KUR) will be installed as a polarizing filter and an analyzer. A 1 T sample magnet and a refrigerator (10 K \sim RT) will also be available.



Figure 1: Measured Reflectivity from a silicon wafer.

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原子炉:JRR-3 装置:SUIREN(C2-2) 分野:中性子散乱(装置)

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1. 中性子散乱 9)超伝導現象

1. Neutron Scattering 9)Superconductivity

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Polarized Neutron Inelastic Scattering Study of Spin Fluctuation in $La_{2-x}(Sr,Ba)_xCuO_4$

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The recent discovery of universal magnetic excitation in the high- T_c cuprates, which shows a novel hour-glass shape dispersion, has provided an important insight into the magnetic origin of the superconductivity. Among the several pictures proposed to explain the hour-glass dispersion, the stripe model is expected to be an important candidate. We have performed inelastic polarized neutron scattering on stripe-ordered La_{1.875}Ba_{0.125}CuO₄(LBCO 1/8) and compared the results with those of $La_{1.92}Sr_{0.08}CuO_4(LSCO 8 \%)$ which has no stripe order. The purpose of this experiment is to understand the effects of the stripe order on the low energy magnetic excitations and hence have an insight into the origin of the universal magnetic excitation.

The experiments have been performed at the TAS-1 triple axis spectrometer operated in a uniaxial polarization mode. Vertically and horizontally focused Heusler monochromator and analyzer were used. Inelastic measurements were done with a fixed final neutron energy of 14.7 meV, and a spin-flipper and a PG filter were placed after the sample.

Figure 1 shows profiles observed at the energy transfer 4 meV in the vertical-field (VF) spin-flip (SF) and the horizontal-field (HF) SF channels along the A-C trajectories shown in the bottom figure. Remarkably, it is shown that for LSCO 8 % the HF-SF signal is almost double of the VF-SF signal indicating isotropic spin fluctuations, whereas for LBCO 1/8 both the channels show comparable cross sections indicating anisotropic spin fluctuations where those along the *c*-axis are suppressed. We have also confirmed by the polarized neutron diffraction that the Cu spins

are confined in the CuO₂ plane, that is, the a - b plane, in the stripe-ordered state.

These results demonstrate that the polarization of the low energy spin fluctuation is different between the samples with and without the stripe order. A possible explanation is that the in-plane gap of the excitation which is observed in the non-doped La_2CuO_4 is recovered in the stripe-ordered sample. Further polarized and unpolarized neutron experiments are in progress to confirm this.



Figure 1: Polarized neutron scattering cross section at the energy transfer of 4 meV observed in the VF-SF and HF-SF channels. The data for LSCO 8 % are measured along the A (circles) and B (squares) trajectories, while those of LBCO 1/8 are measured along the C trajectory. The bottom figures show the scan trajectories in the momentum space and the definition of the polarization axes.

原子炉:JRR-3 装置:TAS-1(2G) 分野:中性子散乱(超伝導)

Magnetic Excitations in Lightly-Doped $La_{2-x}Sr_xCuO_4$

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Recently, detailed inelastic neutron scattering studies have been performed up to high energies in various systems such $YBa_2Cu_3O_{6.6},^{(1)}$ $La_{1.875}Ba_{0.125}CuO_4^{(2)}$ asand La_{1.84}Sr_{0.16}CuO₄.³⁾ All of them show hourglass-shaped magnetic excitations with the parallel incommensurate correlations at low energies. On the other hand, there are few studies of magnetic excitations in the diagonal incommensurate phase in lightlydoped $La_{2-x}Sr_xCuO_4$, although conventional spin wave excitations were reported in the diagonal stripe phase of $La_{2-x}Sr_xNiO_4$.⁴⁾ We previously tried to measure magnetic excitations in the diagonal incommensurate phase using a twinned crystal of $La_{1.976}Sr_{0.024}CuO_4$.⁵⁾ The results suggest that the magnetic correlations change from being incommensurate to commensurate at \sim 7 meV and \sim 70 K. However, since some the assumptions are needed to analyze the data in twinned crystal, information was limited. It is important to compare the magnetic excitatons in both the parallel and diagonal incommensurate phases in detail to clarify what is the intrinsic magnetic properties in the superconducting phase.

We performed inelastic neutron scattering measurements on TAS-2 and LTAS using an almost untwinned crystal of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ $(x \sim 0.04)$, in which elastic magnetic peaks are observed at $(1, \pm \delta, 0)_{\text{ortho}}$ or $(0, 1\pm \delta, 0)_{\text{ortho}}$, to observe magnetic excitations in the diagonal incommensurate phase. We observed energy and temperature dependences of magnetic excitations in the range of $0 \leq \omega \leq 12$ meV and $4 \leq T \leq 290$ K. The results show that the incommensurability (δ) decreases gradually with increasing energy up to 12 meV, as shown in Fig. 1. This is qualitatively consistent with the behavior in the parallel incommensurate phase. The temperature dependence of the magnetic excitations shows that the incommensurability gradually decreases with increasing temperature and becomes almost commensurate below 12 meV at room temperature.



Figure 1: Typical consant-energy spectra at T = 4 K in La_{2-x}Sr_xCuO₄ ($x \sim 0.04$). The diagonal incommensurate peaks are observed at $(1, \pm \delta, 0)$ or $(0, 1\pm \delta, 0)$.

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原子炉:JRR-3 装置:TAS-2(T2-4), LTAS(C2-1) 分野:中性子散乱(超伝導)

1. 中性子散乱 10)残留応力

1. Neutron Scattering 10) Residual Stress

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Intergranular Strain Pole Figure Measurement for ECAPed Al by Neutron Diffraction

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Texture and intergranular stresses are evolved in polycrystalline materials subjected to plastic deformation due to heterogeneous plastic flow. In general, pole figures are measured by X-ray diffraction to evaluate the anisotropic mechanical properties of plastically deformed materials, which is not sufficient. In this study, a neutron diffraction method has been developed to determine the texture as well as intergranular strains called "strain pole figure" for a bulky sample.

A 4N graded pure aluminum bar with 8 mm in diameter and 60 mm in length was ECAPed up to 8 cycles by rotating by 90 degrees at each extrusion. The (hkl) intergranular strains and texture were measured by using RESA at JAEA. The specimen was rotated by 10° steps for texture measurement

and 45° steps for residual strain measurement. And measurements were conducted a gauge volume to measure diffractions from (111), (200) and (220) was adjusted completely inside the sample.

Figure 1 shows the results of texture and hkl intergranular strains. As shown, the ECAPed aluminum shows an asymmetric texture. Residual intergranular strains are observed depending on the texture, and different in the case of three (hkl) oriented family grains. Although the stacking fault energy of aluminum is high, the misfit plastic strains among grains, i.e., heterogeneous plastic flow, seem to be yielded resulting in the generation of internal stresses.



原子炉:JRR-3 装置:RESA(T2-1) 分野:中性子散乱(残留応力)

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Quantitative Evaluations of Microstructural Factors by Neutron Diffraction for Cold Rolled austenitic Stainless Steels

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Cold rolled stainless steels show anisotropic mechanical properties which are dependent on texture, substructure (dislocation structure and density) and intergranular stresses, and hence, it is expected to determine these microstructural factors as macroscopically averaged values. Neutron diffraction enables us to measure these values for cm-ordered bulky specimens. In this study, texture measurements and profile analysis were simultaneously performed to determine the above microstructural factors by an angler dispersion neutron diffraction method for two stainless steels.

The samples used in this study were a 316 type stainless steel without N addition, 316SS, and a 0.325 mass% N bearing 310 type stainless steel, 310SS. After solution treatments to obtain a single austenitic phase, the specimens were subjected to 25% cold rolling. The diffraction profiles of (111), (200) and (220) reflections were measured using the neutron diffractometer for residual stress analysis (RESA) located in JRR-3 at Japan Atomic Energy Agency in Japan. Texture and residual strains were determined by the conventional method, and the dislocation density and the block size were analyzed for the diffraction profiles of (111) reflection using a profile analysis software developed by Ryufuku et al.

Figure 1 shows the gradation images of the intergranular strain pole figure superimposed on the texture contour map for (200) reflections. The textures obtained for 316SS and 310SS are the typical rolling texture of austenitic stainless steels showing little difference. A significant difference between 316SS and 310SS is found in the intergranular strain pole figure; the strain of 310SS is higher than that of 316SS. This large difference in the intergranular stain must be explained by the difference in substructure which is mainly caused by nitrogen addition. That is, the planer dislocation array and network including Lomer-Cottrell immobile dislocations reaction has been observed in 310SS while dislocation cell structure in 316SS. Being consistent with Ikeda et al.'s work of in situ neutron diffraction study for 310SS with different N contents, higher intergranular stresses evolve in a higher N bearing steel. Although the dislocation structure is different in the present two steels, the dislocation density determined from the profile analysis was almost the same, i.e., approximately $2.0 \times 10^{15} / \text{m}^2$, and it gradually decreased with increase in angle from normal direction. To be noted is the comparison of the crystal orientation pole figure and the strain pole figure, where the compressive and tensile residual strains are closely related to the crystal orientation density.



Figure 1: Gradation images of the intergranular strain pole figure superimposed on the texture contour map for (200) reflections of (a) 316SS and (b) 310SS.

原子炉:JRR-3 装置:RESA(T2-1) 分野:中性子散乱(残留応力)

Attempt of Residual Stress Measurements in Multi-Purpose Thermal Neutron Application and Science (MUSASI)

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Recently in Japan, the residual stress measurement and strain measurement for industrial use have been increasing. We feel a growing need for a secondary residual stress analysis port other than RESA. Therefore, the residual stress measurement that using MUSASI was examined.

The standard specimen was a shrink-fitted ring and pulg made of aluminum alloy A7075. The already-known residual stress can be introduced into the specimen by a shrink-fitted ring and plug method, and it has used for round-robin tests of VAMAS. The monochromator was using the bending silicon crystal, and the wavelength was 0.2203 nm.

It is possible to measure the three directions of strain using neutron diffraction. In the cartesian coordinate system, the relation between the lattice spacing d and the strain ε is as follows.

$$\varepsilon_{(h,k,l)x,y,z} = \frac{d_{(h,k,l)x,y,z} - d_{0(h,k,l)}}{d_{0(h,k,l)}}$$

Where d_0 is lattice spacing for the stress free state, and hkl is Miller's indices for stress measurement.

Next, the strain and stress in the cartesian coordinate system can be expressed as follows.

$$\sigma_x = \frac{E}{(1+\nu)(1-\nu)} \left[(1-\nu)\varepsilon_x + \nu(\varepsilon_y + \varepsilon_z) \right]$$

$$\sigma_y = \frac{E}{(1+\nu)(1-\nu)} \left[(1-\nu)\varepsilon_y + \nu(\varepsilon_x + \varepsilon_z) \right]$$

$$\sigma_z = \frac{E}{(1+\nu)(1-\nu)} \left[(1-\nu)\varepsilon_z + \nu(\varepsilon_x + \varepsilon_y) \right]$$

Figures 1 and 2 show the results of the measured residual stress. The solid line in the figure indicates the theoretical value. The measurement stress and the theoretical value are corresponding, however it opens to dispute





Figure 2: Radial stress of specimen.

about the resolution. In the future, improvements of the beam intensity are scheduled, and MUSASI high angle port is scheduled to operate as RESA-II.

原子炉:JRR-3 装置:MUSASI(T1-3) 分野:中性子散乱(残留応力)

Performance Test of Radial Collimator Basic Performance Test

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An engineering materials diffractometer TAKUMI with time-of-flight method is recently proposed to build in Japan high intensity proton accelerator project (J-PARC). TAKUMI needs radial collimators located between the sample position and detectors, to define gauge sizes precisely and to control divergences of the scattered neutrons, i.e., to limit scattered neutrons from parts except the gauge size. Since TAKUMI has a large detector solid angle surrounding the sample position, radial collimators that enable all of detector elements with different positions to observe the same gauge size are needed. However, there was not a clear description showing a relation between gauge size and collimator design parameters. Therefore, we firstly derive both relational expressions, and then to produce a prototype radial collimator to confirm the expression. Here, we report the derivation process of the relational expression and a performance evaluation test result of the prototype collimator.

The basic design concept of a radial collimator is shown in Fig. 1^{1} . Here, we ignore the thickness of the blade for simplification and think a collimator with just twin blade. In general, the radial collimator design parameters are: sample-collimator path length l_1 , collimator blade length l_2 , sample-detector path length L_2 , collimator blade intervals at the entrance s_1 and the exit s_2 , and angular aperture of blade α . Here, we adopted other parameters to explain the effective widths of gauge W_g and detector W_d , geometrical maximum widths of gauge W_{qmax} and detector W_{dmax} . In our radial collimator design, the following conditions were applied for the definitions of W_q and W_{qmax} . (1) The scattered neutron from the sample shows a normal distribution



Figure 1: Definitions of radial collimator parameters

curve, and W_g is FWHM when W_{gmax} is assumed to have 95 % confidence interval of $\pm 2 \sigma$, and (2) α is assumed to be a solid angle of the detector width seen from the sample center. First of all, equation (1) consists of W_{qmax} .

$$W_{gmax} = \frac{(l_1 + l_2)s_1 + l_1s_2}{l_2} \tag{1}$$

By using a constant R, s_1 and s_2 are expressed as equations (2).

$$R = \frac{W_d}{L_2} = \frac{s_1}{l_1} = \frac{s_2}{l_1 + l_2}$$

$$\therefore \begin{cases} s_1 = Rl_1 \\ s_2 = R(l_1 + l_2) \end{cases}$$
(2)

By substituting s_1 and s_2 in equation (1) with equations (2) l_1 is obtained as follows.

$$W_{gmax} = \frac{(l_1 + l_2)Rl_1 + l_1R(l_1 + l_2)}{l_2}$$
$$\therefore l_1^2 + l_1l_2 - \frac{W_{gmax}l_2}{2R} = 0$$
$$l_1 = \frac{\sqrt{l_2^2 + \frac{2}{R}W_{gmax}l_2} - l_2}{2} \quad (\because l_1 > 0) \quad (3)$$

Next, the following expressions comprise be-

原子炉:JRR-3 装置:RESA(T2-1) 分野:中性子散乱(残留応力)

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cause W_{gmax} has 95 % confidence interval of the normal distribution, the FWHM value becomes W_q .

$$FWHM = W_g = 2\sigma\sqrt{2\ln 2} = \frac{W_{gmax}}{2}\sqrt{2\ln 2}$$
$$\therefore W_{gmax} = \frac{2}{\sqrt{2\ln 2}}W_g \quad (4)$$

When W_g , W_d , L_2 and l_2 are set to be 1 mm, 3 mm, 2 m and 350 mm, respectively, the calculated l_1 , s_1 and s_2 are 303.331 mm, 0.455 mm and 0.98 mm, respectively.

A prototype of radial collimator with the parameters shown above was made to have a total angular coverage of about 5° considering the cost balance. Mylar films coated by the gadolinium oxides (total thickness is $50\mu m$) are used for the blades. The performance tests of this radial collimator were carried out at RESA of JRR-3. In this measurement, the sample position of RESA was matched to a focal point of the radial collimator, and the scattered neutron intensities from the sample moving along the incident beam (x) direction were observed. The used sample was a nylon fiber of 1 mm in diameter, and the displacements with a range of $x = \pm 2$ mm from the focal point were given. An incident beam slit with enough size was chosen not to give any influences during sample movements.

Figure 2 shows the experimental result, average scattered intensities of the sample are plotted as the function of the displacement along x direction. The focal point position is around zero. The dotted line shows the result of the McStas simulation using the same collimator parameters. In this simulation, since statistics of the scattered neutrons were too low, the neutron source with the width equivalent to the sample size of nylon was placed at the sample position, and again was moved along the x direction. Similarly, the simulated curve is a plot of the average intensity versus the displacement. It can be seen that the plotted data indicates a normal distribution function of the intensity and displacement. The FWHM of the experimental data fitted by the Gauss function is 1.04 (1) mm, while that of the simulated one is 1.070 (9)



Figure 2: Intensity distribution of incoherent scattering from nylon with 1.0 mm diameter as a function of displacement along the incident beam direction. The solid line is a fitting line by Gauss function. The calculation result by McStas is shown in the dotted line.

mm. These values are very close to the design value of FWHM = 1 mm. Therefore, it can be concluded that the validity of the derived relational expressions and the performance of the prototype collimator have high reliabilities. The peak position of the experimental data shifts from the focal point by 0.1 mm. It may be due to the miss-alignment of the collimator or the sample. Since we positioned the collimator and the sample using a theodolite, such an alignment error might have appeared.

Transmission experiments were performed by measuring the peak intensities of (110) reflection of iron wire with ϕ 1 mm for the cases with and without radial collimator prototype. The ratio of intensitive with and without radial collimator, for (110) reflection of iron wire was 65.6 %. It seems that this value is mostly due to the normal distribution of beam that goes through the radial collimator.

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Performance Test of Radial Collimator Application Test on PSZ Material

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A relational expression between the design parameters of radial collimators and the defined gauge sizes, which are needed to develop radial collimators, has been established, and from the basic performances tests using a radial collimator prototype at RESA, the reliability of the expression were confirmed¹). Now, this radial collimator prototype was tried to use on the real applications. As an example of the application, mapping measurement on poled/unpoled PZT ($Pb(Ti,Zr)O_3$) was performed at RESA. PZT is a conventional piezoelectric ceramic containing a large amount of Pb. Developments of new Pbfree materials having piezoelectric (domain switching) properties as excellent as PZT are necessary from the environmental issues. Here, establishing materials design including piezoelectric properties will help to design microstructures of materials in a short time and will lead to the production of new materials with high troughput and multi functions. The domain switching properties of PZT are usually measured by means of X-ray diffraction (XRD) which measures only the near surface and needs a polished surface. On the contrary, we can measure the domain switching properties as a whole sample or in a defined gauge volume, by means of neutron diffraction (ND).

A tetragonal PZT (sintered at 1503 K) was used as samples. The lattice constants a and care 0.40401 nm and 0.41087 nm, respectively, and the spontaneous polarization direction is [100]. Block specimens with 4 mm width were cut from the sintered sample and polarization treatments on the width direction with 1.9 kV/mm at 373 K were conducted for 10 min. The poled and the unpoled specimens were serialised (layered) as shown in Fig.1. The specimens were set on the sample table in such a way that the scattering vector is parallel to the polarization (width) direction. The incident beam slit with 1 mm width and the radial collimator prototype for 1 mm width were used in the neutron diffraction experiment. The neutron diffraction scanning measurements were performed with 1 mm steps.



Figure 1: Specimen arrangement for ND measurement.



Figure 2: Typical (002) and (200) diffraction patterns of poled/unpoled PZT layered specimen shown in Fig.1.

Typical (002) and (200) diffraction patterns

原子炉:JRR-3 装置:RESA(T2-1) 分野:中性子散乱(残留応力)

1. 中性子散乱 11)その他

1. Neutron Scattering 11) Others

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Hydration Properties of Low Heat Portland Cement

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Low Heat Portland Cement (LHPC) clinkers have occupied important positions in materials of huge buildings. The compressive strength of the hardened LHPC may be strongly associated with the hydration properties of LHPC. Recently, quasielastic neutron scattering (QENS) technique has attracted much attention, because the QENS experiments provide us dynamical information of water molecules in materials. Even though cement clinkers have a lot of components, the hydration properties can be easily investigated from the point of view of the bound water in the hydrated cement.

In this work, the hydration properties of LHPC were studied using the highresolution pulsed cold neutron spectrometer, AGNES. The energy resolution is 120 μ eV, using PG002 monochromator (λ = 0.422 nm). The LHPC clinkers were hydrated with light water (H2O) at 28 degree in air. The H2O to LHPC mass ratio was kept constant at 0.5.

The time evolution of the QENS spectrum of the LHPC was obtained until 5 days of hydration at Q ~ 20 nm-1, where Q is the momentum transfer. The QENS spectrum is extremely broad in the early hydration period, while the elastic peak at around E = 0 meV is drastically grown in later hydration period. This behavior can be safely interpreted; the hydration process changes free water into -OH or water of crystallization. The signals of bound water (BW) and free water (FW) in the whole QENS spectrum were separated. In the first instance, the QENS intensities, I(Q,E), were represented as follows:

$$\begin{split} I(Q,E) = & \{(BW0+BW1)d(Q,E) \\ + & (FW1)L(Q,E)\}R(Q,E)+BG, \end{split}$$

where the first and second terms on the right-hand side indicate elastic and quasielastic scatterings for BW and FW, and BG is the constant background. d(Q,E) and L(Q,E) are represented as the delta function and Lorentzian, respectively. Note that the BW0 corresponds to the component of gypsum in the LHPC and was employed as the constant value. The R(Q,E), which is described by Gaussian, indicates the resolution function of the AGNES spectrometer. Finally, the excellent fits between the observed and calculated patterns could be obtained for all QENS data.

The ratio of the signal from the BW1 of bound water to the total signal of water, BW1 + FW1, was defined as BWI (= BW1 / (BW1 + FW1)), and calculated. The BWI as a function of t is shown in Fig. 1. The hydration process in three different stages could be clearly observed in our experiments using QENS. In the induction period, no hydration products are created up to ~ 0.1 in day. The consumption of FW is ~ 20% after 1 day of hydration, and then the hydration rate decreases gradually.



Fig. 1. Bound water index, BWI, of the hydrated LHPC as a function of hydration time.

Advanced KINKEN Triple-Axis Neutron Spectrometer, AKANE

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We have completed the renewal of the former double-axis diffractometer (KSD), and reconstructed it to a conventional tripleaxis spectrometer, AKANE, last year. As a second phase of renovation, we began to improve its performance, in particular, toward inelastic neutron scattering measurements. This year, we set up a new Ge (311) monochromator in order to gain high-flux neutron beam. As shown in Fig. 1(a), the new [previous] monochromator has the following specifications: (i) 20-cm height [10 cm], (ii) 13 blades with each vertical size of 1.5 cm [5 blades with 2-cm height each] and (iii) tunable vertical focus [a fixed bent]. As a consequence of these features, the beam focus is improved in space and a high luminescence is produced at the sample position. Figure 1(b) actually shows that the phonon intensity increases double with keeping the resolution as well as the S/N ratio.

In addition to the conventional triple-axis mode, AKANE has several options. First, a horizontally focused supermirror can be inserted in the incident beam path. Second, a postion-sensitive-detector bank can be set up after a sample under the doubleaxis mode. A combination of these new equipments has an advantage for taking diffraction patterns over a wide Q range in short time by using a small crystal. Further, Ohoyama et al. performed magnetic neutron diffraction experiments under 30-T pulsed magnetic fields on AKANE using a small MnF2 single crystal. In fact, they succeeded in detection of magnetic signals, which indicates a spin-flop transition under high fields. Thus, AKANE is challenging to develop new techniques of neutron scattering.

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Fig. 1. (a) Previous and new Ge(311) monochromators. (b) Comparison of phonon intensity between the two cases of monochromators.

1-11-3

Kinken Powder Diffractometer HERMES

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The main purpose of HERMES is to obtain high quality powder diffraction data by short time measurements with easy operation. HERMES is quite suitable for many cases of experiments such as measurements of a sample of a very small amount, measurements of a lot of samples, measurements at a lot of temperatures, measurements of very weak magnetic scattering. By its user friendly GUI, even beginners can enjoy neutron experiments on HER-MES.

Recently, HERMES is an important tool for structural investigations on hydrogen storage materials. In developments of novel hydrogen storage materials, understand of hydrogen structure is indispensable. Fig.1 shows the one of the recent results obtained on HERMES: the crystal structure of hydrogen compound Li2NH. Though hydrogen atoms seem to form cages centred on each nitrogen atom, the occupancy of the hydrogen cage is much smaller than 100% so that only one hydrogen exists around one nitrogen; owing to spatial or/and time average operation of the diffraction technique, the average structure seems like that in fig.1.

In 2006, the measurement system has been replaced from the previous UNIX base system on a workstation to the Labview base system on a Windows PC. This replacement has increased expandability of measurements of HERMES. Thus, the IRT group has been trying development of novel experiments techniques using HER-MES, as well as structural investigation by normal powder diffraction experiments; for instance, the neutron holography technique and scanning neutron diffraction technique, development of beam focusing device. Since these techniques need quite high experimental efficiency, HERMES is the best instrument for the experiments.

In 2006, 64 groups had experiments on

HERMES, 23 papers were published.

The detailed and latest information on HERMES can be obtained in the Web site: http://www.yamadalab.imr.tohoku.ac.jp/HERMES/index.html

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Contact person: Kenji OHOYAMA. Institute for Materials Research, Tohoku Univ.



Fig. 1. Crystal Structure of Li2NH determined on HERMES

1-11-4

Present Status of Tohoku University Triple-Axis Spectrometer TOPAN (6G)

Kazuaki Iwasa Department of Physics, Tohoku University

Up to the beginning of FY2006, the control system of TOPAN has been replaced to the LabVIEW PXI environment common for the spectrometers owned by ISSP. The stepping motors and the encoders were also renewed, and the automatic diaphragms and attenuators were installed. These upgrades were based on the financial supports of Grant-in-Aid for Scientific Research from MEXT and of Yamada Science Foundation.

Hereafter, some research subjects using the IRT beam time will be reviewed.

(1) Search for electronic ordering under high pressure: Phase transitions of electron orbital or multipolar degrees of freedom have been topics in condensed matter physics. Collaborators of Tohoku University have studied the ordering of vanadium 3d electron orbital in RVO3 under high pressure (D. Bizen et al.: J. Magn. Magn. Mater. in press (Proceedings of ICM)). In addition, collaborators of Tokyo Metropolitan University have been interested in the drastic change of transport properties in filled skutterudite PrFe₄P₁₂ under high pressure, which is expected to correlate with switch of the order parameter of Pr-ion 4f electrons (D. Kawana et al.: J. Phys. Soc. Jpn. 75 (2006) 113602). In order to understand the ordering mechanisms under high pressures in these systems, we established collaborations with JAEA group that has recently developed a compact anvil-type high-pressure apparatus (T. Osakabe et al.: J. Magn. Magn. Mater. in press (Proceedings of ICM)). We have succeeded in detecting magnetic ordering in TbVO₃ up to 4.3 GPa and $PrFe_4P_{12}$ up to 3.9 GPa. We obtained the stable experimental condition with this high pressure cell and the cryomagnet of ISSP producing magnetic field up to 5.8 T.

(2) Detection of the magnetic polariza-

tion of Ce ions due to octupolar ordering in $Ce_{0.7}La_{0.3}B_6$: Higher rank multipolar ordering has been recently observed in several *f*-electron systems. One of the most attractive systems is CeB₆ and La substituted ones. CeB₆ has been well known for the antiferro-quadrupolar ordering owing to the quartet crystal-field ground state of $Ce^{3+} J = 5/2$ multiplet. On the other hand, Ce_{0.7}La_{0.3}B₆ shows a so-called phase IV below 1.5 K, in which antiferro-type octupolar ordering was suggested from the resonant x-ray scattering result (D. Mannix et al.: Phys. Rev. Lett. 95 (2005) 117206, H. Kusunose and Y. Kuramoto: J. Phys. Soc. Jpn. 74 (2005) 3139). Such ordering is accompanied by the magnetic polarization within the Ce ion without net magnetic dipole moment, and the diffraction peaks are expected to appear in the large scattering vectors. The experiment for Ce_{0.7}La_{0.3}B₆ based on the collaboration with Tokyo Metropolitan University and ISSP was carried out, and we succeeded in detecting antiferromagnetic reflections whose intensities become larger in the higher scattering angles. This result is consistent with the octupolar ordering scenario.

(3) Application of PSD to polarized neutron experiments: We have examined the installation of position sensitive detectors (PSD) in TOPAN for observing reflections in the wide scattering-angle. Although the background level is high when it is used with the cryomagnet, we found that it can be applicable in polarized neutron spinflipping measurement at Bragg reflection points. Now we are trying to install neutron polarization option together with PSD in the LabVIEW system, to accomplish the search for electron ordering phenomena in the near future.

The description of TOPAN is seen in the

web site: http://sheat.phys.tohoku.ac.jp/ ~iwasa/TOPAN/index-j.html. The operation of TOPAN is based on the IRT of Tohoku University shown in the web site.

Detection of Hydrogen Trapped by Nano-scale Carbide by SANS

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Even a trace amount of hydrogen (H) can cause a premature fracture in high strength steels through concentrating at microstructural heterogeneity. Suppressing a diffusive H-concentration is one of the approaches to reduce the susceptibility of hydrogen embrittlement by introducing a nano-carbide (VC, TiC, NbC, etc.) as a H-trap site. A quantitative correlation of the dimensions of nanosized TiC to the amount of trapped H suggests that H is trapped at the TiC/matrix interface¹). However, due to the difficulty of detection of H and monoatomic layer segregation, no structural evidence has been obtained yet. SANS is one of the suitable techniques for detecting H-segregation in a nanoscale sub-Therefore, we measured SANS of stance. 97.62Fe-0.23C-0.25Nb-1.90Ni(at%) alloy with and without H.

The alloy was annealed at 873 K for 10800 sec for forming coherent nano-size NbC. NbC was chosen since it has the same crystal structure as TiC while it gives a larger scattering contrast of H compared to the TiC. 20×20 mm^2 plate samples with 2 mm thickness were cathodically charged with H. The concentrations of H in charged samples after the SANS experiment were 0.03 at% (6 wt ppm). Two different SANS experiments were conducted to determine the effect of H and to confirm reproducibility. In the 1st experiment, two pieces of samples with and without H-charge were adopted. In the 2nd experiment, the sample with H-charge was measured and then annealed at 473 K for 6000 sec for desorbing H. After the heat treatment, the sample was re-measured as a H-free sample. Because the alloy is ferromagnetic, we applied the magnetic fields of 1 T (1st ex.) and 0.5 T (2nd ex.) for separating nuclear and magnetic components of the scattering.

Figure 1 shows the nuclear components of

原子炉:JRR-3



Figure 1: Nuclear components of SANS profiles. \bigcirc & dotted curve: without H, \triangle & solid curve : with H

the SANS profiles obtained from parallel direction to the magnetic field. The difference between the alloys with and without H is detected as shown in Fig.1. In both experiments, the profiles of the alloys with H show higher intensity than those without H with good reproducibility. In the 2nd experiment, the H-charged sample shows same profiles with that of the 1st experiment, while the same sample shows weaker scattering intensity after annealing at 473 K. The possible origin of the change is only the difference of H-concentration. The difference of the intensity can be explained by both H-segregation at the interface of TiC/matrix and trapped H inside TiC precipitates. Although wider q-range measurements are required for determining which trap site is dominant, the results show the high potential of SANS to detect the trapped H even in the case that the total amount of H is in the wt ppm range.

References

 F. G. Wei and K. Tsuzaki, Metal. Mater. Trans. A, <u>37</u>, 331(2006).

装置: SANS-J(C3-2) 分野: 中性子散乱(その他)

2. 中性子ラジオグラフィ

2. Neutron Radiography

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2-1

研究テーマ:ダイナミック中性子トモグラフィ流動計測技術の開発(散乱線に関る基礎的試験) 表 題:ダイナミック中性子トモグラフィ基礎試験

ダイナミック中性子トモグラフィ基礎試験

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液体金属冷却型高速増殖炉の炉心熱 流動評価手法の信頼性向上に資する詳 細データを整備するため、ダイナミッ ク中性子トモグラフィ(DNCT)と命 名した4次元熱流動計測技術の開発に ついて報告する。平成18年度は、DNCT 装置を開発し、JRR-4で基礎試験を実 施した。

中性子ラジオグラフィ¹⁾を基盤技術 とした DNCT装置の概略図を図1に示 す。DNCT技術開発では、特に6ビームを 生成させる中性子制御系の開発が重要で ある。このため、モンテカルロ解析コード MCNPを用いて中性子およびγ線分布を 解析し、中性子制御系を設計した(図2)。 本装置では、投影角度が異なる6投影像を 3枚のコンバータ上に同時に生じさせ、こ れらを3台の高速度ビデオカメラで同時記 録する。

JRR-4 中性子ビーム設備に、回転体が組 み込まれている試験体と DNCT 装置を設 置して基礎試験を実施した。回転体は、ア ルミニウム円柱内にカドミウム線等を埋 め込んであり、0.5~1.5rps の範囲で回転 させた。記録速度は、125~500fpsで実施 した。瞬時 CT 値分布のデータ処理結果の 一例を図3に示す。本基礎試験により、改 良の余地はあるが6投影分の中性子ラジオ グラフィ映像を同時に高速度で記録する DNCT の基本原理が確認できた。

参考文献 1) 呉田昌俊、噴流工学、Vol. 20 [3], (2003), pp.24-31

本研究は、旧電源開発促進対策特別会計法 に基づく文部科学省からの受託研究として、 東京大学、日本原子力研究開発機構が実施し た平成 18 年度「液体金属熱流動評価のため の高速度 3 次元直接計測技術開発」の成果です。

原子炉:JRR-4 装置:中性子ビーム設備



図1 DNCT装置の概略図



図2 MCNP による熱中性子束解析結果



図3 瞬時 CT 値分布のデータ解析結果例

分野:中性子ラジオグラフィ (熱水力)

Neutron Tomography Analysis of Metal Hydride Canister with/without Hydrogen Charging and Discharging Cycle

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Hydrogen is expected as an ideal clean energy medium in the future, but it is difficult to store hydrogen compactly, lightly and safely. Metal hydride (MH) is one of the practical hydrogen storage methods, which can absorb and desorb a large amount of hydrogen atoms in the interstitial sites at ordinary temperatures and low pressure. MH is commonly manufactured by vacuum induction melting, and crushed into grain for expanding the reactive area with hydrogen. The MH grain becomes a fine powder with hydrogen charge/discharge cycle, because the lattice volume change with the cycle makes many cracks on MH grains. This pulverizing phenomenon makes the apparent MH volume larger and changes the internal structure of a MH tank. Because such structural change may cause performance degradation, the authors tried to visualize the internal structure of MH tanks by neutron tomography analysis.

Two MH canisters, MH-1 and MH-2, were prepared for neutron tomography analysis. Both canisters' rated hydrogen amount was 50 NL (normal liter). The dimension was O.D. 50 mm \times H 132 mm and the weight is about 700 g. Each canister contained 330 g MH grain (composition: La-Ce-Ni-Mn-Co) and six tubular glass sleeves (O.D. 2.8 mm) for improving hydrogen ventilation. MH-1 had been charged and discharged hydrogen once. On the other hand, MH-2 had undergone 1000 cycles. Both canister were discharged almost hydrogen and filled with 0.2 MPaG argon gas.

Figure 1 is the neutron tomography analysis result. The upside of Fig.1 shows the partially integrated images of the vertical crosssections of MH-1 (left) and MH-2 (right) and the downside shows the horizontal slice images at dashed line. It is easy to distinguish the six glass sleeves in MH-1 as dark straight lines in the vertical cross-section image and dark circles in the horizontal slice image, respectively. But the sleeve shapes become unclear after 1000 cycles test. The volume expansion of MH might collapse the tubular structure of the glass sleeves. The rising of the MH filling level also proves the MH volume expansion.

The neutron tomography analysis was carried out on 1-cycle and 1000-cycle MH canisters. The analysis revealed the filled MH expands its volume by the charge/discharge cycle, and collapsed the glass sleeves by hydrogen ventilation.



Figure 1: Neutron tomography analysis result of 1-cycle (MH-1, left) and 1000-cycle (MH-2, right) canister.

原子炉:JRR-3 装置:NRF(7R, C2-3-3-1) 分

分野:中性子ラジオグラフィ(新素材)
Development of Neutron Imaging Techniques for PEM Fuel Cells (II)

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The proton exchange membrane fuel cell (PEMFC) is a promising power source for transportation and consumer electronics because of its efficient energy conversion. The Japan Automobile Research Institute (JARI) standard type PEMFC was modified for this study such as replacements of stainless steel made fastening bolts and nuts with duralumin made ones.

Neutron images of the non-operated JARI standard type PEMFC for computed tomography (CT) were captured by a cooled CCD camera system. Projection images were obtained for three conditions: 1) dried condition, 2) anode side flow channel filled with water condition ("one-side-wet") and 3) anode/cathode side flow channels filled with water condition ("both-sides-wet"). Two types of reconstruction calculation were applied such as: 1) conventional FBP(filtered back projection) method, and 2) FBP method using specialized shading images as projection images for dried condition (specialized-FBP).

All figures are 2-D vertical slices reconstructed from CT images and aligned such as left: specialized-FBP, right: conventional FBP. Figures 1 and 2 show the results for "one-side-wet" condition. The left image of Fig.1 shows no water in the flow chnnel but the right image shows residual water. This is due to the insufficient dried-condition of the cell. Both images in Fig. 2 show water existence in the flow channel. As clearly understood, the quality of left image is better than that of the right one. Similar images are also obtained in Fig. 3 and 4 for "both-sides-wet". The left images clearly show water condition in both flow channels as compared to the right ones.

In this study, it was confirmed that the specialized-FBP method is superior to the convetional-FBP method and is useful for the visualization of water existence in a PEMFC.



Figure 1: 2-D vertical slice reconstruction at the cathode side carbon separator under anode side flow channel filled with water condition.



Figure 2: 2-D vertical slice reconstruction at the anode side carbon separator under anode side flow channel filled with water-condition.



Figure 3: 2-D vertical slice reconstruction at the cathode side carbon separator under anode/cathode side flow channels filled with water condition.



Figure 4: 2-D vertical slice reconstruction at the anode side carbon separator under anode/cathode side flow channels filled with water condition.

原子炉:JRR-3 装置:NRF(7R, C2-3-3-1)

分野:中性子ラジオグラフィ (その他)

Evaluation Research for Long Term Stability of Metal

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Neutron imaging technique was applied to improve the estimation of the amount of corrosion in an iron-remainder left underground for geologic isolation research and development.

Carbon steel (SM400B, $30 \times 30 \times 2$ mm thick) was macerated in simulated seawater under atmospheric conditions for almost 5 years, and its surface was corroded as shown in Fig.1 (left). It was used as a corroded carbon steel sample for neutron computed tomography (neutron CT). Copper plate (pure copper $30 \times 30 \times 2$ mm thick) was macerated in H₂S-contained dilute NaS solution for 3 days, and its surface was corroded as shown in Fig.1(right). It was used as a corroded copper plate sample for neutron imaging. The neutron CT of the corroded carbon steel sample was obtained by half rotation projection images with even angle increment. A filtered back projection method was applied as the reconstruction calculation algorithm.

Fig.2 shows projection images of the corroed carbon steel sample and computed tomograms. Horizontal lines in the projection image indicate the cut position of computed tomograms. Reduction of base metal of the carbon steel plate was clearly observed in the computed tomograms. Meanwhile, significant differences were not observed for the corroded copper plate sample as shown in Fig.3 except boundary of flaking. Because the corrosion layer was very thin, then the thickness of the base metal did not change. Experimental results show the effectiveness of neutron imaging to corrosion evaluation for carbon steel but not for copper.

This study was conducted as a collaborative study between Quantum Beam Science Directorate and Geological Isolation Research and Development Directorate.



Figure 1: Sample photograph: corroded carbon steel sample (left), corroded copper plate sample (right).



Figure 2: Projection image of corroed carbon steel sample (upper) and computed tomograms (lower) at the cutlines indicated in the projection image.



Figure 3: Projection image of corroded copper sample (upper) and vertically averaged plofile (lower).

「植物試料における水動態解析~特に根圏の研究について」

Analysis of the water statement in plant tissue.

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中西 友子

研究の目的と意義

植物体の実に9割は水が占め、植物におけるあら ゆる生理反応は水溶液中で行われ、植物の活動は水 の媒介無しにはおこりえない。特に、養分吸収や養 分の転流においては水が大きな役割を果たしている ことは周知の通りである。生きた植物において最も 重要な役割を果たしている化学物質は何といっても 水であるにもかかわらず、水そのものの知見につい ては非常に少ない。そこで我々は、生きたままの植 物体中の水の動きや分布を探るために、中性子ラジ オグラフィーを採用し、水に特異的な像を得ること を目的に実験を進めた。NRG は正確には水素の像の 可視化であるが、植物試料、特に根周辺の水につい て詳細に調べることができる方法は NRG が唯一の 手段に近い。

本研究では、マメ科植物の中で特に乾燥に耐性で あるササゲを使用し、土壌中の根周辺、いわゆる根 圏における水動態を観察した。これらのササゲはア フリカで自生してたササゲ約 2000 種から選抜され た乾燥に耐性な品種と乾燥に感受性な品種である。 ササゲは、根付近に水が全くない状態を2週間以上 続けても、再び水を与えると吸収を開始し生育を継 続することができる植物である。しかし、なぜこの ような強い乾燥耐性能を保持しているかについては 不明な点が多い。一般に自然環境下におけるササゲ は菌根菌と共生し、リン酸など必要な元素を菌根菌 から受け取る代わりに、根から光合成産物を菌根菌 に供与しかつ根の一部を菌根菌の住まいとして分け 与えている。この際に、菌根菌からも水分をも受け 取っているのではないか、もしくは、菌根菌が土壌 水分保持に寄与しているのではないか、という仮説 がある。そこで、ササゲと菌根菌が共生した状態に おける根圏水分量の測定を試み、共生が乾燥耐性に 関与しているか否かについての解析を行うことを目 的に研究を進めた。

根箱に播種後6日目のササゲを移植し、土壌水分 含量を30%に設定した砂(豊浦の標準砂)で2週間 生育させ、その後 NRG 撮影を行った。砂の最大容 水量は0.28ml/g、1枚の根箱に100g前後の砂を入れ た(図1)中央にナイロンメッシュで根箱を仕切り、 植物の根は上部まで、菌根菌は下部にもいき生育で きるように設定した。つまり、植物根は中間ナイロ ンメッシュよりも上部でのみ生育する一方、菌根菌 は砂全面を生育場所とすることができる設定にした。

使用したササゲは、各々、選抜された乾燥耐性品 種の、11979と感受性品種である、7778である。菌 根菌を接種していない区とした区を用意した結果、 全4区の設定となった。それぞれについて3連ずつ 根箱を用意し、合計12枚の根箱の撮影を行った。

撮影後、IP-Lab にて、輝度値を水分含量として検 量線を作成したのち、サンプル砂中の水分含量につ いて定量解析を行った。検量線用サンプルの土壌水 分量は、10、20、30、40%と設定した。



図 1a 根箱の条件設定の模式図

その研究をどのように行ったか



図 1b 用意した根箱(全 12 枚+ a)



図 1c 実際の根箱の写真

どのような結果を得たか

土壌水分量と画像の輝度値(中性子の透過度)と の検量線について図2示した。



図2 土壌水分量と中性子透過度との検量線

図 2 に示されるように、土壌水分量が 10%から 40%までの間において、土壌水分量と画像の輝度値 の間には liniar の関係があった。しかし、その相関 係数の二乗は 0.942 であり、より精度の高い解析に はさらなる検量線を求める工夫が必要であると思わ れる。

以後は、この検量線を基に、根箱砂中の水分含量を 算出した。

図3は実際に撮影した図と、それに擬似カラーを 施した図である。全ての画像は、左が乾燥感受性品 種である7778で、右が乾燥耐性品種の11979である。 また、図 3a が菌根菌未接種、図 3b が菌根菌接種し た場合の中性子線像である。一部の区では根が中央 のナイロン網を突き抜けていたが、ほとんどの区で は図に示されているように、根の生長は上部の砂の 中にとどまっていた。菌根菌がどこまで生育してい るかの判断については、中性子ラジオグラフィー撮 影用の試料はアルミ板で根箱を作成する必要があっ たため、撮影前の段階では確認することはできなか った。また撮影後、サンプルの放射線量が十分減衰 した後日に試料箱を開封して砂を調べてみたが、砂 が完全に乾燥していたこともあり菌根菌の生育状況 については把握することができなかった。どのよう に菌根菌の生育を把握するかが今後の課題として残 った。なお、撮影は菌根菌接種から4日目に行った。

結果(菌根菌を接種しなかった区)



左7778;中央:検量線用サンプル(上から土壌最大容水量の0%、10%、20%、30%、40%の水分を含む);右11979

図3a 菌根菌を接種しなかった場合の中性子線像。 右図は左図に擬似カラーを付したものである。画 像中の左根箱:7778(乾燥感受性ササゲ)、右根箱: 11979(乾燥耐性ササゲ) 中央:検量線用砂サンプ ル



左7778;中央:検量線用サンプル(上から土壌最大容水量の0%、10%、20%、30%、40%の水分を含む);右11979

図3b 菌根菌を接種した場合の中性子線像。

右図は左図に擬似カラーを付したものである。画 像中の左根箱:7778(乾燥感受性ササゲ)、右根箱: 11979(乾燥耐性ササゲ) 中央:検量線用砂サンプ ル

画像解析では根を含まないように砂中の水分含量 算出を行った。つまり、画像から該当箇所に ROI を かけ、輝度値を求め、得られた検量線を基に砂中の 水分含量を%で示した。その結果を図4に示す。上 部の水分含量は下部に比べて減少していた。その原 因としては、重力により水分が下部に移動したこと、 上部には根が張っているので、根が水分を吸収した ことなど考えられた。また、植物を植える前の砂中 の水分含量を30%に設定したにもかかわらず、ほと んど区において水分含量が30%以上となった。これ は検量線用サンプルが撮影までの間に乾燥したこと ならびに、今回は H を多量に含むアクリル棒を使用 して小さい検量線用サンプル箱を作成したことによ る中性子の散乱効果が影響したのではないかと思わ れる。

結果(土壌水分量(透過度から推測)の比較)



図4 砂中の水分含量の推定値(%)

菌根菌の接種の有無で砂中水分含量には変化がほ とんど見られなかった。また、乾燥耐性品種・感受 性品種間でも差が見られなかった。以上のことから、 当初の仮説であった菌根菌による土壌水分保持能力 については確認することはできなかった。

ちなみにササゲは乾燥耐性のものは通常あまり水 分を吸収しないが乾燥時において水分を多量に吸収 し始める。NRG 撮影施設においては照射後砂が飛散 する恐れがあるため極力試料はそのままの状態とし て箱の中は見なかったが、図3bでは右のササゲ(乾 燥耐性)の方が土壌水分量が減少していることが示 された。このことは、試料が撮影した4日目にはか なり乾燥負荷がかかった状態ではなかったかと推察 される。

菌根菌存在下におけるササゲの根の水分吸収動態 についてはまだ知見が無いため、今回の予備実験を 踏まえてこれからも本研究を進めていきたいと考え ている。

成果の公表

本研究成果については、学会発表等では公表してお りません。

2-6

| 研究課題名:造山帯の熱年代学的研究 | | | | | |
|---|-----------------------|------|--|--|--|
| 岡山理科大学自然科学研究所 兵藤 博信 | | | | | |
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| *Hiruzen Institute for Geology and Chronology | | | | | |

| 目的と意義 | 要因から単純な解釈ができない事象も多数存在す |
|---------------------------|-----------------------------|
| 造山帯はそれが形成される過程において複雑な | る。K-Ar年代法を改良した原子炉での放射化を用 |
| 地殻変動の歴史を経験する。その過程で形成さ | いる40Ar/39Ar法はそのような場合に段階加熱法を |
| れた岩石や変成を受けた岩石にはその記録が同 | 用いることで一度閉鎖系になった岩石がその後、熱 |
| 位体の拡散移動や元素分布として残り、特に放 | 的・鉱物学的変化をうけているかを判断する基準を |
| 射性崩壊をする同位体系ではそれを時計として | 提供する。 |
| 活用し、形成年代や変動年代とともにそれらが | この研究の目的は複数の事象が記録されていると |
| 起きた条件を推定することができる。それらの | 予想される造山帯の未知の岩石に対し40Ar/39Ar段 |
| 核種の中で40Kを用いたK-Ar年代測定法は、熱的 | 階加熱法を適用することにより精細な熱的履歴の |
| 擾乱に対するいくつかの鉱物中のアルゴン拡散 | 解析を行うことにある。それにより今まで測定して |
| パラメータがよく研究されており造山帯の冷却 | 得られた数値を単に年代とするのではなく、アルゴ |
| 過程でK-Ar系が閉鎖されたと考えることができ | ン同位体のmobilityを活用して岩体の削剥・上昇過 |
| る温度を閉止温度と定義して直接的に推定する | 程あるいは一度鉱物が形成された後でおきた事象 |
| ことが可能になっている。その半面、純粋な物 | のインジケータとして地質学的意味を明らかにす |
| 理系では推定できないいろいろな地質学的 | る。 |
| JRR-3、HR-2パイプ、地球科学試料放射化分析 | |

JRR-4、TBパイプ、地球科学試料放射化分析

実験及び結果

照射実験

対象とした岩石・鉱物はアイルランド北部のカ レドニアン造山運動の後期に貫入した花崗岩の母 岩におそらく花崗岩の熱水作用で生成した考えら れる2段階の成長をみせるトレモラ閃石(図1.図 2)、エジプトのパンアフリカン造山運動に伴って 噴出した火山岩の角閃石とカリウム長石の年代測 定を行った。エジプトの試料については測定が完 い。

対象とする鉱物を2ミリ径のドリル孔があいた アルミトレイにのせ、4-5段積みにしてボルトナ ットで固定する。この試料ホルダをJRR-3は簡易 アルミ容器、JRR-4は石英管に真空封入した後 0.5 ミリ厚のカドミウムを巻いて、6時間照射を1-4 サイクル行った。JRR-3の最初の試料については アルミ容器の内部にカドミウムシールドを入れて 照射したが、内部温度が上昇しすぎたためカドミ ウムが溶融した(>321℃)。ほとんどがアルミ製 であるにもかかわらず、放熱が効率的でないため 考えられ、今後 JRR-3 でカドミウムを用いるには 試料容器と照射用アルミ製カプセルとの熱的伝導 性を改善する必要がある。JRR-4 では石英容器の 外側にカドミウム板 0.5 ミリをかぶせたが、溶融 することはなかった。各アルミトレイには未知試





| かはまだすべてのデータが出そろっていないので | いく必要がある。 |
|--------------------------------|--|
| 早急な結論はできない。しかしトレモラ閃石がそ | これらの結果はまだ公の場で発表されていな |
| の結晶度から期待される予想に反して安定な年代 | い。それは照射後 3 ヶ月以上の冷却期間をおくこ |
| の記録を失っている可能性は高い。それは貫入岩 | とや、測定そのものに時間がかかること、マシン |
| 体の年代よりも若くなっていることからおおよそ | タイムが前年度からの試料を測定しているためあ |
| 推定される。すなわち貫入という事象よりさらに | いていないことなどによる。従って多くの測定は |
| 軽度な地質学的事象がアルゴン拡散を引き起こし | 実質平成 19 年度になってから実施されたもので |
| てしまったと考えられる。 | 発表の機会を得ていない。今後学会、論文誌など |
| 今回の申請は当研究室においてのJRR-3, | に発表していく予定である。 |
| JRR-4 での40Ar/39Ar年代測定用の初めての試料照 | 研究の性格上、同じ年度内に具体的業績を報告 |
| 射であるので中性子束密度の均質性についても評 | することは著しく困難である。今回の共同利用に |
| 価できるよう標準試料を試料サンプル内の各部に | よる照射とは無関係ではあるが、参考として 18 |
| 配置した。 | 年度以前に京都大学原子炉で行った中性子照射に |
| まず中性子束の均質性であるが、同じ照射条件 | よる40Ar/39Ar年代測定の結果から発表された論文 |
| で水平に配置した試料はややばらつきをみせる。 | を以下に参考のために列挙する。 |
| この現象は産業総合研究所の地質情報研究部門火 | 1) <u>Hyodo, H.</u> (2007) Laser Probe ${}^{40}\text{Ar}/{}^{39}\text{Ar}$ dating: |
| 山活動研究グループの年代研究室が行った JRR-3 | History and development from technical view. |
| における同様の実験でも報告され、中性子束の勾 | Gondwana Research, in press |
| 配がある程度存在することを示唆している。今回 | 2) Kawamura, M., Uchino, T., <u>Gouzu, C.</u> and <u>Hyodo,</u> |
| の実験では京都大学原子炉実験所の研究炉で行っ | <u>H.</u> (2007) 380 Ma 40 Ar/ 39 Ar ages of the high-P/T |
| た結果と比較すると、個々のデータのばらつきは | schists obtained from the Nedamo Terrane, Northeast |
| やや大きい。しかしばらつきはランダムであり、 | Japan. J. Geol. Soc. Japan, in press. |
| 系統的な中性子束密度の勾配による変化は特定で | 3) Kunimatsu, Y., 他 14 名 <u>兵藤 6 番目, 板谷 7 番目</u> |
| きなかった。今後いくつかの照射実験から集積す | (2007) A new Late Miocene great ape from Kenya and |
| る標準年代試料のデータを総合的にみて | its implications for the origins of African great apes |
| | and humans. Preceed. Nat. Acad. Sci. USA. in press. |

改造CNRFを利用する冷中性子ラジオグラフィのための要素技術の開発 Development of Digital Neutron Radiography Using Pulse Neutron Beam

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玉置 昌義

1. 本研究の目的

JRR-3M 高強度中性子ビームを利用したラジオグ ラフィ基礎技術開発の経験を基に、大強度パルス中 性子源建設進捗に合わせて,パルス中性子ラジオグ ラフィ対応基本技術を創製して,冷中性子と物質の 相互作用の特性を生かした科学研究用解析手段とな る中性子画像分光学と呼べる新たな学問分野確立に 必要な技術的支援を進める。

(1)先端的中性子画像撮像システム構築にむけて CNRF を用いて実験的に抽出した課題を解決するた めの要素技術開発の研究を進める。

(2)物質と冷中性子の相互作用の中性子スペクト ルによる変化を高中性子束およびパルスNRの開発 によって新しい分光学的利用法開発に関する基礎研 究を CNRF で進める。

2. 結果の概要

単色中性子ラジオグラフィ法の概念的および実験 的検討を進めた.結果の概要を以下にまとめる.

2-1 単色冷中性子ビームを利用するラジオグラフ ィ試行実験

速度選別器による単色冷中性子ビームを用いて, 冷中性子ラジオグラフィ実験を試行した。ブラッグ カットオフ波長(0.4nm)を挟む長波長と短波長域の 透視像から,鉄溶接部の歪みの影響が可視化出来た.

(1)<u>緒言</u>核種に固有の中性子全断面積を利用す る中性子ラジオグラフィの特性は冷中性子領域では より顕著に現れ、冷中性子を用いることによって熱 中性子の場合よりコントラストの強まった画像を得 ることが可能である。特にブラッグカットオフ波長 域では、熱中性子領域では得られない情報を得るこ とができる。グラファイトモノクロメータにより得 られる特定波長の中性子を用いた単色中性子ラジオ

JRR-3M, CNRF, 中性子ラジオグラフィ

グラフィの可能性を検討した。さらに中性子エネル ギースペクトルの影響を軽減するために速度選別器 による比較的エネルギースペクトル幅の小さい冷中 性子を用いてラジオグラフィ試行実験を行い、単色 冷中性子ラジオグラフィの可能性について検討し、 課題を明らかにした。

(2) 実験 実験はスイスのPSI SINQの新設冷中性 子照射施設ICONで行った。この施設に中性子源から の連続白色スペクトルビームの波長をvelocity selector装置を通して得られるスペクトル幅の狭め られた冷中性子を用い、CCDカメラにより画像を得た。 被写体としてFe、A1、黒鉛を用い、被写体のブラッ グカットオフ波長に応じていろいろな波長のビーム で撮影した。ビームの2次元強度分布歪みを補正し て得られた画像からそれぞれの物質の中性子透過率 を評価し、中性子断面積と中性子ビーム波長の関係 を求めた。Feの溶接部を含む部分をブラッグカット オフ前後の波長のビームで撮影し、溶接部の判別を 試みた。

(3)<u>結果・考察</u>求めたFe、A1(図1)、黒鉛の中 性子断面積は計算で求めた値とエネルギー依存では 相対的に合致し、ブラックカットオフも識別できる 結果を得た。断面積の絶対値としてみた場合には計 算による予想値と少し異なる値を示し定量性の面で は課題が多い。Feの溶接部の画像(写真(左))もブ ラッグカットオフ付近のエネルギーに対しては微小 な断面積の差も画像として識別できるという冷中性 子ラジオグラフィの可能性を確認できた。溶接部の 歪み、結晶構造,あるいは析出物の影響が可視化出来 る.本実験で用いたビームがまだ比較的広いエネル ギースペクトルを持ち、場所によるエネルギー分布 の違い(写真(右))を持っていることに由来する見か け上の断面積の分布が現れた。定量的には熱中性子 ラジオグラフィと同様に散乱中性子の影響、γ線の 影響も見られる。

(4) <u>今後の課題</u> 単色中性子ラジオグラフィの定 量化を向上させるために、γ線の影響除去法、ハニ カムコリメータを用いた散乱線の除去法、スペクト ル幅の狭い単色中性子を得るための単結晶フィルタ 一法などを統合し、単色冷中性子ラジオグラフィ技 術の体系的な確立を図る必要がある。



図1. AI中性子断面積の実験値と計算値、文献値との比較



写真(左) 0.4nm にピークをもつ中性子による Fe 溶接部の透視像(溶接部が明るく見える)

写真(右) 0.65nm にピークをもつ中性子による黒 鉛の見かけ断面積分布(黒鉛ブラッグカットオフ波 長 0.671nm)

2-2 相対微傾斜した単結晶群を用いる波長選別 器の原理とその検証

黒鉛単結晶を傾斜させて組み合わせた波長選別器 を提案・試作し、その単色冷中性子ビームを用いる ラジオグラフィ実験を試行し、その可能性を示した. (1) <u>緒言</u>特定波長欠損の中性子ビームを用い る中性子ラジオグラフィ(NR)を発展させ、複数組み 合わせた単結晶により、波長・スペクトル幅を任意 に制御した中性子ビームを得る方法を提案する.原 理検証と中性子波長選別器(スリット)の可能性を、 特定波長欠損および単色ビームによるNR撮像を行う ことにより、実験的に示す.

(2) <u>原理</u> スペクトルをもつ中性子ビームは、 ブラッグカットオフ(BC0)型およびスーパーミラー (逆ブラッグカットオフ:ABC0)形フィルターを透過 する事により、スペクトル幅の狭い単色中性子ビー ムになる(図 1).フィルターは、モザイク度相当の 角度を傾けて重ねた単結晶群で構成される。透過中 性子ビームは、それぞれの単結晶により特定波長の 回折を起こし、幅広い波長域に欠損をもつスペクト ルに変形する. λ1 およびλ2 に対応する回折角に 設定した単結晶を基準に、BCO型フィルターでは低角 度側に、ABCO型フィルターでは高角度側に、順次単 結晶を傾斜させて重ねる.両フィルターの組み合わ せが、λ1からλ2の波長域をもつ単色中性子ビーム を得る波長選別器(スリット)として機能する.

(3) <u>実験</u> NRによる検証実験はJAEA JRR-3M TNRF・CNRFで行った.モザイク度公称値 0.4、0.7、 1.0 および 2.0 度の黒鉛単結晶 4 個の設定角を種々 組み合わせて、BCO型およびABCO型のフィルター、お よび両フィルターによる中性子波長選別器(スリッ ト)を構成し、C-CCDおよびBAS-NDによるNR撮像系に 組み込んで使用した(図2は単結晶群設定例).ま ず、フィルターの機能を確認するために中性子透過 率評価用のNR像を得た.さらにフィルターの中性子 波長調整機能を検証するために、鉄のBCO(0.40nm) 前後の波長域にわたって巨視的中性子全断面積(Σ t)評価用のNR像を得た.

(4) <u>結果・考察</u> 黒鉛単結晶のモザイク度およ びその組み合わせに対応して変化する中性子透過率 からフィルター効果を確認した. 傾斜させて組み合 わせた黒鉛単結晶群を透過した中性子ビームによる 鉄被写体のNR像から評価したBCO前後の鉄の Σ tは、 波長フィルターの検証とスリットの可能性を示して いる(図3). しかし、限られた単結晶群で選別でき る波長域は冷中性子スペクトルの裾野除去には不十 分で、求めた鉄の Σ tの波長依存性は相対的傾向に とどまった.

(5) <u>今後</u>中性子速度選別器による波長域幅の 制限およびスペクトルのTOF計測を併用して、定量的 検証をすすめる.



図1 中性子波長スリットの原理



図2 黒鉛単結晶群の角度設定例



図3 鉄の見かけΣ_tの中性子波長依存性

3. 本研究の成果

(1)玉置 昌義、"解説 中性子ラジオグラフィ(N RT)の将来展望"、非破壊検査 第53巻、2号、
84-87ページ(2004).

(2) Masayoshi Tamaki, "Conceptual monochromatic digital neutron radiography using continuous cold neutron", Nuclear Instruments and Methods in Physics Research A32-37(2005).

(3) Masayosgi Tamaki, Kazuhiro Iida, Noriaki Mori, Eberhard H. Lehmann, Peter Vontobel, Mirko Estermann, "Dy-IP characterization and its application for experimental neutron radiography test under realistic conditions", Nuclear Instruments and Methods in Physics Research A320-323(2005)

イメージングプレートを用いる定量的中性子ラジオグラフィの開発と応用研究

Development of Dy-IP for Neutron Imaging for Nuclear Materials under Realistic Conditions

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1. 本研究の目的

JRR-3M 高強度中性子ビームを利用したラジオグ ラフィ基礎技術開発の経験を基に、定量性確立を進 めてきたイメージングプレート・冷却型 CCD を利用 する広ダイナミックレンジ・デジタルラジオグラフ ィ画像取得・処理・解析システムの開発研究をさら に高度化するとともに、中性子と物質の相互作用の 特性を生かした科学研究用解析手段となる中性子画 像分光学と呼べる新たな学問分野確立に必要な技術 的支援を進める。

先端的中性子画像撮像システム構築にむけて CNRF・TNRF を用いて実験的に抽出した課題を解決す るための要素技術開発の研究を進める。具体的には、 冷却型 CCD 中性子カメラ,中性子用およびX線用イ メージングプレートの併用による定量的画像情報の 取得・処理・解析方法の高度化を図っていく。

2. 結果の概要

核燃料照射後試験を念頭に、γ線不感処理式イメ ージングプレートの原理を提案した.酸化ジスプロ シウム(Dy203)を揮尽性発光体(PSL体)に混ぜ込ん だイメージングプレート(Dy-IP)を製作し、機能の検 証、特性の評価、最適仕様の確定などを進めた.開 発した Dy-IP を、照射後の核燃料、スポレーション ターゲット、核融合材料の非破壊透視検査に実用的 に応用した.

(1)<u>緒言</u>:中性子イメージング技術を科学研究手段として高度化するために、散乱中性子除去および γ線カブリ評価に関する手法の確立につづいて、更なる中性子イメージング技術の高度化と実用的応用 のために、核燃料の照射後試験に使用可能なγ線不 感式撮像法の開発に取り組んだ. (2) <u>背景</u>: BAS-ND(酸化ガドリニウム入りIP)の開 発と商品化は中性子科学研究に関わるイメージング 手法に飛躍的な高度化をもたらした。しかし、実験 場におけるIP画像のγ線によるカブリは、BAS-NDに とって避けられない解決すべき課題であった(図 la). ジスプロシウム(Dy)とX線用イメージングプレ ート(XIP)を組み合わせる間接中性子イメージング 法(図 lb)でこの問題を克服し、マルチチャンネルコ リメータ(MC)による散乱中性子除去法を併用して科 学研究への応用に必要とされる定量性の確保を検証 した. この間接撮像手法を高度化するために、Dyを XIP内に混ぜ込むことで、γ線不感処理式中性子イメ ージングの新概念を提案した.

 (3) <u>原理</u>: 中性子イメージングデバイスとしての Dy入りIP(Dy-IP)による撮像原理を示す(図 2 左).
 中性子イメージング過程において、照射中性子線量 に比例してDy-IP中のDyが放射化されると同時に、 PSL体自身もγ線やベータ線に感光する.

時には飽和して画像情報を失う.そこで中性子照射 直後に可視光線を当てて IP の潜像を一旦消去する. 続いて遮光した状態で放射化した Dy からのβ線に よって IP を自己露光させ、二次元潜像を形成させる. 最後に IP 読み取り器でデジタル画像化し、画像解析 を行う.

(4) 検証: 揮尽性蛍光体 (PSL体: BaFBr: Eu) とDy203 を等モル比に混ぜたDy-IPを試作し、JRR-3M TNRFに おいて、標準的には、1-10 秒間照射、5-15 分間可視 光下 y 線カブリ消去、遮光下 1-24 時間自己露光後、 IP読み取り・画像解析を行って中性子透視画像が得 られることを検証した(1). Dy/XIPの組み合わせの 間接撮像法に比べてより良好な中性子イメージが得 られた. 更にMCを併用して散乱中性子の影響を取り 除くことによって高い定量性が確保できることを検 証した.

JRR-3M, TNRF, 中性子ラジオグラフィ

(5) 評価: Dy-IPの感度・空間分解能の蛍光体層厚 さおよび(Dy203/PSL体)混合比依存性を明らかにし た(図3)。さらにGd203 層をPSL体層に裏打ちしてIP 後方からの散乱中性子の影響を除去することで、更 によい定量性が確保できることを明らかにした. PSL体にDy203を40モル%混合した150μ厚さの蛍光 体層と 100μ厚さのGd203 後方散乱中性子吸収体層 からなるDy-IPが最適仕様である.

(6) <u>応用</u>:スイス ポールシェラー研究所 (PSI) の中性子イメージング施設NEUTRA にて、照射後核 燃料ピンの中性子イメージングに応用し(図 2b)、燃 料ペレット・ジルカロイ被覆管の寸法、ジルカロイ 被覆管壁の水素析出物、燃料濃縮度(U-235 換算)の 評価を行った(図 4). PSI中性子源SINQや世界各国 のスポレーションターゲット開発のために、鉛、水 銀などの照射後ターゲットの中性子イメージングに Dy-IPを応用した(図 5).現在,次世代ターゲットの 照射後試験を進めている.また、照射後核融合炉材 料の中性子透視試験にもDy-IPを応用した.

(7)<u>結言</u>:開発したDy-IPは定量性を確保できる高 性能中性子イメージングデバイスであり、核燃料、 核融合材料およびスポレーションターゲットの照射 後非破壊透視検査に有用であることを確認した.











図4 半影法によるウラン濃縮度の評価



図5 スポレーションターゲットNR像と集合体内配置

3. 本研究の成果

(1) Masayoshi Tamaki, "Conceptual monochromatic digital neutron radiography using continuous cold neutron", Nuclear Instruments and Methods in Physics Research A32-37(2005).

(2) Masayosgi Tamaki, Kazuhiro Iida, Noriaki Mori, Eberhard H. Lehmann, Peter Vontobel, Mirko Estermann, "Dy-IP characterization and its application for experimental neutron radiography test under realistic conditions", Nuclear Instruments and Methods in Physics Research A320-323 (2005) 3. 即発ガンマ線分析

3. Prompt Gamma-ray Analyses

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Determination of Cadmium in Polymer Samples by MPGA

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Prompt gamma ray analysis (PGA) is a high-sensitive, high-precision, multi-element and non destructive method¹). The method is used in various fields, such as geology, archaeology, earth science, industry and environmental science. However, the difficulty of quantification arises when the gammaray intensity from the trace element of interest is not strong enough in comparison with the background gamma rays from the large amount of other elements in the sample. In order to improve the sensitivity of PGA, we proposed to introduce multiple gamma ray detection method to the PGA, and constructed a neutron beam line for multiple prompt gamma ray Analysis $(MPGA)^{2-4}$.

In summer 2000, the EU commission approved drafts of the guidelines for waste electrical and electronic equipment (WEEE) and the guidelines for the restriction of the use of certain hazardous substances in electrical and electronic equipment (RoHS). The guidelines establish that users can return waste electrical and electronic equipment to the manufacturers free of charge. This regulation applies to electrical household equipment, electrical tools, consumer electronics, IT and telecommunication equipment, lamps and lights, toys, medical equipment, monitoring and control instruments as well as slot or vending machines. Lead, mercury, cadmium, chromium (VI), polybrominated biphenyls (PBB) and polybrominated diphenyl ethers (PBDE) are prohibited. The following experimental work on the investigation of cadmium containing polymers demonstrates the efficiency of the MGPA technique as a screening method according to the RoHS guidelines. Cadmium as a toxic heavy metal shows the most intensive gamma ray signal at 558 and 651 keV. A cadmium standard sample provided by the Institute for Reference Materials and Measurements (IRMM) was measured for about 10 minutes at the JRR-3 reactor (C2-3-2). The total event rate was about 1.7 k count/sec. Figure 1 shows a typical signal profile of the gamma ray of cadmium in IRMM B6 sample on two dimensional spectrum. The IRMM B6 sample contains 54 ppm cadmium. From the experiment, we estimated the quantification limit of cadmium in a polymer sample to be about 0.1 ppm with a new MPGA detector system which consists of 8 clover Ge detectors, 4 coaxial Ge detectors and 2 twin Ge detectors. MPGA does not require any sample preparation. Therefore, MPGA may be used as a screening analysis for RoHS related samples.



Figure 1: Cadmium gamma ray peak of IRMM B6 sample on two dimensional spectrum. Cadmium emits strong gamma ray pair of 558 and 651 keV.

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- 2) Y.Toh, et al., Appl. Radiat. Isotopes, $\underline{64}$, 751(2006).
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原子炉: JRR-3 装置: MPGA(C2-3-2) 分野: 即発 y 線分析実験(工業材料)

火山岩, 堆積岩試料の即発γ線分析

Neutron-induced prompt gamma ray analyses of volcanic and sedimentary rocks

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楠野 葉瑠香, 新藤 智子,

| 国立科学博物館 | 佐野 貴司 |
|---------|-------|
| 東京経済大学 | 新生 裕尚 |

我々の研究グループは4つの異なる研究機関に属 するメンバーから構成されている.マシンタイムを 100%有効に使うことが難しいので,お互いが助け合 って分析準備や測定を行ってきた.しかし個々のメ ンバーの研究テーマは独立しているので以下に各メ ンバーごとに研究成果の報告をさせていただく.

A. 北部九州玄武岩類中のホウ素含有量の時 間的・空間的変化

1. はじめに

北部九州は、四国海盆(15~26 Ma)と古いフィ リピン海プレート(40~60 Ma))の年代が異なる二 枚の海洋プレートがユーラシアプレート下に沈み込 む複雑なテクトニックセッティングに置かれている. そのような特異な構造場で、海洋プレートから放出 された流体が生成するマグマ組成にどの程度反映さ れているのかを調べることは、地球における物質循 環を理解する上で重要である.

海洋底堆積物,変質 MORB に多量に含まれるホウ 素は,他の沈み込み成分に比べ非常に流動性に富む ため,マグマソースへの流体の寄与の良いトレーサ ーとなる.研究協力者の三好は,沈みこむフィリピ ン海プレートが北部九州直下のマグマソースに与え た影響を,玄武岩~安山岩のホウ素含有量を用いて 検討した.

2. 分析試料

火山岩試料は、壱岐火山、玄海島、北松浦地域、 由布火山、鶴見火山、鬼箕火山、九重火山、耶馬渓 地域、阿蘇火山、雲仙火山、多良岳火山、大矢野島、 天草地域から採取し、全試料について即発ッ線分析

JRR-3M,即発ガンマ線分析装置

を行った.

3. 分析結果・考察

フィリピン海プレートの北部九州への沈み込みが 開始する前(11~6 Ma)に活動した玄武岩類は前弧 側,背弧側の両方で低い B/Sm (0.5~1.3), B/Zr (0.02 ~0.05), B/Nb (0.2~0.5)比を示す.特にそれらの B/Nb 比は,マントルの B/Nb 比(0.05~0.5)と同等 である (Fig. A1).このことは11~6 Ma の間には海 洋プレートの沈み込みの影響はほとんどなかったと いうことを示している.



中性子利用分析・即発ガンマ線分析

た後(6 Ma 以降)に活動した玄武岩類のうち,火山 フロントに位置する阿蘇火山の玄武岩類は北部九州 玄武岩類の中で最も高い B/Sm (1.6~4.3), B/Zr (0.07 ~0.16), B/Nb (1.4~3.7) 比を示す (Fig. 1). 由布, 鶴見,九重火山も阿蘇と同様に火山フロントに位置 するが,それらの玄武岩類は阿蘇玄武岩類に比べて 著しく低い B/Sm (0.9~1.9), B/Zr (0.04~0.07), B/Nb (0.5~0.9) 比を示す.また,背弧側に分布する玄武 岩類の B/Sm, B/Zr, B/Nb 比は,フィリピン海プレ ートの沈み込み開始前後でほとんど変化しない (Fig. A1).

阿蘇玄武岩類の B/Nb 比は,比較的古く冷たい海 洋プレート(太平洋プレート:130 Ma)が沈み込む 東北日本弧,カムチャッカ弧,伊豆-マリアナ弧な どの玄武岩類と同等である.それに対し,由布,鶴 見,九重火山の玄武岩類の B/Nb 比は,比較的若く 熱いプレートが沈み込むカスケード,メキシコ

(MVB)の玄武岩類の B/Nb 比と同等である. 以上のことは、阿蘇火山直下には古い(冷たい)フィリピン海プレート、由布、鶴見、九重火山直下には若い(熱い)四国海盆がそれぞれ沈み込んでいることを示唆しているのかもしれない.

4. 今後の課題

これまでの分析結果から,北部九州における海洋 プレート由来物質の循環が,これまで東北日本など で提唱された沈み込み帯物質循環モデルと大きく異 なる可能性がわかってきた.今後,西南日本~琉球 弧に分布する火山岩のホウ素含有量を調べ,広域的 にフィリピン海プレート由来物質の循環を明らかに したい.他に,1)地設構成物質(特に深成岩体)の ホウ素含有量分析によって,1億年以上前の物質循 環を明らかにし,さらに,玄武岩マグマへの地殻混 成作用の影響を定量的に理解すること,2)フィリピ ン海プレートの海洋底堆積物および海洋地殻玄武岩 のホウ素含有量から,火山直下マントルに付加する 流体の化学組成を推定することが課題である.

B. 即発γ線分析によるホウ素の地球化学図

1. はじめに

地球化学図は地殻表層における元素の濃度分布を 示し、自然環境の固相における化学的バックグラウ ンドの情報を得ることができる。また、人為的環境 変化を評価する上での指標ともなる。立正大学地球 環境科学部宇宙地球化学研究室では 2000 年度から 埼玉県西部に位置する秩父市の荒川上流域における 地球化学図を多元素にわたり作成してきた。その中 でもホウ素は生活環境情報を知るうえで重要である。

2. 試料

試料は尾根に囲まれた流域の平均化学組成を示す ものとして河川堆積物を用いた。平成16,17,18 年度は荒川上流の中津川,河原沢川,赤平川流域か ら試料を採取した。

3. 分析

試料の分析手順を図 B1 に示した。即発γ線分析 (PGA) 用の分 析試料は分析上不都合な水を 900℃で乾燥し完全脱水させたものを用いた。

4. 結果・考察

平成 16, 17, 18 年度の試料の 分析結果を表 B1 に、その結果を 元に作成した地球化学図を平成 16 年度以前の値も含めて図 2 に示し た。試料採取地域の地質は砂岩・ 泥岩を主体として、中津川流域の 北中央部には花崗岩が分布して いる。

試料 T 自然乾燥 IJ. 粉末化 Ð 110℃乾燥(乾燥器) ↓ 重量測定 900℃乾燥(電気炉) ↓ 重量測定 ペレット作成 テフロン袋に封入 中性子照射 (JRR-3炉PGA装置) Ū **即発γ線測定**

図 B1. 分析手順

地球化学図から、中津川流域の北中央部を中心に ホウ素が高濃度であることが分かった。これは花崗 岩の貫入による鉱物化作用でホウ素が濃集したため と考えられる。



図 B2. ホウ素の地球化学図

5. まとめ

図 B2 は 2000~2006 年度までの 224 試料の分析 結果をもとに地球化学図を作成した。2006 年度採取 地域の赤平川流域は中津川流域ほどの濃度分布差が 見られない。これは背景の地質が主に泥岩を主とし 似た地質であるためと考えられる。

| 試料名 分析値 ppm 試料名 分析値 ppm 0401 111 0523 72 0619 74 0402 152 0524 63 0620 63 0403 131 0525 84 0621 49 0404 132 0526 82 0622 78 0405 121 0527 83 0623 83 0406 124 0528 156 0624 79 0407 104 0529 158 0625 70 0408 103 0530 136 0628 83 0410 108 0532 96 0628 43 0411 10 0533 80 0620 78 0413 148 0535 79 0631 49 0414 98 0536 61 0632 56 0413 148 0537 66 0633 33 0414 | 21 = | 1 /// 4 | | ~ ~ ~ ~ | | VI/HZIS |
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| 0402152 0524 63 0620 63 0403 131 0525 84 0621 49 0404 132 0526 82 0622 78 0406 124 0527 83 0623 83 0406 124 0528 156 0624 79 0407 104 0529 158 0625 70 0408 103 0530 136 0626 86 0409 115 0531 114 0627 70 0410 108 0532 96 0628 43 0411 110 0533 80 0629 41 0412 130 0534 89 0630 78 0411 138 0535 79 0631 49 0414 98 0536 61 0632 56 0415 83 0537 66 0633 50 0416 111 0538 81 0634 60 0417 112 0539 76 0635 46 0418 115 0540 68 0636 33 0420 146 $05801-3$ nd 0642 71 0422 91 $05801-3$ nd 0642 71 0422 91 $05802-3$ 60 0642 71 0424 228 $05802-3$ 60 0644 43 0425 246 $05802-3$ 60 0644 43 </td <td>0401</td> <td>111</td> <td>0523</td> <td>72</td> <td>0619</td> <td>74</td> | 0401 | 111 | 0523 | 72 | 0619 | 74 |
| 0403131 0525 84 0621 49 0404 132 0526 82 0622 78 0405 121 0527 83 0623 83 0406 124 0529 158 0625 70 0407 104 0529 158 0625 70 0408 103 0530 136 0626 86 0409 115 0531 114 0627 70 0410 108 0532 96 0628 43 0411 110 0533 80 0629 41 0412 130 0534 89 0630 78 0413 148 0535 79 0631 49 0414 88 0536 61 0632 56 0415 111 0538 81 0634 60 0417 112 0539 76 0635 46 0418 115 0540 68 0636 33 0420 146 $05R01-2$ 3 0639 101 0422 91 $05R01-3$ nd 0640 60 0421 85 $05R01-5$ 10 0642 71 0424 228 $05R02-1$ 25 0644 71 0425 80 $05R02-3$ 60 0644 43 0421 156 $05R02-3$ 60 0644 43 0502 375 $05R06$ <td>0402</td> <td>152</td> <td>0524</td> <td>63</td> <td>0620</td> <td>63</td> | 0402 | 152 | 0524 | 63 | 0620 | 63 |
| 0404 132 0526 82 0622 78 0405 121 0527 83 0623 83 0406 124 0528 156 0624 79 0407 104 0529 158 0625 70 0408 103 0530 136 0626 86 0409 115 0531 114 0627 70 0410 108 0532 96 0628 43 0411 100 0533 80 0630 78 0413 148 0535 79 0631 49 0414 98 0536 61 0632 56 0415 83 0537 66 0633 33 0416 111 0538 81 0637 43 0420 146 05R01-1 3 0638 85 0421 85 05R01-2 3 0641 73 | 0403 | 131 | 0525 | 84 | 0621 | 49 |
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| 0406 124 0528 156 0624 79 0407 104 0529 158 0625 70 0408 103 0530 136 0626 86 0409 115 0531 114 0627 70 0410 108 0532 96 0628 43 0411 110 0533 80 0629 41 0412 130 0534 89 0630 78 0413 148 0535 79 0631 49 0416 111 0538 81 0634 60 0417 112 0539 76 0635 46 0418 115 0540 68 0637 43 0420 146 05R01-1 3 0643 74 0422 91 05R01-3 nd 0644 71 0422 91 05R02-1 25 0644 71 | 0405 | 121 | 0527 | 83 | 0623 | 83 |
| 0407 104 0529 158 0625 70 0408 103 0530 136 0626 86 0409 115 0531 114 0627 70 0410 108 0532 96 0628 43 0411 108 0532 96 0628 43 0411 110 0533 80 0629 41 0412 130 0534 89 0630 78 0413 148 0535 79 0631 49 0414 98 0536 61 0632 56 0415 83 0537 66 0633 50 0416 111 0538 81 0634 60 0417 112 0539 76 0635 46 0418 115 0540 68 0637 43 0420 146 $05701-2$ 3 0639 101 0422 91 $05701-3$ nd 0644 71 0424 228 $05701-4$ 13 0644 71 0424 228 $05702-1$ 25 0644 71 0426 246 $05702-3$ 8 0647 71 0424 150 $05702-3$ 8 06457 73 0501 160 05705 16 0648 43 0502 375 05706 19 06552 64 0503 136 05707 | 0406 | 124 | 0528 | 156 | 0624 | 79 |
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| 0412 130 0534 89 0630 78 0413 148 0535 79 0631 49 0414 98 0536 61 0632 56 0415 83 0537 66 0633 50 0416 111 0538 81 0634 60 0417 112 0539 76 0635 46 0418 115 0540 68 0636 33 0419 62 0541 368 0637 43 0420 146 $05R01-1$ 3 0639 101 0422 91 $05R01-3$ nd 0640 60 0423 76 $05R01-3$ nd 0640 60 0423 76 $05R01-4$ 13 0641 73 0424 228 $05R01-5$ 10 0642 71 0425 80 $05R02-1$ 25 0644 71 0426 246 $05R02-3$ 60 0646 48 0429 94 $05R03$ 8 0647 71 0430 81 $05R05$ 16 0649 43 0502 375 $05R06$ 19 0655 32 0503 136 $05R07$ 15 0651 36 0504 603 $05R07$ 73 33 33 0506 146 0602 62 0654 47 0507 314 0603 | 0411 | 110 | 0533 | 80 | 0629 | 41 |
| 0413 148 0535 79 0631 49 0414 98 0536 61 0632 56 0415 83 0537 66 0633 50 0416 111 0538 81 0634 60 0417 112 0539 76 0635 46 0418 115 0540 68 0636 33 0420 146 05R01-1 3 0638 85 0421 85 05R01-2 3 0639 101 0422 91 05R01-3 nd 0640 60 0423 76 05R01-4 13 0641 73 0424 228 05R01-5 10 0642 71 0425 80 05R02-1 25 0644 71 0427 193 05R02-3 60 0646 48 0428 156 05R05 16 0649 43 | 0412 | 130 | 0534 | 89 | 0630 | 78 |
| 0414 98 0536 61 0632 56 0415 83 0537 66 0633 50 0416 111 0538 81 0634 60 0417 112 0539 76 0635 46 0418 115 0540 68 0636 33 0419 62 0541 368 0637 43 0420 146 05R01-1 3 0638 85 0421 85 05R01-2 3 0639 101 0422 91 05R01-3 nd 0640 60 0423 76 05R01-4 13 0641 73 0424 228 05R01-5 10 0642 71 0425 80 05R02-3 60 0644 48 0429 94 05R03 8 0647 71 0430 81 05R05 16 0649 43 | 0413 | 148 | 0535 | 79 | 0631 | 49 |
| 0415 83 0537 66 0633 50 0416 111 0538 81 0634 60 0417 112 0539 76 0635 46 0418 115 0540 68 0636 33 0419 62 0541 368 0637 43 0420 146 05R01-1 3 0638 85 0421 85 05R01-2 3 0639 101 0422 91 05R01-3 nd 0640 60 0423 76 05R01-5 10 0642 71 0425 80 05R01-6 8 0643 74 0426 246 05R02-1 25 0644 48 0429 94 05R03 8 0647 71 0430 81 05R04 31 0648 31 0501 160 05R07 15 0651 36 <td>0414</td> <td>98</td> <td>0536</td> <td>61</td> <td>0632</td> <td>56</td> | 0414 | 98 | 0536 | 61 | 0632 | 56 |
| 0416 111 0538 81 0634 60 0417 112 0539 76 0635 46 0418 115 0540 68 0636 33 0419 62 0541 368 0637 43 0420 146 05R01-1 3 0638 85 0421 85 05R01-2 3 0639 101 0422 91 05R01-3 nd 0640 60 0423 76 05R01-4 13 0641 73 0424 228 05R01-5 10 0642 71 0425 80 05R01-6 8 0643 74 0426 246 05R02-1 25 0644 71 0427 193 05R02-3 60 06464 48 0429 94 05R03 8 0647 71 0430 81 05R07 15 0651 <td< td=""><td>0415</td><td>83</td><td>0537</td><td>66</td><td>0633</td><td>50</td></td<> | 0415 | 83 | 0537 | 66 | 0633 | 50 |
| 0417 112 0539 76 0635 46 0418 115 0540 68 0636 33 0419 62 0541 368 0637 43 0420 146 05R01-1 3 0638 85 0421 85 05R01-2 3 0639 101 0422 91 05R01-3 nd 0640 60 0423 76 05R01-4 13 0641 73 0424 228 05R01-5 10 0642 71 0425 80 05R02-1 25 0644 71 0427 193 05R02-1 25 0644 71 0427 193 05R02-3 60 06448 31 0428 156 05R05 16 06449 43 0501 160 05R05 16 06449 43 0502 375 05R06 19 0655 | 0416 | 111 | 0538 | 81 | 0634 | 60 |
| 0418 115 0540 68 0636 33 0419 62 0541 368 0637 43 0420 146 05R01-1 3 0638 85 0421 85 05R01-2 3 0639 101 0422 91 05R01-3 nd 0640 60 0423 76 05R01-4 13 0641 73 0424 228 05R01-5 10 0642 71 0425 80 05R02-1 25 0644 71 0426 246 05R02-2 58 0645 63 0428 156 05R03 8 0647 71 0430 81 05R04 31 0648 31 0501 160 05R05 16 0649 43 0502 375 05R06 19 0650 66 0503 136 05R07 15 0651 <t< td=""><td>0417</td><td>112</td><td>0539</td><td>76</td><td>0635</td><td>46</td></t<> | 0417 | 112 | 0539 | 76 | 0635 | 46 |
| 0419 62 0541 368 0637 43 0420 146 05R01-1 3 0638 85 0421 85 05R01-2 3 0639 101 0422 91 05R01-3 nd 0640 60 0423 76 05R01-4 13 0641 73 0424 228 05R01-5 10 0642 71 0425 80 05R01-6 8 0643 74 0426 246 05R02-1 25 0644 71 0427 193 05R02-2 58 0645 63 0428 156 05R03 8 0647 71 0430 81 05R04 31 0648 31 0501 160 05R05 16 0649 43 0502 375 05R06 19 0650 66 0503 136 05R07 15 0651 | 0418 | 115 | 0540 | 68 | 0636 | 33 |
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| 0422 91 05R01-3 nd 0640 60 0423 76 05R01-4 13 0641 73 0424 228 05R01-5 10 0642 71 0425 80 05R01-6 8 0643 74 0426 246 05R02-1 25 0644 71 0427 193 05R02-2 58 0645 63 0428 156 05R02-3 60 0646 48 0429 94 05R03 8 0647 71 0430 81 05R05 16 0649 43 0502 375 05R06 19 0650 66 0503 136 05R07 15 0651 36 0504 603 05R08 19 0652 64 0505 82 0601 94 0653 33 0506 146 0602 62 0654 <td< td=""><td>0421</td><td>85</td><td>05R01-2</td><td>3</td><td>0639</td><td>101</td></td<> | 0421 | 85 | 05R01-2 | 3 | 0639 | 101 |
| 0.423 76 $05R01-4$ 13 0641 73 0423 76 $05R01-5$ 10 0642 71 0425 80 $05R01-6$ 8 0643 74 0426 246 $05R02-1$ 25 0644 71 0427 193 $05R02-2$ 58 0645 63 0428 156 $05R02-3$ 60 0646 48 0429 94 $05R03$ 8 0647 71 0430 81 $05R05$ 16 0648 31 0501 160 $05R05$ 16 0649 43 0502 375 $05R06$ 19 0655 66 0503 136 $05R07$ 15 0651 36 0504 603 $05R08$ 19 0655 32 0505 82 0601 94 0653 | 0422 | 91 | 05R01-3 | nd | 0640 | 60 |
| 0.424 228 $05R01-5$ 10 0642 71 0425 80 $05R01-6$ 8 0643 74 0426 246 $05R02-1$ 25 0644 71 0427 193 $05R02-2$ 58 0645 63 0428 156 $05R02-3$ 60 06466 48 0429 94 $05R03$ 8 0647 71 0430 81 $05R05$ 16 0649 43 0501 160 $05R05$ 16 0649 43 0502 375 $05R06$ 19 06550 66 0503 136 $05R07$ 15 06651 36 0505 82 0601 94 0653 33 0506 146 0602 62 0654 47 0507 314 0603 70 0655 | 0423 | 76 | 05R01-4 | 13 | 0641 | 73 |
| 0425 80 $05R01-6$ 8 0643 74 0425 246 $05R02-1$ 25 0644 71 0427 193 $05R02-1$ 25 0644 71 0427 193 $05R02-2$ 58 0645 63 0428 156 $05R02-3$ 60 0646 48 0429 94 $05R03$ 8 0647 71 0430 81 $05R05$ 16 0648 31 0502 375 $05R06$ 19 0650 66 0502 375 $05R06$ 19 0650 66 0503 136 $05R07$ 15 0651 36 0504 603 $05R08$ 19 06553 33 0506 146 0602 62 0654 47 0507 314 0603 70 0655 | 0424 | 228 | 05R01-5 | 10 | 0642 | 71 |
| 0.125 0.35 0.5161 $0.5602-1$ 25 0.644 71 0.426 246 $05R02-1$ 25 0.644 71 0.427 193 $05R02-2$ 58 0.645 63 0428 156 $05R02-3$ 60 0.646 48 0429 94 $05R03$ 8 0.647 71 0430 81 $05R04$ 31 0.648 31 0501 160 $05R05$ 16 0.649 43 0502 375 $05R06$ 19 0.650 66 0503 136 $05R07$ 15 0.651 36 0504 603 $05R08$ 19 0.652 64 0505 82 0601 94 0.653 33 0506 146 0602 62 0.654 47 0507 314 0603 70 0.655 32 0508 256 0604 84 0.656 58 0509 278 0.605 66 0.657 73 0510 222 0.606 76 0.658 54 0511 80 0.607 77 0.659 29 0512 141 0.608 55 0.660 52 0513 118 0610 75 0.662 38 0516 94 0612 75 0.664 48 0517 75 0.613 80 0.665 42 <tr<< td=""><td>0425</td><td>80</td><td>05801-6</td><td>8</td><td>0643</td><td>74</td></tr<<> | 0425 | 80 | 05801-6 | 8 | 0643 | 74 |
| 0.125 1.13 $0.5R02-2$ 58 0.645 63 0.427 193 $05R02-2$ 58 0.646 48 0.429 94 $05R02-3$ 60 0.646 48 0.429 94 $05R03$ 8 0.647 71 0.430 81 $05R05$ 16 0.649 43 0.502 375 $05R06$ 19 0.650 66 0.503 136 $05R07$ 15 0.651 36 0.504 603 $05R08$ 19 0.652 64 0.505 82 0.601 94 0.653 33 0.506 146 0.602 62 0.654 47 0.507 314 0.603 70 0.655 32 0.508 256 0.604 84 0.656 58 0.509 278 0.605 66 | 0426 | 246 | 05802-1 | 25 | 0644 | 71 |
| 0427 153 05402 2 053 0645 48 0428 156 05R02-3 60 0646 48 0429 94 05R03 8 0647 71 0430 81 05R04 31 0648 31 0501 160 05R05 16 0649 43 0502 375 05R06 19 0650 66 0503 136 05R07 15 0651 36 0504 603 05R08 19 0652 64 0505 82 0601 94 0653 33 0506 146 0602 62 0654 47 0507 314 0603 70 0655 32 0508 256 0604 84 0656 58 0510 222 0606 76 0658 54 0511 80 0607 77 0659 29 | 0427 | 103 | 05802-2 | 58 | 0645 | 63 |
| 04299405R038064771 0430 8105R0431064831 0501 16005R0516064943 0502 37505R0619065066 0503 13605R0715065136 0504 60305R0819065264 0505 82060194065333 0506 146060262065447 0507 314060370065532 0508 256060484065658 0509 278060566065773 0510 222060676065854 0511 80060777065929 0512 141060855066052 0514 118061075066238 0516 94061275066448 0517 75061380066542 0518 75061490066652 0519 51061599JB-1a 20047.98 0522 76061859JB-1a 2057.81 | 0428 | 156 | 05802-3 | 60 | 0646 | 48 |
| 0.123 3.4 0.503 3 0.643 31 0430 81 $05R04$ 31 0648 31 0501 160 $05R05$ 16 0649 43 0502 375 $05R06$ 19 0650 66 0503 136 $05R07$ 15 0651 36 0504 603 $05R08$ 19 0652 64 0505 82 0601 94 0653 33 0506 146 0602 62 0654 47 0507 314 0603 70 0655 32 0508 256 0604 84 0656 58 0509 278 0605 66 0657 73 0510 222 0606 76 0658 54 0511 80 0607 77 0669 29 < | 0420 | 04 | 05802 | 00 | 0647 | 71 |
| 0500 01 05004 01 0504 01 0501 160 05R05 16 0649 43 0502 375 05R06 19 0650 66 0503 136 05R05 15 0651 36 0504 603 05R08 19 0652 64 0505 82 0601 94 0653 33 0506 146 0602 62 0654 47 0507 314 0603 70 0655 32 0508 256 0604 84 0656 58 0509 278 0605 66 0657 73 0510 222 0606 76 0658 54 0511 80 0607 77 0659 29 0512 141 0608 55 0660 52 0513 118 0609 71 0661 20 <td>0430</td> <td>81</td> <td>05804</td> <td>31</td> <td>0648</td> <td>31</td> | 0430 | 81 | 05804 | 31 | 0648 | 31 |
| 0501 100 05010 10 0645 43 0502 375 05R06 19 0650 66 0503 136 05R07 15 0651 36 0504 603 05R08 19 0652 64 0505 82 0601 94 0653 33 0506 146 0602 62 0654 47 0507 314 0603 70 0655 32 0508 256 0604 84 0656 58 0509 278 0605 66 0657 73 0510 222 0606 76 0658 54 0511 80 0607 77 0659 29 0512 141 0608 55 0660 52 0513 118 0610 75 0662 38 0515 139 0611 82 0663 49 <td>0501</td> <td>160</td> <td>05805</td> <td>16</td> <td>0649</td> <td>43</td> | 0501 | 160 | 05805 | 16 | 0649 | 43 |
| 0502 0503 136 05060 13 05030 136 0503 136 05R07 15 0651 36 0504 603 05R08 19 0652 64 0505 82 0601 94 0653 33 0506 146 0602 62 0654 47 0507 314 0603 70 0655 32 0508 256 0604 84 0656 58 0509 278 0605 66 0657 73 0510 222 0606 76 0658 54 0511 80 0607 77 0659 29 0512 141 0608 55 0660 52 0513 118 0610 75 0662 38 0515 139 0611 82 0663 49 0516 94 0612 75 0664 | 0502 | 375 | 05806 | 19 | 0650 | 66 |
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| 05054 0505 82 0601 94 0653 33 0506 146 0602 62 0654 47 0507 314 0603 70 0655 32 0508 256 0604 84 0656 58 0509 278 0605 66 0657 73 0510 222 0606 76 0658 54 0511 80 0607 77 0659 29 0512 141 0608 55 0660 52 0513 118 0609 71 0661 20 0514 118 0610 75 0662 38 0515 139 0611 82 0663 49 0516 94 0612 75 0664 48 0517 75 0613 80 06665 52 0518 75 0614 90 JB-1a 200447 | 0504 | 603 | 05808 | 19 | 0652 | 64 |
| 0500 14 0601 64 0602 62 0654 47 0506 146 0602 62 0654 47 0507 314 0603 70 0655 32 0508 256 0604 84 0656 58 0509 278 0605 66 0657 73 0510 222 0606 76 0658 54 0511 80 0607 77 0659 29 0512 141 0608 55 0660 52 0513 118 0609 71 0661 20 0514 118 0610 75 0662 38 0515 139 0611 82 0663 49 0516 94 0612 75 0664 48 0517 75 0613 80 06665 52 0519 51 0615 99 J | 0505 | 82 | 0601 | 94 | 0653 | 33 |
| 0500 110 0602 02 0201 0301 11 05007 314 0603 70 0655 32 0508 256 0604 84 0656 58 0509 278 0605 66 0657 73 0510 222 0606 76 0658 54 0511 80 0607 77 0659 29 0512 141 0608 55 0660 52 0513 118 0609 71 0661 20 0514 118 0610 75 0662 38 0515 139 0611 82 0663 49 0516 94 0612 75 0664 48 0517 75 0613 80 06655 42 0518 75 0614 90 06666 52 0519 51 0615 99 JB-1a 200447 | 0506 | 146 | 0602 | 62 | 0654 | 47 |
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| 0500 278 0605 66 0657 73 0510 222 0606 76 0658 54 0510 222 0606 76 0658 54 0511 80 0607 77 0659 29 0512 141 0608 55 0660 52 0513 118 0609 71 0661 20 0514 118 0610 75 0662 38 0515 139 0611 82 0663 49 0516 94 0612 75 0664 48 0517 75 0613 80 0665 42 0518 75 0614 90 0666 52 0519 51 0615 99 JB-1a 20047 7.88 0520 100 0616 96 JB-1a 20057 7.89 0521 75 0617 93 JB-1a 20057 <td< td=""><td>0508</td><td>256</td><td>0604</td><td>84</td><td>0656</td><td>58</td></td<> | 0508 | 256 | 0604 | 84 | 0656 | 58 |
| 0500 210 0500 70 0500 70 0658 54 0510 222 0606 76 0658 54 0511 80 0607 77 0659 29 0512 141 0608 55 0660 52 0513 118 0609 71 0661 20 0514 118 0610 75 0662 38 0515 139 0611 82 0663 49 0516 94 0612 75 0664 48 0517 75 0613 80 0665 42 0518 75 0614 90 0666 52 0519 51 0615 99 JB-1a 2004年 7.88 0520 100 0616 96 JB-1a 2005年 7.89 0521 75 0617 93 JB-1a 2005年 7.89 0522 76 0618 < | 0509 | 278 | 0605 | 66 | 0657 | 73 |
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| 0511 053 0560 7 0560 22 0512 141 0608 55 0660 52 0513 118 0609 71 0661 20 0514 118 0610 75 0662 38 0515 139 0611 82 0663 49 0516 94 0612 75 0664 48 0517 75 0613 80 0665 42 0518 75 0614 90 0666 52 0519 51 0615 99 JB-1a 2004年 7.98 0520 100 0616 96 JB-1a 2005年 7.89 0521 75 0617 93 JB-1a 2005年 7.89 0522 76 0618 59 JB-1a 205年 7.88 | 0511 | 80 | 0607 | 70 | 0659 | 29 |
| 0512 11 0600 71 0661 20 0513 118 0609 71 0661 20 0514 118 0610 75 0662 38 0515 139 0611 82 0663 49 0516 94 0612 75 0664 48 0517 75 0613 80 0665 42 0518 75 0614 90 0666 52 0519 51 0615 99 JB-1a 2004年 7.98 0520 100 0616 96 JB-1a 2005年 7.89 0521 75 0617 93 JB-1a 2006年 7.81 0522 76 0618 59 JB-1a 公表值* 7.88 | 0512 | 141 | 0608 | 55 | 0660 | 52 |
| 0514 118 0610 75 0662 38 0514 118 0610 75 0662 38 0515 139 0611 82 0663 49 0516 94 0612 75 0664 48 0517 75 0613 80 0665 42 0518 75 0614 90 0666 52 0519 51 0615 99 JB-1a 2004年 7.98 0520 100 0616 96 JB-1a 2005年 7.89 0521 75 0617 93 JB-1a 2006年 7.81 0522 76 0618 59 JB-1a 公奏值* 7.88 | 0513 | 118 | 0609 | 71 | 0661 | 20 |
| 0511 110 0611 82 0663 49 0515 139 0611 82 0663 49 0516 94 0612 75 0664 48 0517 75 0613 80 0665 42 0518 75 0614 90 0666 52 0519 51 0615 99 JB-1a 2004年 7.98 0520 100 0616 96 JB-1a 2005年 7.89 0521 75 0617 93 JB-1a 2006年 7.81 0522 76 0618 59 JB-1a 公表插* 7.88 | 0514 | 118 | 0610 | 75 | 0662 | 38 |
| 0516 94 0612 75 0664 48 0517 75 0613 80 0665 42 0518 75 0614 90 0666 52 0519 51 0615 99 JB-1a 2004年 7.98 0520 100 0616 96 JB-1a 2005年 7.89 0521 75 0617 93 JB-1a 2006年 7.81 0522 76 0618 59 JB-1a 公務4# 7.88 | 0515 | 139 | 0611 | 82 | 0663 | 49 |
| 051.7 75 061.3 80 0665 42 0518 75 0614 90 0666 52 0519 51 0615 99 JB-1a 2004年 7.98 0520 100 0616 96 JB-1a 2005年 7.89 0521 75 0617 93 JB-1a 2006年 7.81 0522 76 0618 59 JB-1a 公表插* 7.88 | 0516 | 94 | 0612 | 75 | 0664 | 48 |
| 0518 75 0614 90 0666 52 0519 51 0615 99 JB-1a 2004年 7.98 0520 100 0616 96 JB-1a 2005年 7.89 0521 75 0617 93 JB-1a 2006年 7.81 0522 76 0618 59 JB-1a 公表插* 7.88 | 0517 | 75 | 0613 | 80 | 0665 | 42 |
| 05110 10 0614 90 0000 32 0519 51 0615 99 JB-1a 2004年 7.98 0520 100 0616 96 JB-1a 2005年 7.89 0521 75 0617 93 JB-1a 2006年 7.81 0522 76 0618 59 JB-1a 公表值* 7.88 | 0518 | 75 | 0614 | ۵0 ۵0 | 0666 | 52 |
| 0510 0510 0513 0514 2004年 7.80 0520 100 0616 96 JB-1a 2005年 7.89 0521 75 0617 93 JB-1a 2006年 7.81 0522 76 0618 59 JB-1a 公表值* 7.88 | 0510 | 51 | 0615 | 00 00 | JB-1a 2004年 | 7 9.2 |
| 0521 75 0617 93 JB-1a 2006年 7.81 0522 76 0618 59 JB-1a 公元64 7.81 | 0520 | 100 | 0616 | 96 | JB-1a 2005年 | 7 80 |
| 0522 76 0618 59 JB-1a 公表值 [*] 7.81 | 0521 | 75 | 0617 | 93 | JB-1a 2006年 | 7.81 |
| | 0522 | 76 | 0618 | 59 | JB-1a 公表值* | 7.88 |

表 B1. 平成 16~18 年度までのホウ素の分析結果

C. 富士山の火山噴出物の即発ガンマ線分析

1. はじめに

富士火山における最後の山頂噴火は約 2200 年前 と報告されている(宮地, 1988).この時に噴出した マグマは山頂から東麓に降り積もり,湯船第2スコ リアと呼ばれるスコリア層を形成した(宮地,1982). またマグマは標高2500m以上で溶結して山体頂部の 表層をつくった.噴出量は約0.5km³と見積もられて おり(宮地,1982),山頂から噴出した最大規模の火 山噴出物である.この湯船第2スコリアは新富士火 山の噴火史および火山防災を考える上で,最も重要 な噴火堆積物の1つであるが,これまでに記載岩石 学的特徴や化学分析値の報告はほとんどなかった. この理由はスコリア層の大部分が赤色~褐色であり, 酸化や風化が激しいと見受けられ,マグマは噴出前 の化学的特徴を保持していない可能性があると思わ れていたからと推定される.そこで,湯船第2スコ リアの酸化や風化による化学組成の変化を調べた. 更に,新鮮部分について岩石記載および全岩分析を 行った.

2. 分析試料

試料は山頂火口から東へ 8.5km の地点の崖から採 取した(図 C1). ここは湯船第2スコリアの等層厚 線図の主軸部分であり,スコリアの厚さは 1.7 mで あった. 宮地(1982)で報告されているように5つ の fall-unit が確認された. 我々は下位から上位まで 順番に B から J までの 9 つの場所から大きなスコリ ア (>2g)を採取した.



図 C1 対象試料(湯船第2スコリア層)の採取地 点(静岡県-山梨県境)

3. 方法

岩石の記載と空隙率測定を行った後、即発y線分 析により B, Cl, Gd, Sm の定量を行った(Sano et al., 1999, 2004, 2006). そして蛍光 X 線分析装置を用い て主成分およびいくつかの微量成分の定量も行った (佐野, 2002). また B, C, G, H, J の 5 層から採取し たスコリアについては酸化・変質部分を含んだ部分 の全岩化学分析も行った.

4. 結果・考察

全てのスコリアは班晶としてカンラン石(0~4 vol.%)および斜長石(2~16 vol.%)を含んでいた. みかけの密度と真の密度から計算される空隙率は 20~70%と様々であった.

酸化・変質部分を含む試料の全岩化学分析値は新 鮮部分と比べて MgO および Ni の含有量が低い

(MgO は 10%低下, Ni は半分に低下) 以外は分析 誤差を超えた差は見られなかった.従って,他の元 素は酸化や変質の影響はほとんど受けていないと考 えられる.



図 C2 湯船第2スコリアの空隙率に対する全岩 化学組成のプロット

ハーカー図における新鮮部分の組成バリエーションは明瞭なトレンドを形成し、これは斑晶鉱物の7%の分別により説明可能である. 斑晶モードと全岩化学組成との間に明瞭な相関は見られなかった.しかし空隙率はSiO₂, TiO₂, FeO*, B, Cl, Ba, Zr, Yと正の相関, CaO, Sr, Crと負の相関をなし、分化した組成のスコリアほど空隙率が高いという事実が明らかになった(図C2).

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D. 瀬戸内火山岩および外帯花こう岩のホウ素含有 量について

1. 試料,分析

研究協力者の新正は,瀬戸内火山岩および外帯花 こう岩から広域的に採集した試料について,即発ガ ンマ線分析によるホウ素含有量の測定を行なった.

日本海拡大に伴う西南日本弧の時計回り回転直後 の時期(14Ma頃)に活動した火成岩類のうち外帯 域に分布するものは大部分が珪長質〜中間質の貫入 岩類であり,外帯花こう岩質岩と一括される.また 瀬戸内区には,マントルに由来する玄武岩,高マグ ネシア安山岩(HMA)および珪長質の火山岩類が分 布し,瀬戸内火山岩類と呼ばれる.広域的に採取し た,瀬戸内火山岩類のデイサイト〜流紋岩および外 帯花こう岩質岩について 30 余りの試料を選び,即 発ガンマ線分析によりそのホウ素濃度を求めた.

2. 結果,考察

外帯花こう岩質岩のホウ素濃度は 7 ~ 426 ppm と極めて広い組成範囲をもつが、電気石を含み 100 ppm を超える極めて高いホウ素濃度をもつ試料を 除外した平均のホウ素濃度は 28 (±24) ppm であっ た (図D1).なおSタイプ、Iタイプ花こう岩で系統 的な差はなかった.SiO2量とホウ素含有量には相関 が見られず、単独の貫入岩体について複数の試料を 分析した場合にはしばしば試料により大きな組成差 が見られた.これらの事実から、外帯花こう岩のホ ウ素濃度は固結前のマグマ組成を必ずしも反映して おらず、固結時~固結後の流体等による元素移動の 影響を大きく受けているものと考えられる.

瀬戸内火山岩類のデイサイト~流紋岩のホウ素濃 度の範囲は10 ~ 110 ppm で, 平均は57 (±30) ppm であった. 瀬戸内火山岩類の珪長質火成岩の一部は 四国海盆上の堆積物が深部で融解したスラブメルト でありそれがマントルウェッジかんらん岩と反応し て HMA となったという提案がある(Shimoda and Tatsumi, 1999). 今回測定した瀬戸内火山岩のデイ サイト~流紋岩は B/Nb-B プロット上で広く分散す るが,高マグネシア安山岩(新正ほか,未公表)の それと分布範囲はよく似ている(図 D2). HMA の



図 D1 外帯花こう岩類の B 量のヒストグラム(S/I タイプ を区分)

ホウ素と液相濃集元素の B/Nb 比に大きな分散があ るのは、スラブ由来成分(≒珪長質火山岩)の B/Nb 比にそもそも大きな分散があったためかも知れない.



図 D2 瀬戸内火山岩類の B/Nb-B plot

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南極隕石試料の即発ガンマ線分析

Prompt gamma-ray analysis of Antarctic meteorites

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1.はじめに

日本原子力研究所の研究用原子炉 JRR-3 が改 造され、中性子ビームを利用した即発γ線分析 (PGA)が実施可能となって以来、主に隕石試料 を分析対象として即発γ線分析を実施してきた。 これまでの研究を通して、PGA は隕石の全岩組 成(特に、主成分元素組成)を求める手段として、 大変優れていることを実証した。それは、隕石 を構成する主成分元素をほぼ全元素定量するこ とができる他に、PGA は全岩試料に対して非破 壊分析できる点で大きな利点をもつ点に集約さ れる。

平成16年度から18年度の間、標記課題で原研施設を利用した共同研究を行った。この3年の研究期間に行った研究は2つに分類できる。1 つはこれまでの経験を生かして、各種隕石試料の非破壊分析を行ったことで、ほとんどの場合が粉末試料か、或いは塊状であっても中性子のビーム径(2cm x 2cm)以内に収まる程度の試料で、比較法により定量をおこなった。もう一つは、隕石中の特定元素の存在度と存在状態を知ることを目的にして行った研究で、従来の研究

エコンドライト Dhofar 007 を用いた。同隕石 はオマーンの砂漠で見つかった隕石で,約 27 kg が回収された。隕石は初め集積岩ユークライト と分類されたが,その種の隕石のわりには金属 相を多く含み,その結果 Ni や Co の含有量が高 いことから,メソシデライト(石鉄隕石)のケイ を発展させた、新しい試みである。本報告では、 このうちの1番目の課題を中心にまとめる。

既に述べたとおり、PGA を用いて隕石試料の 元素組成をほぼすべての主成分元素に対して求 めることができる。また、PGA で利用する中性 子束は通常の炉内照射で行う機器中性子放射化 分析(INAA)に比べて桁違いに低いことから、 PGA で利用した試料を再度 INAA に用いること は可能であり、その結果、微量元素を効率よく 分析することができる。その意味で、PGA と INAA を相補的に利用することにより、限られ た量の隕石試料から最大限の元素組成に対する 情報を引き出すことが可能になる。本報告書で 述べる結果も、PGA と INAA の併用によってえ ら得たものであり、試料によっては PGA 後の試 料を誘導結合プラズマ質量分析法に利用した例 もある。

2.実験

2.1 試料

酸塩相と関連があるのではないかと指摘されて いた。そこで、同隕石 0.883 g を粉末にし、その うちの約 200 mg を用いて PGA を行った。また、 粉末試料約 50 mg を INAA に、10 mg、200 mg を ICP-MS による希土類元素、及び白金族元素の定 量にそれぞれ用いた。

研究施設名と装置

JRR-3M (PGA)

研究分野 宇宙化学

2.2 即発γ線分析

PGA は日本原子力研究所(現 日本原子力研究 開発機構)のJRR-3M に設置されている熱中性子 ガイドビームを用いて行った。試料約 200 mg を FEP フィルムに溶封し、ヘリウム雰囲気化にて 約 3 時間測定した。定量は比較法で行い、比較 標準試料には玄武岩試料 JB-1 とスミソニアン製 Allende 粉末試料を用いた。

2.3 その他の元素分析

今回は初めの粉末状試料が低く的多く準備出 来たので、PGA に使った残りを INAA、ICP-MS を用いた実験を行った。INAA では照射時間と 冷却時間を適当に組み合わせて、限られた試料 から最大限の元素組成情報を引き出すことを心 がけた。それぞれの方法に関して既に本研究室 から論文が公表されており、それに従って実験 を行った。

3.結果と考察

3.1 表1に定量に用いた方法と共に,元素 組成のデータを示す。%で表示されている元素 はすべて PGA で定量することが可能である。ま た,そのうち Si を除く主成分元素は INAA によ っても定量可能であり、表1の値はこの2つの 分析方法によって定量された値をもとに、もっ とも妥当な定量値として吟味したものである。 後段の希土類元素(ラインタノイド)と白金族元 素は ICP-MS によって求めた値である。表1で 分かるとおり,ニッケル含有量は約1000 ppm に も及び、通常の集積岩タイプのユークライト中 のNi含有量に比べて桁違いに高いことが分かる。 それに伴って、白金族元素存在度も高く、例え ば代表的な白金族元素である It の含有量は約 50 ppb と、コンドライト隕石のもつ含有量の約半 分の濃度値を示す。

3.2 Dhofar 007 の起源

図1は Dhofar 007 の希土類元素存在度をコン ドライトの値で規格化した相対存在度パターン である。図中にはユークライト隕石の存在度パ ターンも比較の為に示されているが, Dhofar 007 のパターンは Binda 隕石のそれと酷似してい ることがわかる。このことは, Dhofar 007 隕石 の母天体はユークライト的なものであることを

示唆する。

元素組成と鉱物学的観察から Dhofar 007 隕石 の起源について考察した。同隕石の鉱物学的観 察からこの隕石の形成過程として以下のことが 推察される;(i)母天体深部に於ける結晶化, (ii) 衝突による溶融,(iii) 今回測定した岩石片 の再結晶化をもたらした熱的出来事,(iv) 高温 での速い冷却,(v)低温でのゆっくりとした冷 却,(vi) 再度の衝突による衝突脈の形成。表1 に示されるように、この隕石にはかなりの量の 金属相と、それに伴う高濃度の親鉄性元素が含 まれている。これらの金属や親鉄性元素は恐ら く、この隕石の母天体における衝突によっても たらされたものであり、その衝突した物体(プロ ジェクタイル)は鉄ニッケル合金からなる鉄隕石 であったと考えられる。白金族元素の CI コンド ライト組成(太陽系の元素組成を近似するものと 考えられている値)で割った相対存在度を図2に 示す。NiとCoがコンドライトの値に比べて分化 しており、Coに相対的にとんでいることや、Os と Ir も分化していてメソシデライトの比に近い ことを考えると、この相対的な元素組成からは、 プロジェクタイルがメソシデライト的なもので あることを示唆する。

以上のことより, Dhofar 007 隕石はメソシデ ライトの大きなケイ酸塩質インクルージョンで ある可能性が考えられる。しかしながら,特殊 なユークライト隕石である可能性も残されてい る。この種の隕石の化学組成を通じて,原始太 陽系における物質の進化がより詳細に記述され ることが可能であり,今後の研究の進展が待た れる。

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表 1 Dhofar 007 の元素組成

| | | Dhofar 007 CG | | | |
|-------------------------------|-------|---------------|------------|------------|---------------|
| SiO | (04) | 16.9 | + | 1 9 | |
| 510_2 TiO ₂ | (%) | 40.2 | | 1.3 | 0.17 |
| | (%) | 12.6 | ± | 0.008 | 10.71 |
| $A12O_3$ Cr_2O_3 | (%) | 0.446 | - - | 0.3 | 10.71 |
| E ₂ O ₃ | (%) | 15 7 | - - | 0.009 | 0.62 15.57 |
| MnO | ()() | 15.7 | | 0.0 | 10.07 |
| MaO | (%) | 0.52 | т | 0.04 | 15.94 |
| MgO CaO | (%) | 9.0 | т | 0.7 | 10.04 |
| NacO | ()() | 0.246 | | 0.0 | 0.26 |
| Na ₂ O | (%) | 0.540 | ± | 0.001 | 0.26 |
| K2U S | (%) | 0.029 | ± | 0.002 | |
| с. С. | (ppm) | 4000 | - T | 0.01 | 145 |
| SC V | (ppm) | 21.01 | ± . | 0.01 | 14.0 |
| V Co | (ppm) | 01.0 50.9 | ± | 6.0 0.7 | 11 0 |
| C0 N: | (ppm) | 09.0 | ± | 0.7 | 11.0 |
| IN1 | (ppm) | 929 | ± | 32 | ə.7 |
| AS | (ppm) | 0.50 | ± | 0.06 | |
| CP-MS | | | | | |
| Y | (ppm) | 3.17 | ± | 0.08 | 3.22 |
| Ru | (ppb) | 52 | ± | 1 | |
| Rh | (ppb) | 7.9 | ± | 0.2 | |
| Pd | (ppb) | 37 | ± | 4 | |
| Ba | (ppm) | 13.9 | ± | 0.3 | 6.0 |
| La | (ppm) | 0.386 | ± | 0.003 | 0.382 |
| Ce | (ppm) | 0.908 | ± | 0.005 | 1.01 |
| \Pr | (ppm) | 0.152 | ± | 0.003 | 0.154 |
| Nd | (ppm) | 0.705 | ± | 0.004 | 0.773 |
| Sm | (ppm) | 0.261 | ± | 0.005 | 0.261 |
| Eu | (ppm) | 0.330 | ± | 0.003 | 0.277 |
| Gd | (ppm) | 0.393 | ± | 0.009 | 0.355 |
| Tb | (ppm) | 0.077 | ± | 0.008 | 0.0705 |
| Dy | (ppm) | 0.58 | ± | 0.01 | 0.507 |
| Ho | (ppm) | 0.132 | ± | 0.002 | 0.118 |
| \mathbf{Er} | (ppm) | 0.406 | ± | 0.005 | 0.356 |
| Tm | (ppm) | 0.0611 | ± | 0.0007 | |
| Yb | (ppm) | 0.427 | ± | 0.003 | 0.387 |
| Lu | (ppm) | 0.067 | ± | 0.001 | 0.0624 |
| Os | (dag) | 30 | ± | 1 | |
| \mathbf{Ir} | (ppb) | 49 | ± | 2 | |
| Pt | (ppb) | 49 | ± | 1 | |
| Au | (ppb) | 92 | + | 1.0 | |

*¹Uncertainties for NAA/PGA are due to counting statistics and those for ICP-MS are standard deviation of replicated measurements. ^{*2}Barrat et al. (2000).

固体環境試料および地球化学的試料の即発ガンマ線分析 (Ⅳ)

Neutron-induced prompt gamma-ray analysis of solid environmental samples and geochemical samples

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1. はじめに

固体環境試料や地球化学的試料中に含有され る元素を定量し、その分布を明らかにすることは、 試料自体の形成過程を知る上でも、試料の置かれ た環境を理解する上でも重要な課題と考えられ る。中性子誘起即発 γ線分析法(PGA)は、通常の 機器中性子放射化分析法(INAA)と同様に、多元素 同時定量分析が可能なため、多くの元素の分布を 総合的に判断するのに適した分析法と言える。さ らにPGAは、INAAでは分析が困難な H, B, S, Si 等の軽元素やCd 等の有害元素の定量が可能 である、試料の誘導放射能が低く同分析法で使用 した試料を他の分析法で再使用することが可能 である、といった特長を持つ優れた分析法である。 本研究では、同法を用いることにより、次に掲げ る試料について種々の環境化学的、地球化学的な 検討を行ったので、それぞれの試料ごとに研究内 容およびその結果を報告する。

2. 谷津干潟および三番瀬底質中の元素と化学状 態の垂直分布

【序】これまでに多くの干潟が埋め立てられ消失 したが、環境浄化作用や生物多様性などの側面か ら干潟の重要性が認識されるようになってきた。

その例として、千葉県の三番瀬埋め立て計画の白 紙撤回や、有明海の漁業不振を理由とした諫早湾 干拓事業の差し止め訴訟などがあり、干潟と埋め 立てに関する事例が社会的にも大きな関心事と なり、干潟の機能や役割の解明が求められている。 本研究では千葉県の谷津干潟と三番瀬を対象と して、干潟周辺の埋め立てが干潟底質の環境に与 えた影響を評価する。谷津干潟は四方を埋め立て られ海とは直接面していないのに対し、三番瀬は 周囲で埋め立てはあったものの、現在でも広い面 で海と面しており、この2つの干潟での埋め立て による影響は異なっていると考えられる。この2 地点で底質試料を採取し、中性子誘起即発γ線分 析(PGA)、および機器中性子放射化分析(INAA) により約 30 元素の定量を行った。また、干潟底 質中では嫌気性の細菌である硫酸還元菌の活動 により硫化水素が発生し、底質中の鉄イオンと反 応し硫化鉄やPyrite(FeS2)を生成することから、 メスバウアー分光法により鉄の化学状態を測定 した。

【実験】 試料として、東京湾奥に位置する谷津 干潟の底質を垂直方向に採取した。採取には内径 6cm のアクリルパイプを用い、得られた約 50cm のコアを現地で 3cm ごとに切り分け、酸化を防ぐ

研究施設と装置名

JRR-3M、即発γ線分析装置

研究分野 環境化学、地球化学、分析化学 ためN2中に封入した。得られた試料はN2を用いた 加圧濾過により間隙水を取り除き、メスバウアー 測定とXAFS測定に用いた。また、その後、凍結 乾燥を施し、めのう乳鉢で粉砕し均一にした。そ の中から約200mgを精秤し、錠剤成型器を用いて 直径 10mm、厚さ約 1mmのペレットに成型した。 これを中性子ビームサイズである 20mm四方以 内に収まるように、厚さ12μmのFEPフィルムに 封入し、テフロン製の専用ホルダーに固定したう えで、日本原子力研究開発機構JRR-3Mの中性子 ビームガイドに設置し、He雰囲気中で3600秒間 即発γ線を測定した。中性子束の変動を補正する ために、24 時間に一回、一定のTi板(Ti flux monitor)を測定して得られる 342keVと 1381keV ピークの計数率の平均値で割り、比較標準試料に ついて報告されているTi flux monitorの計数率で 規格化した分析感度を用いて各元素の含有量を 計算した。INAA法に関しては、日本原子力研究 開発機構のJRR-4 にて照射を行い、大学開放研の γ線スペクロトメーターにて測定を行った。

【結果及び考察】 PGA, INAA 法により、30 数 元素の垂直分布を得ることができた。採取した谷 津干潟底質コアは深さ約25cm までが泥質でそれ 以深が砂質となっており、この変化はもともと東 京湾の海岸線の一部であった谷津干潟が、四方が 埋め立てられたことによって東京湾から隔離さ れ、水の流れが変化したためと考えられる。得ら れた元素の垂直分布の多くも25cm 前後で変化し ており、その変化の特徴に従って4つのグループ に分けることができた。図1に4つのグループの 代表の元素の垂直分布を示す。表層部から徐々に 減少し、25cm 以深でほぼ一定になる元素として、 ClとBrがあった。これらは海水中に豊富である ため、海水からの影響が大きいと考えられる。逆 に表層部から徐々に増加し、25cm 以深で濃度が 高い元素として Fe や Mn などがあった。メスバ ウアー分光法により Fe の化学状態別の割合を求 めると、25cm より浅い部分では Pyrite が多く、 それより深い部分では磁性成分が多くなってい た(図 2)。これより、埋立ての影響で水の流れが 変わり、砂鉄など Fe の磁性成分を含む物質の供



図1. 谷津干潟底質中の Cl, Mn, S, Si の垂直分布



図2. 谷津干潟底質中のPyriteと磁性成分の垂直 分布

給が減り、また、東京湾から隔離されたために、 還元的環境下で活発に活動する硫酸還元菌が発 生する硫化水素により Pyrite が多く生成するよ うになったことが示唆された。また、25cm より 浅い部分で多く、それ以深で少ない元素として、 S, H, B などが挙げられる。S は Pyrite を構成す る元素の一つであり、その垂直分布は、メスバウ アー分光法によって得られた Pyrite 存在割合の 垂直分布とよく一致した。また、XAFS 法を用い たSの状態分析からも、25cmより浅い部分では 硫化物の割合が高く、谷津干潟が還元的状態に変 化したことを示した。最後に Ca, Na, Si の濃度が 25cm 以浅で低く、それ以深で高くなっていた。 これらの元素は風化により岩石から溶脱しやす いものである。表面積の大きな泥質部分では深さ に応じ溶脱が進むが、砂質部分では表面積が小さ いため、溶脱が進まずに多くが残っていると考え られた。

3. 遠洋性海洋堆積物表層における供給源の推定

【序】 海洋堆積物中にはさまざまな供給源より もたらされた元素が混在する。堆積物の粒径別化 学組成や同位体組成から供給源を推定する研究 報告は多数見受けられるが、プローブ以外の元素 濃度変動要因を明らかにすることは難しい。本研 究では堆積物中に異なる供給源を持つ場合、それ ぞれの元素組成パターンが異なるという観点か ら、堆積物定量値に多変量解析を適応し、その供 給源分別を試みた。

【実験】 海洋堆積物は白鳳丸((独)海洋研究開発 機構(JAMSTEC))による KH04-05 航海にて 2004-2005 年にかけて西経 170 度沿いに採取し た南大西洋の遠洋性コア(4 コア)を用いた。堆積 物は鉛直方向に 0.5-1.0cm 毎にカットした後 110℃、2時間の乾燥を行った。150-200mg 程度 を精秤し、直径 10mm 厚さ 1mm 程度のペレッ トを作成した。ペレットを清浄な FEP フィルム に内包し PGA (即発ガンマ線分析法, JRR-3M)の 測定試料とした。同様にして INAA(機器中性子 放射化分析法, JRR-4)による多元素分析も適応 した。得られた定量値を多次元ベクトルとみなし 多変量解析(主成分分析)を適応し、堆積物中での 元素濃度変動因子を抽出した。なお、主成分分析 にあたり測定誤差をもとにした加重を測定点に 対して加えた計算を行った。

【結果及び考察】 測定を行った元素中、コア別 に29-36元素の定量を行うことが出来た。定量値 から得られた主成分分析のパラメータの中から、 陸源元素の固有ベクトルを因子別にFig.3 に示す。 また、各因子の寄与率をTable 1 に挙げた。固有 ベクトルのパターンの挙動の類似性から因子を Group1 [SX09 (factor1) & SX18 (factor1)] & Group2 [SX16 (factor1)とSX21 (factor2)]に分別 した。詳細な考察の結果、Group1 は大陸起源砕 屑物(風送塵)であり、Group2は火山岩(玄武岩)と 推定した。特にSX09 に関しては南極大陸起源の 漂流岩屑(IRD)のベクトルパターンと酷似するこ とから、その供給源が南極大陸であることが強く 推定される。また堆積物のK/Ti, Euアノーマリー (Eu/Eu*)の挙動からもこれらの推定を支持するこ とができた。



Fig. 3. Eigenvectors of terrigenous elements of the South Pacific sediments

| | | Sample | | | |
|----------|----------|-----------|-----------------|-----------------|-------------------------|
| | | SX09 | SX16 | SX18 | SX21 |
| | Location | 65.18° S | 43.18° S | 39.99º S | $24.79^{\rm o}~{\rm S}$ |
| | | 174.08° W | 171.17° W | 170.00° W | 169.98° W |
| Variance | Factor 1 | 26 | 54 | 49 | 28 |
| /% | Factor 2 | 20 | 26 | 9 | 22 |
| | Factor 3 | 12 | 18 | 7 | 20 |
| | K/Ti | 4.39 | 4.89 | 8.33 | 3.34 |
| | Eu/Eu* | - | 1.22 ± 0.06 | 1.08 ± 0.05 | 1.18 ± 0.06 |

Table 1. Sampling sites and factors loading from principal components analysis

4. 成果の公表

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- 19. "放射化分析法およびメスバウアー分光法に よる干潟底質の環境評価"、諸町大地・久野章 仁・松尾基之、第50回放射化学討論会(2006 日本放射化学会年会)(2006年10月)
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4. 放射化分析

4. Neutron Activation Analyses

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4-1
 研究テーマ: 放射化法による中性子捕獲断面積の測定技術開発
 表 題: 安定核種の断面積測定と中性子束モニタの開発

研究炉 JRR-3 を用いた熱中性子捕獲断面積測定技術開発

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中性子捕獲断面積データは、核変換や核燃料の 燃焼による生成量評価を考える上で重要である。 放射化法により断面積を測定するにあたり、照射 設備の中性子束の現状を実験的に知っておく必 要がある。そこで、研究炉 JRR-3 における照射 設備 PN-3、PN-1、HR-1 (図1)の中性子束の成分 を、Westcott's Convention^{1) 2)}に基づいて調べたの で報告する。更に、中性子束モニタ開発として、 数点の安定核種の熱中性子捕獲断面積の測定を 実施した。



図1 研究炉 JRR-3 照射設備

照射設備の中性子束情報として、熱中性子束成分 と熱外中性子成分の2成分に着目した。中性子束 モニタとして、主として¹⁹⁷Au/Alと⁵⁹Co/Al合金 線のセットを用い、適宜、W 箔、Mo線を追加し て中性子束情報を補足することとした。熱外中性 子成分を求める場合にはCd 遮蔽管にモニタ線の セットを入れて照射した。本実験では、Cd 遮蔽 管の照射における安全性を確認する目的もあっ た。研究炉JRR-3の20MW 定格運転において、 PN-3にて遮蔽無しで10分照射を行い、中性子束 モニタと一緒に数点の安定核種も照射した。 PN-1にて Cd 遮蔽有り/無しの照射を10分ずつ、 HR-1にて Cd 遮蔽有り/無しの照射を1時間ずつ 行った。

照射後、中性子東モニタからのγ線を高分解能 Ge 検出器で測定し、それぞれの生成放射能を求 めた。モニタの放射能を、Westcott's Convention に基づき解析し、各照射設備における中性子束の 成分を調べ図2の結果を得た。a) 気送管照射設 備 PN-3:熱中性子束は、約1×10¹³n/cm²s であり、十 分良く熱化されていることが確認された。PN-3 を用 いれば、熱中性子捕獲断面積を測定することが可能 であると考えられる。このことを、モニタと一緒に 照射した Mo-98 及び Zr-96 の断面積を測定すること により実証した。更に、中性子束モニタの開発とい う観点から、更に W-186、In-113、Sc-45、Fe-58、Cu-63 の熱中性子捕獲断面積の測定を実施した。

b) 気送管照射設備 PN-1:約 5×10¹³ n/cm²s 程の熱中 性子成分を有し、熱外中性子成分が 0.1% しかないこ とを確認した。そのため、Cd 遮蔽を用いて共鳴積分 を測定することは困難であると判断された。



図2 Westcott's convention に基づき測定した中性子束成分

c)水力設備 HR-1:約 8×10¹³n/cm²s の高い熱中性子 成分と熱外中性子成分約 1%を有することを確認し た。本照射において、Cd 遮蔽管の照射の安全性を確 認することができたので、本照射設備は、共鳴積分 の測定に適用できることが分かった。本照射設備は、 1 サイクル(26 日間)照射が可能であるので、中性子 捕獲断面積の小さい核種や生成核の半減期が非常に 長い場合に対しても生成量を稼ぐことが期待される ので断面積測定に有効である。

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原子炉: JRR-3 装置:気送管及び水力設備 分野:放射化分析(その他)

4-2

研究テーマ: 40Ar/39Ar 年代測定による火山活動史及び地殻構造発達史の解明—日本周辺海域 及び活動的火山に関する研究—

表 題:火山岩の 40Ar/39Ar 年代測定

大陸棚限界画定調査によるフィリピン海地域の火成活動史に関する新知見

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本研究では、フィリピン海海域およびその周辺の小笠原海台や南鳥島周辺海域において,採取された地質試料に関する地球科学的分析データ(特に岩石の形成年代)をもとに,各海域におけるマグマ活動およびマントルダイナミクス等を含めた火成活動史を把握することを目的とする.また本研究は現在国により準備されている国連への我が国の大陸棚限界画定申請のための調査の一環である。日本周辺海域の基盤岩の精密な形成年代を決定することを通じて、国連への提出情報作成をサポートする。

測定試料は、海底においてボーリングマシ ンにより掘削された、あるいはドレッジによ り回収された火山岩試料を用いた。火山岩の うちもっとも新鮮な石基部分を主に使用し た。試料から厚さ約 1mm の板状試料を切り 出し、それを軽く粉砕して約 1mm 角の小片 にした。その後変質により生じている可能性 のある粘土鉱物や炭酸塩鉱物の除去を目的 として、3MHCl 中で約 30 分、さらに 4MHNO₃ 中で約 30 分超音波洗浄後、脱イオン水で洗 浄した。洗浄時間は、試料の変質程度によっ て調整した。洗浄後温水中で約2日間脱塩処 理を行った。乾燥後、顕微鏡下で変質部や斑 晶の混入のない試料をハンドピックし、測定 用試料とした。試料の中性子照射は、JRR4 にて行った。Sパイプで6時間照射(途中回 転)を行った。またカドミウム箔による熱中 性子カットを行った。

アルゴンの同位体比分析は、産業技術総合 研究所のレーザ加熱⁴⁰Ar/³⁹Ar 年代測定シス テムにより行った。分析法等については、 Ishizuka et al. (2003) に準じた。

今年度得られた多くの成果のうち、特に興味深いのは伊豆小笠原弧背弧地域の火山と四国海盆中軸部に存在する紀南海山列と呼ばれる火山列との関係である。紀南海山列の玄武岩類からは7.4-15.5Ma(1Maは百万年)の Ar/Ar 年代が得られた。現段階では年代値に地域による系統的な差は認められない。この 年代は、四国海盆の拡大が停止したと考えら れる 15Ma より概ね若い年代である。紀南海 山列における火山活動が、四国海盆の拡大停 止後、約 800 万年間起きていたことが明らか になった。

一方紀南海山列と背弧海山列の間の海山 群からは 8.9-14.4 Ma の年代が得られた。こ の年代値は、これまで背弧海山列で得られた 年代範囲(17.3-3Ma: Ishizuka et al., 2003)と 重なるが、古い時代に限られている。これら の海山が伊豆小笠原島弧の背弧域の(島弧) 火山活動であることを示唆すると同時に、背 弧域の火山活動が時代とともに東側、すなわ ちより火山フロント近傍に限られていった とする従来の考え(Ishizuka et al., 2003)を支 持する結果である。

上記の結果は、上記2地域の火山がほぼ同 時期に活動していたことを示している。しか しながらこれら火山の溶岩の化学的特徴は 大きく異なる。紀南海山列の溶岩は、それよ り東の火山の溶岩が示すいわゆる島弧の火 山岩が示す特徴、すなわち沈み込む太平洋プ レート由来の物質のマグマへの寄与が全く 認められない。したがっていわゆるプレート の沈み込みに伴う島弧のマグマ活動によっ て形成されたものではない。さらに溶岩の年 代と化学組成との間に驚くべきほど明確な 相関関係が発見された。この関係は、四国海 盆拡大停止後、時代とともに紀南海山列下の マントルの温度が低下あるいはマントルの 上昇流が弱まることにより、マントルの溶融 度が低下し、かつ低温で融けやすい部分のみ が溶融してマグマを生成するようになった ことを示していると解釈できる。背弧海盆拡 大停止以後の背弧地域のマグマティズムと マントルダイナミクスの解明に重要な制約 を与える発見と考えられる。

参考文献 1) Ishizuka, O., K. Uto, and M. Yuasa (2003), Geol. Soc. Spec. Publ., 219, 187-205.

原子炉:JRR-4

装置:Sパイプ

分 野:放射化分析(地質学)
研究テーマ:核破砕核種に対する線量評価法の開発 表 題:水銀中生成トリチウムの性状解明

水銀中で生成するトリチウムの化学形割合

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大強度陽子加速器施設 J-PARC における核 破砕中性子源のターゲットとして使用される 水銀中には様々な浮遊性放射性核種が生成し、 特にトリチウムは生成量が多く、潜在的な内 部被ばく源となる。トリチウムの吸入による 内部被ばく線量を計算する際に使用する線量 係数は化学形によって大きく異なり、トリチ ウム水(HTO)の線量係数はトリチウムガス (HT)のそれの1万倍である。したがって線 量を評価するにあたり、放出されるトリチウ ムの化学形に関する知見は重要である。

昨年度、我々は、大強度陽子誘導トリチウ ムを模擬するために、水銀に少量の金属リチ ウムを溶解して得た液体アマルガムを試料と し、熱中性子照射して水銀中にトリチウムを 生成させる方法を考案した。これにより、HTO および HT の生成を確認した。本年度は、図1 に示すように試料を封入する容器の形状を改 良して試料を直接パージすることで収率の向 上を図り、水銀中で生成するトリチウムの化 学形割合についてデータを得ることを目的と し、液体アマルガム照射実験を行った。

約1gの試料を照射容器に封入し、照射試料 とした。JRR-4 中性子ビーム設備のビーム孔前 に照射試料と Co フラックスモニタを設置し、 熱中性子モード I で 6 時間照射した。放射化 した Co の γ 線スペクトロメトリにより求めた 熱中性子フラックスは約 1.7 × 10⁹ cm⁻² s⁻¹で あった。生成したトリチウムは HTO と HT に



分別、回収し、液体シンチレーションカウン タにより放射能を計測した。照射容器の形状 改善により、収率はほぼ100%となった。図2 に、生成したトリチウムの化学形割合を試料 毎に示す。全試料の平均割合はHTOが40%、 HTが60%、標準偏差は10%であった。

平成 19 年度は、試料容器の気相の成分を操作し、試料に不純物として含まれる酸素や水分の量を変化させ、生成するトリチウムの化学形割合に与える影響を明らかにする予定である。



成果の公表

- a) 真辺健太郎, 横山須美, 遠藤章. 水銀中生 成トリチウムの性状. 日本原子力学会 2007 年春の年会.
- b) K. Manabe and S. Yokoyama, Ratio of tritiated water and hydrogen generated in mercury through a nuclear reaction, Appl. Radiat. Isotopes (2007), in press.

doi:10.1016/j.apradiso.2007.07.028.

使用原子炉: JRR-4 装置名: 中性子ビーム設備 利用分野: 放射化分析・その他

4-4
 研究テーマ:中性子放射化分析法による環境試料の分析
 表 題:大気エアロゾル粒子のキャラクタリゼーション

大気エアロゾル粗大粒子中でのアルミニウム(AI)とバナジウム(V)の濃度比

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大気中に浮遊している粒子、大気エアロゾル 粒子の化学的そして物理的挙動を明らかにす るために、大阪府堺市で大気エアロゾル粒子 を捕集して、その組成分析を行っている。今 回分析した試料は、2006年にロープレッ シャーアンダーセンサンプラーで捕集した試 料で、粒子の大きさ(粒径)を13粒径範囲に分 けて捕集された。この試料を、JRR-3、気送管 照射装置(PN-3)で照射し、A1, Ca, C1, V, Ti, Mn, Naの分析を行った。この中で、粒径 の大きい粗大粒子中での、A1とVの濃度比 (V/A1)の試料ごとの変化について報告する。

試料は、Table 1で示す期間に捕集された。 Table 1

| Period | Start | End |
|--------|--------------|---------|
| P1 | 2006 Jan. 04 | Jan. 31 |
| P2 | 2006 Mar. 28 | Apr. 25 |
| P3 | 2006 Jul. 03 | Jul. 24 |
| P4 | 2006 Oct. 16 | Nov. 13 |

粒径範囲を、C(粗大)とF(微小)に分けて、塵 (PM),A1,Vの濃度をFig1. に示す。粒径範囲 C:>2.2µm,F:<2.2µmとした。PMの濃度 は、期間P2で、粒径範囲CとFともに他の期間 と比べて高くなった。これは、粗大粒子のA1 の濃度が他の期間と比べて4倍以上高くなって おり、土壌粒子つまり黄砂等の中国大陸飛来 の土壌粒子の影響によるものである。Vについ ても土壌粒子の影響で濃度が高くなった。

Vについては、夏期のP3で微小粒子で濃度が高 くなった。微小粒子のVは、石油燃焼由来とさ れており、この時期に、火力発電所等からの 影響が大きくなったと推定される。さら に、P3では粗大粒子でP2に次いでVの濃度が高 くなった。この時期のA1の濃度は、一番低く 土壌粒子の影響を大きく受けてない。さら に、Fig.2で示すように、粗大粒子のVとA1の 濃度比(V/A1)はP3で他の期間と比べて10倍ほ

| 原子炉: JRR-3 | 装置: 放射化分析用照射設備 |
|------------|----------------|
| 原子炉: JRR-4 | 装置: Tパイプ |

ど高くなっていた。これは、微小粒子のVの粗 大粒子への付着又は、土壌粒子のVによる汚染 が考えられる。



分野:放射化分析(環境) 分野:放射化分析(環境)

研究テーマ:関東甲信静地方における浮遊粒子状物質中の金属成分濃度の把握 表 題:関東における大気エアロゾルのキャラクタリゼーション(第26報)

> 内藤季和、米持真一¹ 千葉県環境研究センター ¹埼玉県環境科学国際センター 関東地方環境対策推進本部大気環境部会浮遊粒子状物質調査会議

本研究では、関東地方の1都9県(関東地方の1都6県+山梨県・静岡県・長野県)におい て浮遊粒子状物質の汚染実態を把握し、その濃 度や組成等の動向を知ることを目的とした。

[調査方法] 平成 17 年 7 月 25~29 日(夏期)と 12 月 5~9 日(冬期)に 18 地点で行い、石英ろ紙 およびポリフロンろ紙を装着したアンダーセ ンサンプラーにより、粒子を粒径 2.1~11 μ m(粗大粒子)と2.1 μm 未満(微小粒子)に分級捕 集した。捕集したろ紙試料は秤量後、日本原子 力研究開発機構の原子力科学研究所(茨城県那 珂郡東海村)の JRR-3 原子炉において気送管

(PN-3)での熱中性子放射化分析により、40秒
 照射・180秒測定で9種の短寿命核種(Mg, A1, C1, Ca, Ti, V, Mn, Cu, Br)を分析した。イオンクロマトグラフ法により水溶性成分、CHN コーダー(熱分離法)により、炭素成分についても分析した。

[調査結果](1)粒子状物質濃度:結果を図1に 示した。粗大粒子の平均濃度は夏期が11.2µ g/m³、冬期は7.4µg/m³、微小粒子は夏期12.6 µg/m³、冬期16.1µg/m³であった。微小粒子/(粗 大粒子+微小粒子)の平均値は夏期が0.55、冬期 は0.69 で夏期に粗大粒子の占める割合が多か った。(2)金属成分:バナジウムは東京湾岸で 高い傾向にあり、湾岸部で重油燃焼が多いこと を示唆している。マンガンは例年同様、冬期に 東京湾岸で高くなる傾向があり、鉄鋼工場に由 来すると考えられる。アルミニウムとカルシウ ムは粗大粒子に多く存在し、土壌粒子や道路粉 じん由来と考えられる。ナトリウムと塩素は海 に近い粗大粒子で濃度が高くなり、海塩粒子の 影響と考えられた。臭素は例年微小粒子で濃度 が高いが、昨年度に続いて夏期の粗大粒子で高 くなり、その原因は不明である。



図1 調査地点における浮遊粒子状物質濃度

放射化分析と水溶性成分との比較では、ナト リウムはほぼ一致したが、塩素は放射化分析の 結果が低く、カルシウムとマグネシウムは逆に 放射化分析の結果が高い結果となった。カルシ ウムとマグネシウムについては、非水溶性成分 が多いためと考えられる。

原子炉:JRR-3 装置:気送管 分野:放射化分析(環境)

研究テーマ:放射化分析による家畜・家禽の土壌摂取量推定 表 題:家畜・家禽の土壌摂取が畜産物の生産に及ぼす影響

繁殖雌豚の土壌摂取量の推定

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屋外に放飼した家畜・家禽は土壌を摂取 する。表層土に吸着されている重金属や残 留農薬等の有害物質が土壌摂取を介して 畜産物へ移行すると、ヒトへの汚染も危惧 される。しかし、その影響は十分に検討さ れていない。今年度はスカンジウムを標準物 質として用い、放射化分析法で繁殖雌豚の土 壌摂取量を検討した。

供飼前まで舎飼いしていた繁殖成雌豚(5歳)を屋外区(3頭・平均体重238kg)および屋内区(3頭・平均体重237kg)に分けて 群飼した。1日量2.5kgの配合飼料を朝夕2 回に分けて給与した。試験開始後45~46日 目(1回目)、73~74日目(2回目)ならび に101~102日目(3回目)に1日10点以上 の排糞を採取した。豚糞、給与飼料ならびに 放飼場の土壤を風乾・微粉砕して試料とした。 豚糞(300mg)、給与飼料(300mg)、土壌(100mg) ならびに標準物質のスカンジウム水溶液を 吸着させたろ紙をポリエチレン製袋に二重 封入し、日本原子力研究開発機構JRR-4炉簡 易照射筒(熱中性子束 5.3×10¹⁷×m⁻²)で、 20分間照射した。30~45日間の冷却後、外 側のポリエチレン製袋を交換し、γ線スペク トロメトリによって 500秒間測定した。

試料中のスカンジウム含有率と土壌含 有率は表1のとおりであった。給与試料中 のスカンジウムは、試料材料の穀実に付着 した土壌や同じく添加ミネラルに由来し たものと考えられる。また、給与飼料の乾 物消化率を80%とすると、屋外区および屋内 区の繁殖雌豚の1日1頭当たり土壌摂取量 は図1のとおりとなった。両区の差から、繁 殖雌豚の土壌摂取量は1回目では109g/ 頭/日、2回目では277g/頭/日、3回目 では232g/頭/日となった。この量は繁殖 雌豚が摂取した飼料の4~11%の量に相 当し、必須ミネラル欠乏による異嗜行動時 のような高い値ではなく、通常な飼育では この範囲の土壌摂取量と考えられる。

| <u>表1</u> 試料中のスカンシ | ジウムと土壌の含有る | 举 |
|--------------------|------------|-------|
| 試 料 | スカンジウム | 土壌 |
| 給与飼料 | 0.035ppm | 0.22% |
| 豚糞·屋外区1回目 | 3.95 | 24.2 |
| 豚糞·屋外区2回目 | 9.58 | 58.9 |
| 豚糞·屋外区3回目 | 7.92 | 48.7 |
| 豚糞·屋内区1回目 | 0.39 | 2.4 |
| 豚糞·屋内区2回目 | 0.58 | 3.6 |
| 豚糞・屋内区3回目 | 0.37 | 2.3 |
| 土壤 | 16.3 | _ |



原子炉:JRR-4 装置:簡易照射筒 分野:放射化分析(農・水産物)

研究テーマ:中性子放射化分析法の農業環境研究に対する利用法の開発と適用

表 題:作物の無機元素集積能力を評価するための土壌からの移行係数算出法の開発

作物の無機元素集積能力を評価するための土壌からの移行係数算出法の開発

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1. はじめに

土壌ー作物移行係数は、土壌中に存在し ている対象元素が作物にどの程度移行する のかの指標であり、作物中(特に可食部) の元素の濃度を、その作物を育てた土壌中 の濃度で割った値である。土壌ー作物移行 係数を有害元素に適用した場合には、有害 成分の作物への集積しやすさの指標となり、 稀少資源元素に適用した場合には、作物の 資源回収能力の指標になるため、これを簡 易に算出する意義は大きいと考えられる。 また機器中性子放射化分析(放射化分析と 略す)は、植物と土壌を化学的な分離操作 なしで、同じ条件のもとに照射、測定でき るという特徴を持つ多元素同時分析法であ る。

植物と土壌を同時に放射化すれば、標準 物質や近年放射化分析で用いられるko法 のような複雑な計算なしに、土壌-作物移 行係数を求めることができると考え、検討 を行った結果について報告する。

2. 実験方法

つくば市の農業環境技術研究所畑ほ場 (黒ボク土および造成土)より葉菜類・根 菜類・麦類・豆類・水稲等の作物および土 壌を採取し、風乾後微粉砕して試料とした。 ポリエチレン製袋に2重封入した試料を茨 城県東海村にある日本原子力研究開発機構 JRR3 炉 PN1, PN2 気送照射孔および JRR 4 炉 水力 T パイプ (A系統)で、短半減期核種 用に1分、中長半減期核種用に20分照射し、 冷却後外側のポリエチレン製袋の包み替え を行ない、同軸型 HPGe 半導体検出器を装備 した γ線スペクトロメトリにより 500 秒か ら 24,000 秒かけて測定を行った。

3.結果および考察

短半減期核種用には作物 50mg および土 壌 10mg を秤取し、1 分照射した後、3 時間 から 1 日冷却時間を置き、500 秒の測定を 行うことで、 γ 線スペクトロメトリにおけ る測定距離などの測定条件を土壌と植物と で同じにできることがわかった。

中長半減期核種用には作物 300mg および 土壌 100mg を秤取し、20 分照射した後、6 日以上冷却時間を置き、1000秒から24,000 秒かけて測定を行うことで、土壌・植物同 一条件下での測定が可能であった。 半減期が1日以内の短寿命放射性核種では ⁴⁰K, ⁵⁶Mn, ²⁴Na 等が、半減期が1週以内の 中寿命放射性核種では⁸²Br,¹⁴⁰La,¹⁵³Sm 等が、半減期が1週を越える長寿命放射性 核種では¹⁴¹Ce,⁶⁰Co,⁵¹Cr,¹⁵²Eu,⁵⁹Fe,⁸⁶Rb, ⁴⁶Sc, ⁶⁵Zn 等が検出される作物があり、移 行係数が算出できた(表1)。表1の結果は、 各作物で Rb および Zn の移行係数が比較的 高いことを示した。短半減期核種において も移行係数が算出できるものがあった。標 準試料を入れない場合には、定量に関する 情報は得られないが、移行係数は算出でき る (表 2)。

4. 結論

以上の結果、土壌一植物移行係数の算出 を容易に行う手段として、放射化分析法が 有効であり、高い集積特性を有する作物の スクリーニングに使用できる可能性が示さ れた。

参考文献

1)第44回アイソトープ・放射線研究発表会 要旨集,IIp-01,(2007),p150

表1 同一畑ほ場から採取した各種畑作物 の土壌-作物移行係数(長寿命核種からの 計算値、土壌;黒ボク土)

| | | | | 2. | | <u></u> | | <u></u> |
|----------|--|-----------|--------------|------------------------|---------|---------------|----------------|-------------------|
| 1 | | | mg/kg | od 移行係数 | mg/kg | oe 移行函数 | mg/kg | |
| I | 4 - 12 Jan 1997 - 17 | 2001年 | 189 | - | 40 | - | 40 | - 一 |
| | ><ば畑圃場 | 2002年 | 159 | - | 40 | - | 38 | - |
| I | レタス | 2001年 | | nd | | nd | 0.4 | 0.010 |
| | ブロッコリー | 2001年 | r | nd | | nd | 0.3 | 0.008 |
| I | キャヘッ | 2001年 | 13 | 0.07 | 0.6 | 0.015 | 0.4 | 0.011 |
| 葉 | キャベツ | 2002年 | 13 | 0.06 | | nd | 0.3 | 0.008 |
| 菜 | チンケンサイ | 2001年 | 14 | 0.08 | | nd | 1.0 | 0.025 |
| 類 | チンケンサイ | 2002年 | 20 | 0.13 | 0.1 | 0.002 | 1.1 | 0.028 |
| | 小松菜 | 2002年 | 9 | 0.06 | | nd | 1.4 | 0.037 |
| | 3月5日ホウレンソウ | 2002年 | r | nd | 0.1 | 0.003 | 1.0 | 0.027 |
| - | 5月10日ホワレンソワ | 2002年 | 1 | nd | 0.1 | 0.003 | 0.5 | 0.012 |
| 根菜類 | ニンソン | 2002年 | 18 | 0.11 | | nd | 0.2 | 0.004 |
| | -/-/ | 2002年 | r | na | | na | 0.0 | 0.015 |
| 芋 | サトイモ(ナ) | 2001年 | 1 | 10 0.02 | | nd | 0.5 | 0.012 |
| 類 | リトイモ(税) | 2001年 | 7 | 0.02 | | nd | 0.0 | 0.013 |
| | 1111(金米) | 2001年 | 25 | 0.03 | 0.3 | 0.007 | 27 | 0.022 |
| 穀 | 燕麦 | 2002年 | 11 | 0.07 | 0.2 | 0.004 | 2.5 | 0.065 |
| 類 | 小麦茎葉 | 2002年 | 36 | 0.23 | 0.2 | 0.005 | 2.1 | 0.055 |
| 豆 | ソラマメ | 2001年 | r | nd | | nd | 1.2 | 0.031 |
| 類 | グリーンピース | 2001年 | 29 | 0.15 | | nd | 0.3 | 0.009 |
| é3 | デントコーン | 2001年 | r | nd | | nd | 0.5 | 0.011 |
| 出 | <i>พ</i> ฦ, พ | 2001年 | 8 | 0.04 | | nd | 2.1 | 0.053 |
| 作 | イタリアンライク・ラス | 2002年 | 16 | 0.10 | 0.4 | 0.009 | 1.7 | 0.045 |
| | 7ルファルファ | 2002年 | 9 | 0.05 | 0.2 | 0.004 | 1.5 | 0.040 |
| (参考) | ホティアオイ | 2001年 | 27 | - | 1.5 | - | 3.1 | - |
| | | | | | r | - | | - |
| I | | | (| Ur 1 # 2 4 = 17 # 4 | | EU 新久公 /大学 | | Fe #2 45 /5 #4 |
| — | | 2001年 | mg/kg | 杨仃係数 | mg/kg | 1917係数 | mg/kg | 炒 仃係数 |
| - | oくば畑圃場 | 2001年 | 94 | _ | 1.5 | | 0014U 78521 | |
| I | レタス | 2002年 | 0.2 | 0.002 | 1.4 | nd – | 96 | 0.0011 |
| 1 | ブロッコリー | 2001年 | V.2 | nd 0.002 | | nd | 71 | 0.0008 |
| I | キャベッ | 2001年 | r | nd | 0.007 | 0.005 | 269 | 0.0008 |
| 葉 | キャベツ | 2002年 | r | nd | | nd | 62 | 0.0032 |
| 菜 | チンケンサイ | 2001年 | r | nd | | nd | 133 | 0.0064 |
| 類 | チンケンサイ | 2002年 | 0.6 | 0.007 | 0.005 | 0.004 | 500 | 0.0016 |
| | 小松菜 | 2002年 | 0.2 | 0.002 | | nd | 134 | 0.0017 |
| | 3月5日ホウレンソウ | 2002年 | 0.3 | 0.004 | 0.004 | 0.003 | 282 | 0.0036 |
| | 5月10日ホリレノフリ | 2002年 | 0.3 | 0.004 | | na | 100 | 0.0020 |
| 根菜類 | | 2002年 | 0.2 | 0.004 | | nd | 27 | 0.0019 |
| | -/-/ サレイエ(エ) | 2002年 | | nd ad | | nd | 27 | 0.0003 |
| 芋 | サトイモ(钼) | 2001年 | 0.2 | 0.002 | | nd | 22 | 0.0003 |
| 類 | サトイモ(基葉) | 2001年 | 0.4 | 0.002 | | nd | 152 | 0.0018 |
| +0 | 大麦 | 2002年 | 0.8 | 0.009 | 0.007 | 0.005 | 367 | 0.0047 |
| 寂 | 燕麦 | 2002年 | 0.7 | 0.008 | 0.007 | 0.005 | 198 | 0.0025 |
| 規 | 小麦茎葉 | 2002年 | 0.6 | 0.007 | 0.009 | 0.006 | 285 | 0.0036 |
| 묘 | ソラマメ | 2001年 | r | nd | | nd | 72 | 0.0008 |
| 類 | グリーンビース | 2001年 | 1 | nd | | nd | 81 | 0.0010 |
| 飼 | テントコーン | 2001年 | 0.4 | 0.004 | 0.005 | nd | 118 | 0.0014 |
| 料 | フルカム ノルリストニノカ [*] ニス | 2001年 | 0.7 | 0.008 | 0.005 | 0.003 | 320 | 0.0038 |
| 作 | 7177777777 | 2002年 | 0.5 | 0.006 | 0.009 | 0.000 | 340 | 0.0043 |
| (余孝) | ホティアオイ | 2002年 | 2.9 | 0.004 | 0.018 | 0.013 | 2022 | 0.0030 |
| (27) | 471741 | 20014 | 2.0 | | 0.025 | | 3300 | |
| | | | | 16 | r | 1 | | DL |
| | | | | 11 按行区数 | ma/ka | LU 投行反为 | ma /lea | RD 段// 医粉 |
| — | | 2001年 | mg∕kg ∕io | 19171ポ釵 | ттg/ кg | 191丁1术叙 | ing/kg | 19171ポ剱 |
| | oくば畑圃場 | 2001年 | 3.4 | | 0.0 | | 48 | _ |
| | レタス | 2001年 | 0.0 | 00 | 0.0 | nd | 34 | 0.86 |
| I | ブロッコリー | 2001年 | 0.0 | 0.0 | 1 | nd | 23 | 0.57 |
| I | キャベッ | 2001年 | 0.035 | 0.009 | | nd | 29 | 0.72 |
| 葉 | キャベツ | 2002年 | 1 | nd | | nd | 21 | 0.45 |
| 菜 | チンケンサイ | 2001年 | 1 | nd | | nd | 29 | 0.71 |
| 類 | チンケンサイ | 2002年 | 0.024 | 0.007 | | nd | 28 | 0.58 |
| | 小松菜 | 2002年 | 1 | nd | | nd | 25 | 0.53 |
| I | 3月5日ホウレンソウ | 2002年 | 0.005 | 0.001 | I | nd | 18 | 0.38 |
| I | 10日本ワレンクク 1-1-1-1-1-1-1-1-1-1-1-1-1-1-1-1-1-1-1 | 2002年 | | IU ad | | nd | 27 | 0.50 |
| 根菜類 | | 2002年 | · · · | nd | | nd | 6 | 0.30 |
| <u> </u> | レーノーノ サレイモ(子) | 2002年 | | nd od | | nd | 9 | 0.12 |
| 芋 | サトイモ(親) | 2001年 | , , | nd | | nd | 6 | 0.15 |
| 頖 | サトイモ(茎葉) | 2001年 | 0.021 | 0.005 | 1 | nd | 20 | 0.50 |
| ±n. | 大麦 | 2002年 | 1 | nd | 0.0004 | 0.00001 | 15 | 0.32 |
| 彩 | 燕麦 | 2002年 | r | nd | | nd | 19 | 0.39 |
| 頖 | 小麦茎葉 | 2002年 | 0.012 | 0.004 | | nd | 12 | 0.25 |
| 豆 | ソラマメ | 2001年 | 1 | nd | | nd | 9 | 0.21 |
| 類 | グリーンピース | 2001年 | 1 | nd | | nd | 6 | 0.16 |
| 飼 | デントコーン | 2001年 | 1 | nd | | nd | 18 | 0.44 |
| 料 | <u> ソルカ ム</u> | 2001年 | r | nd | | nd | 15 | 0.37 |
| 作 | 1917251552 | 2002年 | | nd | | nd | 25 | 0.52 |
| (44.74) | 1510771077 | 2002年 | 1 | nd | 0.0000 | nd | 18 | 0.38 |
| (奓考) | ホナイパオイ | 2001年 | 0.058 | - | 0.0092 | - | 15 | 0.39 |
| | | | | | | | | |
| | | | | | | | | |

表1 つづき

| | | | S | ic | | Zn |
|------|-------------|-------|-------|--------|-------|------|
| | | | mg/kg | 移行係数 | mg/kg | 移行係数 |
| | くげた国語 | 2001年 | 34 | I | 122 | - |
| - | スは注意 | 2002年 | 31 | - | 133 | - |
| | レタス | 2001年 | 0.013 | 0.0004 | 25 | 0.20 |
| | ブロッコリー | 2001年 | 0.004 | 0.0001 | 38 | 0.31 |
| | キャベッ | 2001年 | 0.065 | 0.0019 | 35 | 0.28 |
| 葉 | キャベツ | 2002年 | 0.002 | 0.0001 | 20 | 0.15 |
| 菜 | チンケ`ンサイ | 2001年 | 0.030 | 0.0009 | 34 | 0.28 |
| 類 | チンケ`ンサイ | 2002年 | 0.179 | 0.0058 | 43 | 0.32 |
| | 小松菜 | 2002年 | 0.031 | 0.0010 | 27 | 0.21 |
| | 3月5日ホウレンソウ | 2002年 | 0.088 | 0.0028 | 42 | 0.32 |
| | 5月10日ホウレンソウ | 2002年 | 0.040 | 0.0013 | 67 | 0.50 |
| 坦带粗 | ニンジン | 2002年 | 0.040 | 0.0013 | 31 | 0.23 |
| 复为无法 | ニンニク | 2002年 | 0.004 | 0.0001 | 12 | 0.09 |
| Ŧ | サトイモ(子) | 2001年 | 0.003 | 0.0001 | 18 | 0.15 |
| - 新 | サトイモ(親) | 2001年 | 0.003 | 0.0001 | 15 | 0.13 |
| ×R. | サトイモ(茎葉) | 2001年 | 0.032 | 0.0009 | 23 | 0.19 |
| 志乃 | 大麦 | 2002年 | 0.141 | 0.0045 | 6 | 0.05 |
| 和 | 燕麦 | 2002年 | 0.063 | 0.0020 | 16 | 0.12 |
| XR. | 小麦茎葉 | 2002年 | 0.095 | 0.0031 | 6 | 0.05 |
| 묘 | ソラマメ | 2001年 | 0.002 | 0.0001 | 46 | 0.38 |
| 類 | グリーンピース | 2001年 | 0.004 | 0.0001 | 44 | 0.36 |
| 伯 | デントコーン | 2001年 | 0.021 | 0.0006 | 22 | 0.18 |
| 出日 | ソルカ・ム | 2001年 | 0.086 | 0.0026 | 21 | 0.17 |
| 1/F | イタリアンライク・ラス | 2002年 | 0.118 | 0.0038 | 58 | 0.44 |
| IF | アルファルファ | 2002年 | 0.072 | 0.0023 | 18 | 0.14 |
| (参考) | ホティアオイ | 2001年 | 0.282 | - | 283 | _ |

| 表 | 2 | 短寿命照射 | (1分) | によ | り算出 | された |
|---|---|--------|------|----|-----|-----|
| 7 | ン | ガンの土壌- | 作物移 | 行係 | 数 | |

| 種別 | 作物名 | 採取年 | Mn |
|---------------|--------------|-------|---------|
| | フダンソウ | 1993年 | 0.0411 |
| | ハクサイ | 1994年 | 0.0177 |
| | モロヘイヤ | 1995年 | 0.0551 |
| | カリフラワー | 1996年 | 0.0137 |
| | ネギ | 1996年 | 0.0094 |
| | ブロッコリー | 1996年 | 0.0182 |
| 葉菜類 | コマツナ | 1999年 | 0.0263 |
| | キャベツ(1/27収穫) | 1999年 | 0.0155 |
| | キャベツ(4/21収穫) | 1999年 | 0.0233 |
| | チンゲンサイ | 1999年 | 0.01 55 |
| | ホウレンソウ | 1999年 | 0.0264 |
| | レタス | 2000年 | 0.0217 |
| | 春菊 | 2000年 | 0.0188 |
| | カボチャ | 1995年 | 0.0044 |
| | キュウリ | 1999年 | 0.0101 |
| 用共好 | オクラ | 1999年 | 0.0075 |
| 米采規 | トマト | 1999年 | 0.0071 |
| | ナス | 1999年 | 0.0113 |
| | ピーマン | 1999年 | 0.0111 |
| | ショウガ | 1995年 | 0.0241 |
| 坦苏粨 | ラッキョ | 1997年 | 0.0038 |
| 低未規 | ダイコン | 1999年 | 0.0062 |
| | ニンジン | 2000年 | 0.0096 |
| | ジャガイモ | 1994年 | 0.0038 |
| 芝粨 | ジャガイモ | 1997年 | 0.0036 |
| 丁規 | サツマイモ | 1999年 | 0.0052 |
| | サトイモ | 1999年 | 0.0051 |
| | 玄米 | 1993年 | 0.0686 |
| 古 凸 米石 | 玄米 | 1996年 | 0.0303 |
| 和規 | ソバ | 1995年 | 0.0210 |
| | トウモロコシ | 2000年 | 0.0140 |
| | インゲン | 1995年 | 0.0179 |
| | アズキ | 1996年 | 0.0125 |
| 豆類 | ソラマメ | 1999年 | 0.0090 |
| | キヌサヤエンドウ | 1999年 | 0.0069 |
| | エダマメ | 2000年 | 0.0199 |

原子炉:JRR-3,JRR-4 装 置:気送管,水力Tパイプ 分 野:放射化分析(農・水産物)

研究テーマ: SI トレーサブルな標準物質分析法及び不確かさ評価法の開発 表 題: セラミックス中のクロム、コバルトの放射化分析

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産業技術総合研究所計測標準研究部門で は、国家計量機関として国家計量標準の開 発・供給を行っている。無機化学標準の分野 では、これまで重量分析法、電量分析法、滴 定法、同位体希釈質量分析法等の一次標準測 定法による値付けを行い、基盤的な元素標準 液や社会的にニーズが高い材料系標準物質

(鉄鋼、セラミックス等),環境組成標準物 質(底質、生物試料)を開発してきた。材料 系標準物質、環境組成標準物質の認証値の算 出には、主に同位体希釈法を中心とした複数 の分析法(ID-ICPMS, ICP-MS, ICP-OES)を 適用しているが、これらの手法とは異なる原 理に基づく機器中性子放射化分析法(INAA) を適用することで,開発した標準物質の認証 値の信頼性をさらに向上させることが期待 できる。 INAA は上記の分析法とは異なり, 溶液化することなく定量できることが大き な利点である.しかしながら、日本国内にお いては INAA による分析結果の信頼性評価に ついて、標準物質開発に欠かせない測定不確 かさの観点から評価した例は少ない。そこで 本研究では放射化分析の測定不確かさに基 づいた信頼性評価を行い、標準物質開発に応 用することを目的とする。18年度では、難分 解性試料である窒化けい素セラミックスを モデル試料として INAA によるクロム、コバ ルトの定量を試みた。

線製ポリエチレン袋に二重封入した。Cr、Co の比較標準は、トレーサビリティが確保され た関東化学製 JCSS (Japan Calibration Service System) Cr、Co1000ppm 標準液を 希釈後、洗浄したろ紙 (ADVANTEC No 5C) に 滴下して調製した。窒化けい素5試料、比較 標準 Cr、Co各3水準、ブランク計12試料を カプセルに詰め JAEA 研究用原子炉 JRR-4、T パイプで20分間照射した。短半減期核種を 減衰させた後、原子力科学研究所研究炉実験 管理棟に設置された Ge 半導体検出器により γ 線スペクトルを測定した。計数誤差による ばらつきを軽減するため、試料及び比較標準 の測定は複数回行った。

結果:分析結果を表に示す。クロム、コバル ト両元素の定量値の相対標準偏差は 1.1%、

1.3%と良好であった。18 年度以降は INAA の 測定不確かさを評価するために、照射キャプ セル内の中性子フラックスの分布、さらに適 切な比較標準物質の調製(内部標準法もしく は標準添加法の適用)、放出γ線の自己吸収 の影響、γ線測定時のパルスパイルアップの 影響等を検討する予定である。

INAA の測定不確かさを正しく見積もるこ とで、他の分析法による定量値との比較が可 能になり、標準物質開発への放射化分析法の 適用可能性を評価することができると考え られる。

実験:窒化けい素約 200 mg を清浄な日立電

表 INAA による窒化けい素中のクロム、コバルト分析結果

| | 定量值 (µ g/g) | 相対標準偏差(%) |
|----|--------------|-----------|
| Cr | 9.69 | 1.14 |
| Co | 6.20 | 1. 33 |

原子炉:JRR·4 装置:Tパイプ 分野:放射化分析(工業材料)

「地質特性が河川水質に及ぼす影響に関する研究」

Influence of geological characteristics on the chemistry of river water

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はじめに

かつて鉱山国として知られていたわが国において は,各地の廃鉱山からの流出水による水質汚濁が, 深刻な環境問題を引き起こしている。それらの多く は責任の所在が不明確であることが多く、放置され ている例も少なくない。ホタルの里として知られる 吉野川市美郷地区においても、旧銅山からの硫酸酸 性の坑廃水が流出し続けており、下流域ではホタル の飛翔が見られないことが知られている。その原因 としては,河川底質の重金属が高濃度であるため, ホタルの餌であるカワニナが生育できない環境であ るとの因果関係が判明しているが、未だに坑排水の 対策は採られていない。そこで本研究では、河川水 質,特に溶存態重金属の挙動と底質との関係を明ら かにし、得られた知見に基づいて問題解決に向けた 具体的な対策を提案することを目的に調査を実施し た。

1. 研究の方法

1. 1 調査地

地となっている。

徳島県吉野川市美郷地区は,北緯34度1分,東経 134度15分を中心とし,東西13km,南北 8km,総 面積50.47km²の四国山地の山稜にある山村である (図1)。人口は2005年現在で,1,247人。四国山地 の山稜に囲まれた典型的な山村で,山稜を超えて北 は吉野川市山川地区,川島地区に接し,南は木屋平 村を経て剣山山脈に連なる。南東部は柳水峠の稜線 をもって神山町と境をなし,村の中心部を流れる川 田川に東山谷川が合流して吉野川中流に注いでいる。 地勢は概ね北部で険しいが,川田川から東山谷川を 通り大野を経て柳水庵に至る線以南は緩やかな傾斜

地質的には中央構造線・三波川帯に位置し,当地域 を構成する三波川変成岩は,泥質片岩・砂質片岩・ 珪質片岩・塩基性岩(塩基性片岩・変はんれい岩)か らなり、それらは褶曲しながらも大局的には北に傾 斜する構造を呈している。三波川帯の結晶片岩層の 中には含銅硫化鉄鉱の鉱床があり、そのいくつかは 1960年代まで採掘されていた。それらの中でも東山 谷川上流部に位置する旧東山鉱山は、黄鉄鉱・黄銅 鉱・磁硫鉄鉱を算出する阿波有数の銅山であった。 明治初期の開坑以降, 1900 年から 1930 年代に最盛 期を迎え,1907年と1908年の2年間の精鉱産出高 は 32,694t に達した。当時, 鉱山周辺には, 約 1000 人の従業員と家族が居住していたという。閉山後は, 鉱石残渣の小山を残して周辺は荒れ果て、今に至っ ている。鉱山跡地には自噴井が残されており、高濃 度の重金属排水を流出している。この流出水の析出 物の色から、地元ではこの自噴井からの流出水路を 「赤水谷川」と呼び習わしている。「赤水谷川」は自 噴井の下流約1km の地点で,同地域の主要河川で ある東山谷川に合流している。本研究では、この赤 水谷川と東山谷川本流を中心に河川水・河川底質の 試料採取ならびに流量測定を行った。また当該水域 の溶存化学成分のバックグラウンドを得るために, 東山谷川の支流、および美郷地区を流れるもう一方 の主要河川である川田川の調査も併せて実施した。

1.2 現地調査ならびに試料採取

調査は 2001 年 10 月,2002 年 4 月,2002 年 12 月,2007 年 5 月の計 4 回にわたって実施し,美郷 村東山鉱山跡および東山谷川,川田川水系において 各回とも 20~25 地点から水試料を採取した。また, 2002 年 4 月ならびに 2002 年 12 月,2007 年 5 月に は河川底質(河川土壌)のサンプル採取を合わせて 実施した。水試料は簡易濾過の後,ポリエチレンビ ンに採取・保存した。採水にあたっては,現地にお いてデジタル式pHメータ (DKK HPH-130), ECメ ーター (Hach社製 SensIon 5) あるいはデジタル式 pH-ECメーター (Horiba pH・EC meter D-24) によ

JRR-3 PN、ASC-20、地球化学試料放射化分析



図1 調査地:徳島県吉野川市美郷地区

り水温・電気伝導度(EC)およびpHの測定を行った。 なお,使用した機器は,あらかじめ日本工業規格 K0102 (JIS-K0102)にしたがい校正を行った。電気 伝導度(EC)の定量限界は0.01 mS/mであり,pH, ECともに繰り返し誤差は1%以内であった。また現 地において、メチルレッド・ブロモクレゾールグリー ン混合溶液を指示薬とした硫酸滴定法によりアルカ リ度の測定を行い、HCO3でに換算した。底質試料に ついては、チャック付きビニル袋に封入した後、冷 蔵し、実験室において60℃で3日間乾燥させた後、 測定に用いた。

1. 3 化学分析

試薬類は市販の特級試薬をそのまま使用した。また,使用した水は,錫でメッキした銅製の蒸留器(高 林理化株式会社製)によって得られた蒸留水をさら に Millipore 社製 Milli-Q SP 超純水システムにて 処理した超純水を用いた。

主要陰イオン成分については、 $0.20 \mu m$ のメンブ ランフィルターでろ過の後、イオンクロマトグラフ ィー(Hitachi L-7470)を用いてノンサプレッサ法に より測定した。主要陽イオンについては、島津製作 所 AA-646 を用い、 Na⁺とK⁺はフレーム発光分析 法、Ca²⁺とMg²⁺は 1%ランタン共存下において原子 吸光光度法 (AA) により定量した。各イオンの定量 限界は、F-, Cl⁻, PO₄³⁻, SO₄²⁻, Na⁺およびCa²⁺が 5.0 μ mol/dm³, NO₃が 1.5 μ mol/dm³, K⁺およびMg²⁺ が 1.0 µmol/dm³であった。繰り返し誤差は全イオン において 3 %以内であった。

溶存主要イオンの調査においてMg²⁺, SO₄²⁻など の値が明瞭に高い地点が確認されたため,川田川中 流の6地点,東山谷川水系の10地点について河川 水・河川底質について重金属の分析を実施した。河 川水中のカドミウム,銅,マンガン,亜鉛について はICP発光分光光度法を用いて,鉄についてはチオ グリコール酸ナトリウムによる3価鉄還元の後に, ジピリジル発色法を用いた吸光光度法により吸収波 長525 nmで測定した。

底質試料については, 原子炉中性子を用いた機器 中性子放射化分析法(INAA)により、重金属類の多元 素同時定量を行った(放射化分析研究会, 2004)。 試料は、アルミナ製スタンプミルで粉砕し、さらに メノウ製ボールミルにより20分間粉砕した。こう して均質化した試料 100 mgをポリエチレン製の袋 に入れ空気を除去した後シーリングし、さらにこれ をポリエチレン製袋で二重にシーリングした。この 試料を日本原子力研究開発機構の研究用原子炉 JRR-3を用いて,気送管PN-1(熱中性子束密度: 5.2×10¹⁷ m⁻²·s⁻¹) で5分間照射し, 試料を放射化し た。核種の測定には東京大学・大学開放研究室のGe 半導体検出器ASC-20を用いた。また、定量計算に は検量線法,ならびに解析ソフトKAYZERO/ SOLCOI (オランダ, DMS Research製) によるk0 法を用いた(Simonits et al., 1975)。

またこれとは別に、ICP発光分光光度法等を用い て底質試料の湿式分析を以下の手順で行った。固体 試料 200 mg をテフロン容器に量りとり,濃硝酸 6 cm³,フッ化水素酸 3 cm³を加え、マイクロ波分解装 置で 25 分間の分解を 3 回繰り返した。次に得られ た溶液をホットプレート(約 250 °C)で蒸発乾固し た。冷却後,1N 硝酸 5 cm³ を加え 30 分放置し, 残留物を溶解させた。その後,0.45 μ m メンブラン フィルターで吸引ろ過を行い,純水で定容(50 cm³)し,ICP発光分光光度法および原子吸光光度 法にて測定した。

2. 結果

2. 1 河川溶存成分:主要成分·重金属

過去4回にわたって同地点で水採取,ならびに分 析を実施したが,ECの同一地点における時間変動 は、地理的な変動に比べて小さく、ほとんどの地点 において変動係数(標準偏差/平均値×100%)は 15%以内であった。これに対して空間変動について は、同一調査期間内における各水試料のECの変動 係数はいずれの回も54-69%となり、地理的条件に よる水質変動が時間変動をはるかに上回ることが判 明した。時間変化による水質変動が小さなことが確 認できたため、以下溶存成分については各化学成分 のデータが揃った2002年4月の観測値について議 論を進める。

調査地域の河川成分を代表する項目として,電気 伝導度(EC),pHならびに主要溶存成分の濃度を表 1に示した。また,重金属類の分析結果を表2に示 した。旧東山鉱山からの流出水である赤水谷川(H3) には,高濃度のアルカリ土類金属(Ca²⁺・Mg²⁺), 硫酸イオン (SO_{4²}),および重金属類 (Cu・Fe・ Mn・Zn)が溶存している。しかし、同河川におけ る他の元素(Na+・K+・Cl)については、東山谷川・ 川田川の各採水地点から得られた試料と同程度の濃 度を示し、人為的な影響の指標となるNO3 に関して は東山谷川・川田川の各地点に比べ小さな値となっ ている。また、pHが低いためにHCO3の濃度も低く なっている。これらの分析結果から、赤水谷川の水 質は、典型的な含銅硫化鉄鉱鉱床からの流出水で形 成されていることが示される。なお、環境基本法に 基づく水質汚濁に係る環境基準として指定されてい る重金属項目(Cd・Pb・As・Hg)について赤水谷 川試料の分析をしたところ(ICP: Hgは還元気化・冷 原子吸光法), Cd・Asは環境基準値とほぼ同値の $0.01 \pm 0.001 \text{ mg/dm}^{3}$ となったが、Hgは 0.7 ± 0.1 ng/dm³(基準値:500 ng/dm³), Pbは検出限界以下 (0.01 mg/dm³)であった。また、Cd・As・Pbについ ては、他の試料水についても分析を試みたが、いず れも検出限界以下であった。

2.2 河川底質の重金属

ICP, AA, INAA による河川底質の分析結果を表 2に示す。分析対象となった 11 元素(Cu, Zn, Cd, Md, Pb, As, Fe, Ni, Cr, Co, Mo)のうち, この地域の バックグラウンドとなる川田川の含有量に比べ,赤 水谷川ならびにその下流域において顕著に高い値を 示した元素のみを示してある。その結果,赤水谷川 において顕著に高い値(バックグラウンドの平均値 +変動値の2σ以上)を示したのは, Cu・Fe・Mn・ Zn であった。コバルトはわが国の地殻推定含有量 (Co: 15 mg/kg)に比してやや高い値(Co: 22 mg/kg)を示したが(Togashi *et al.*, 2000),当地域

表1 河川水の溶存主要成分 (n=2)

| | 溶存主要成分 | | | | | | | | | | |
|------|--------------|------|------------------------------|-----------------------------|---|---|--|---|--|--|-----------------------------|
| | EC (mS/m) | pH | Na+ (mg/dm ³) | K+ (mg/dm ³) | Mg ²⁺ (mg/dm ³) | Ca ²⁺ (mg/dm ³) | Cl [.] (mg/dm ³) | NO3 ⁻ (mg/dm ³) | SO4 ²⁻ (mg/dm ³) | HCO3 ⁻ (mg/dm ³) | Si (mg/dm ³) |
| K-7 | 13.70 | 8.22 | 3.84 | 0.82 | 2.64 | 17.4 | 3.89 | 3.42 | 11.3 | 44.7 | 4.06 |
| K-8 | 14.87 | 8.46 | 4.22 | 0.93 | 2.84 | 18.7 | 4.16 | 3.62 | 13.6 | 48.1 | 4.06 |
| K-9 | 17.83 | 8.32 | 4.99 | 1.69 | 3.14 | 21.1 | 6.59 | 11.8 | 16.3 | 44.9 | 4.06 |
| K-10 | 15.09 | 8.58 | 4.48 | 1.16 | 2.92 | 19.2 | 4.81 | 5.45 | 14.2 | 46.4 | 3.73 |
| K-11 | 14.96 | 8.89 | 4.55 | 1.04 | 2.94 | 19.1 | 4.83 | 4.89 | 14.3 | 47.6 | 3.69 |
| K-12 | 15.98 | 8.95 | 4.62 | 0.98 | 3.58 | 19.3 | 4.95 | 4.36 | 16.6 | 46.2 | 3.81 |
| H-1 | 12.02 | 7.83 | 3.99 | 0.50 | 1.71 | 15.4 | 3.70 | 2.50 | 8.85 | 29.5 | 5.02 |
| H-2 | 13.89 | 8.12 | 4.65 | 0.98 | 2.58 | 17.1 | 4.93 | 4.37 | 11.3 | 32.9 | 3.85 |
| H-3 | 51.4 | 4.90 | 4.88 | 1.08 | 20.0 | 47.0 | 2.88 | 0.20 | 224 | 1.0 | 17.0 |
| H-4 | 18.8 | 6.83 | 4.58 | 0.89 | 5.54 | 21.1 | 4.57 | 2.43 | 41.9 | 31.7 | 5.40 |
| H-5 | 12.25 | 7.37 | 4.45 | 0.71 | 3.65 | 13.1 | 5.52 | 2.39 | 6.98 | 33.2 | 4.98 |
| H-6 | 15.39 | 7.83 | 4.66 | 0.82 | 3.50 | 19.4 | 3.56 | 4.53 | 6.84 | 42.2 | 4.19 |
| H-7 | 10.77 | 7.87 | 4.28 | 0.53 | 2.23 | 12.2 | 3.44 | 1.93 | 8.67 | 27.6 | 4.52 |
| H-8 | 16.82 | 7.80 | 4.71 | 0.88 | 4.31 | 18.6 | 4.78 | 3.15 | 22.6 | 43.4 | 4.69 |
| H-9 | 17.07 | 8.25 | 4.70 | 0.87 | 4.20 | 18.7 | 4.74 | 3.02 | 21.2 | 44.7 | 4.56 |
| H-10 | 16.30 | 8.57 | 4.78 | 0.93 | 4.26 | 18.7 | 5.07 | 3.46 | 20.3 | 47.6 | 4.60 |

| | | 河ノ | 川水 | 河川底質 | | | | |
|------|-----------------------|-----------------------|-----------------------|-----------------------|---------|--------|---------|---------|
| | Cu | Fe | Mn | Zn | Cu | Fe | Mn | Zn |
| | (mg/dm ³) | (mg/dm ³) | (mg/dm ³) | (mg/dm ³) | (mg/kg) | (g/kg) | (mg/kg) | (mg/kg) |
| K-7 | 0.0053 | 0.017 | < 0.0006 | 0.0029 | 39.5 | 38.3 | 504 | 81.3 |
| K-8 | 0.0052 | 0.015 | < 0.0006 | 0.0018 | 34.1 | 22.7 | 566 | 71.4 |
| K-9 | 0.0075 | 0.252 | 0.0124 | 0.0034 | 30.9 | 20.5 | 418 | 62.8 |
| K-10 | 0.0012 | 0.094 | 0.0037 | 0.0011 | 24.6 | 20.5 | 470 | 57.9 |
| K-11 | 0.0058 | 0.026 | < 0.0006 | 0.0022 | 33.5 | 32.4 | 893 | 76.3 |
| K-12 | 0.0092 | 0.041 | 0.0063 | 0.0095 | 81.1 | 29.0 | 649 | 186 |
| H-1 | 0.0066 | 0.078 | < 0.0006 | 0.0055 | 30.4 | 12.1 | 423 | 59.6 |
| H-2 | 0.0063 | 0.035 | < 0.0006 | 0.0025 | 32.7 | 24.5 | 350 | 70.0 |
| H-3 | 2.64 | 0.187 | 1.16 | 3.77 | 196 | 40.0 | 503 | 206 |
| H-4 | 0.1039 | 0.015 | 0.0667 | 0.118 | 595 | 22.3 | 465 | 808 |
| H-5 | 0.0115 | 0.089 | 0.0022 | 0.006 | 21.9 | 17.5 | 304 | 60.0 |
| H-6 | 0.0082 | 0.144 | 0.0022 | 0.0034 | 42.8 | 32.7 | 432 | 78.1 |
| H-7 | 0.0059 | 0.024 | < 0.0006 | 0.0011 | 26.2 | 16.4 | 170 | 60.3 |
| H-8 | 0.0208 | 0.020 | 0.0173 | 0.0419 | 105 | 25.1 | 650 | 232 |
| H-9 | 0.0227 | 0.023 | 0.0127 | 0.0312 | 82.8 | 30.3 | 578 | 203 |
| H-10 | 0.0142 | 0.026 | 0.011 | 0.018 | 99.9 | 48.0 | 1074 | 251 |

表2 河川水の溶存重金属類ならびに底質中の重金属類 (n=3)

の各地点から採取された試料の平均からの変動幅1 σ 以内の値となった。

3. 考察

3.1 溶存成分の挙動

旧東山鉱山から流出する重金属類のうち,当該地域 のバックグラウンドに比べ,顕著に高濃度を示した ものは Cu・Fe・Mn・Znであった。これらの成分 の一般河川(東山谷川)への流出後の挙動を明らか にするために,溶存化学成分の河川水による希釈効 果と凝集沈殿について定量的に考察した。合流前後 の河川流量と化学成分との関係を以下に示す。鉱山 からの流出水が東山谷川と合流し,単純希釈される 場合,各成分濃度と流量とは以下の関係式で表現で きる。

$$\left\{ C_{us} (F_{ds} - F_{tr}) + C_{tr} F_{tr} \right\} / F_{ds} = C_{us}^{*}$$
(1)

ただし, C:溶存成分濃度, F:流量, us:東山谷川 上流(坑廃水流入前), tr:赤水谷川(坑廃水), ds: 東山谷川下流(坑廃水流入後)である。

下流域における,ある化学成分の濃度(C)が上流域 での主流と支流との単純混合だけで決定づけられる 場合,上記濃度計算値(C*)と実測値(C)との比率 (C/C*)は1となる。これに対して,主流と支流の合 流により,沈殿作用のような溶存化学成分の水相か らの除去反応が発生した場合は(C/C*)<1となる。

この式に従い、坑廃水の流路である赤水谷川(H3) が東山谷川(H2)へ流入する地点から約 700 m 下流 の H4 地点での各化学成分の濃度を算出し, 化学成 分ごとの計算値と実測値との比率(C/C*)を図2に示 した。その結果、主要成分については理論値と実測 値とがほぼ一致し,同地点での溶液組成は坑廃水と 東山谷川との単純混合で説明できた。しかし重金属 類については、実測値が理論値の20-40%程度と小 さな値を示し、重金属の水相からの除去が示された。 また、河川底質については、Cu・Znの実測値が 7-10 倍程度と顕著に高い値を示した。このような現象 については以前の熱力学的な研究により、東山谷川 との合流に伴う pH 上昇が、これら重金属類の中和 沈殿を誘発するためと説明されている(Anazawa et.al., 2004)。今回の調査結果もそれを裏付けるも のとなった。なお、Fe・Mn については、周辺岩盤 の主要成分であるため、中和沈殿による濃度上昇が 明瞭には検出されなかったものと考えられる。

3.2 対策



 図2 H4地点における溶存化学成分の濃度計算値(C*)と実測値(C)との比率(C/C*)。上流域の H2とH3との単純な混合で濃度が決定される場合はC/C*=1となり、沈殿反応が発生 する場合はC/C*<1となる。

重金属廃液の処理法には、主に凝集沈殿法や吸着 除去法などが採用され、各々特色を生かした処理が 行われている(石油天然ガス・金属鉱物資源機構, 2006a など)。新たな施設の設置による周辺環境への 悪影響や保守に関わるコストを考慮すると,処理費 用の負担責任者が不在のまま含重金属廃水が大量に 流れ続ける当調査地において、これら産業廃液処理 用の施設を設置するのは、環境保全の観点からも経 済的にも適切な方法とはいえない。重金属類を完全 に除去する努力をするよりも、重金属による環境負 荷を軽減するための、安価で周辺の自然環境に即し た重金属除去法を用いることが肝要である。そのた めには、上記天然河川での重金属類の中和沈殿反応 に習い, 流出口における坑廃水の pH を高めて重金 属を沈殿・除去する方法が有効であろう。具体的に は石灰石等の投入と,その結果生じた沈殿物の除去 を繰り返すことが挙げられる。

本調査地域と同様に強酸性の坑廃水が流出し,中 和処理を継続的に行っている例としては,岩手県旧 松尾鉱山,鳥取県旧岩美鉱山などが知られている。 このうち旧松尾鉱山跡からは,pH2.3の強酸性の坑 廃水が毎分 18 m³の割合で流出しており,日量 20 tonの炭酸カルシウムを使った中和処理が行われて いる(石油天然ガス・金属鉱物資源機構,2006b)。 本調査地域では上記例に比べると坑廃水の流出量は 1.6 m³/min(27 dm³/s)と小さく,酸性度もそれほ ど強くない(pH 4.7)。したがって対策としては,流 出水の完全な中和を図るのではなく,重金属の凝集 沈殿を促進するための小規模な中和沈殿槽を設置す ることが考えられる。

そこで、石灰石などの炭酸カルシウム(CaCO₃)を 坑廃水に投入し, 重金属類を中和凝集沈殿させた場 合のCaCO3の必要量,重金属の除去効率,および発 生する沈殿物の量を試算した。まず、坑廃水の流量 (A地点における流量)と各重金属濃度の積を求め, 各重金属の流出量を算出した。次に、主要イオン濃 度およびイオン強度を考慮した上で、坑廃水(赤水 谷川:A)が中和された場合の理論溶液の成分組成 を溶解度積から算出した。このとき、中和反応によ る凝集沈殿物として、Cu4(OH)6SO4, Fe2O3, MnO2, ZnSiO3を想定した。また、反応効率については、赤 水谷川と東山谷川との合流付近(H2)と同程度の 割合でpH上昇が進むものとして、CaCO3の溶解度 積の 1/10 量のCa²⁺が溶出すると仮定した。重金属の 除去効率を求めるための理論凝集量は、溶液中の溶 存態重金属の濃度と流量の積を坑廃水の重金属流出 量から差し引いて算出した。計算に使用した熱力学 データは、米国地質調査所(USGS)が提供する Wateq.datを用いた(Parkhurst and Appelo, 1999)。

その結果,各重金属の除去率は,銅77%,鉄100%, マンガン100%,亜鉛99%となった(表3)。また, 凝集沈殿物の年間発生量は,Cu₄(OH) $_6$ SO₄が3.1 ton, Fe₂O₃が0.23 ton, MnO₂が1.57 ton, ZnSiO₃が 6.88 tonとなり,10 m³程度の沈殿槽を設置した場合, 理論的には1~2回/年程度のスラッジ処理で済む 試算となった。この処理によって新たに発生する環 境負荷としては,石灰石からのCa²⁺の溶出が挙げら れるが,その理論溶出量は32.4 ton/yrであり,調査

| | 衣3 中和処理による功廃水の組成変化と単金属の除去効率(理論値) " | | | | | | |
|----|--|--|---------------------------|---------------------|-------------|--|--|
| | | Precipita | tion | | | | |
| | Pre-treated water (mg/dm ³) | Treated water (mg/dm ³) | Removal efficiency (%) | Chemical Formula | (t/yr) | | |
| Ca | 52.97 | 91.02 | — | $CaCO_3$ | -81.0^{2} | | |
| Cu | 2.64 | 0.59 | 77 | $Cu_4(OH)_6SO_4$ | 3.10 | | |
| Fe | 0.19 | 0.00 | 100 | Fe_2O_3 | 0.23 | | |
| Mn | 1.16 | 0.00 | 100 | MnO_2 | 1.57 | | |
| Zn | 3.77 | 0.04 | 99 | $ZnSiO_3$ | 6.88 | | |

表3 中和処理による坑廃水の組成変化と重金属の除去効率(理論値)¹⁾

1) [Ca²⁺][CO₃²⁻] = 0.1 K_{sp} (calcite)として算出

2) 溶出のため負値となっている。

時における下流域(H3)のCa²⁺流量(369 ton/yr) の10%以下となった。これはH3地点におけるCa²⁺ の時間変動(CV 15.5%)の範囲内であり,環境に 対する悪影響はほとんどないものと考えられる。

おわりに

本研究では,廃鉱山からの流出水中の重金属類の 挙動を,溶存態成分と底質中成分の両面から考察し た。その結果,天然河川で中和凝集沈殿作用により 水相から除去される過程を熱力学的・量論的に説明 することができた。またこの原理による簡易中和沈 殿槽を設置した場合の重金属類の除去率や環境負荷 を試算した。

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成果報告

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「植物・土壌試料の元素分析」

Elemental analysis of plants and soils

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研究の目的と意義

当研究室では、植物および土壌試料中の元素濃度 を非破壊状態で調べるために、放射化分析を採用し てきた。具体的には、食の安全性が重要視されるな か、元素濃度から産地の判別をしようという試みが あり、農産物中の元素を非破壊でマルチに測定する ために、放射化分析を用いた。現在も本研究は遂行 中であるが、今までに得られた結果について報告し たい。

近年、農作物の原産地について消費者の関心は高 まるにつれ、信頼ある情報を提供することが求めら れている。これまでに、GMO 混入については日本 で開発された DNA マーカー等を利用した技術が、 国際基準になってきている。しかし同じ品種の作物 については DNA が等しいため遺伝子を用いる判別 法では原産地を特定することはできない。そこで、 農作物の産地特定のためには、様々な情報を得て複 合的に解析するシステムが求められる。複数の元素 パターンや同位対比などを駆使し、統計処理をする ことで産地を特定する技術の開発では、一部の農産 物については判別が可能になってきている。この元 素パターンによる判別システムでは、通常 ICP-AES もしくは ICP-MS が利用されるが、定量対象とする 元素の範囲を拡大できれば、産地特定の精度の向上 が期待できる。本研究では、次の利点を持つ放射化 分析法を導入する;1)ICP-MS等の前処理である溶液 化が必要ないことから、極微量元素の混入が最小限 に抑えられる。2)高感度に定量できる元素が多くあ る。3)多元素同時分析を行うことができる。これら の利点を最大限活かし、これまで測定できなかった 農作物や食品中の超微量元素の検出を試み、そのデ ータから高精度な産地特定法の開発を試みる。分析 対象としては、産地の明確な試料として農水省の消 費技術センターが他の課題で入手するタマネギを利 用する。これまでに食品総合研究所で蓄積されてき た知見に本研究の成果を融合させていくことにより、 高精度な産地特定システムの構築が期待できる。

その研究をどのように行ったか

消費技術センターより産地が明確なタマネギサン プルの提供を受けた。タマネギの前処理方法として は、以下の通りである。

- オレンジ色または茶色をした外側の皮と上端、 及び基部から上1cmまでを除去した白または緑 色をした部位を採取した。(外皮をとり、純水で 洗浄後、上端と基部から上1cmまでを除去した)。
- 2. 個数は10個で1サンプルとした。
- 10 玉全てを均質化することができない場合は、 10 玉を対象に4等分、あるいは6等分、8等分 など、縦方向に切り分け、対角線部分を採取し て試料とした。
- 分析対象とする元素のコンタミをできる限り少 なくするため粉砕機にはチタンコート刃のフー ドプロセッサーなどを用いた。ステンレスなど の金属部分はできるだけ試料に触れないように 粉砕機を使用した。
- 5. 水分測定は下記の統一した方法により測定した。
 - 1) ルミ箔カップの秤量容器の重さを測る。
 - 2) 粉砕・均質化試料を 5~6g 秤量容器に取り、 重さを測った。
 - 3) 70℃で24時間常圧乾燥した。
 - デシケーター中で放冷後,重さを測り,水 分を求めた。
 - 5) 測定は3点併行で行った。

以上の方法で前処理したタマネギは、60℃で常圧乾 燥を1週間行い、粉末状に粉砕した後、高純度ポリ エチレン袋に2重に封入して放射化分析に供した

どのような結果を得たか

北海道産タマネギを 14 種類、佐賀産タマネギを 20 種類について、放射化分析で測定を行った。一方で 並行して同サンプルを PGA 測定も行った。産地の詳 細な場所と品種については、Figure 1 に記した。

PN-3 による短半減期を対象とした放射化分析については、²⁴Na, ²⁷Mg, ²⁸Al, ³⁸Cl, ⁴²K, ⁴⁹Ca and ⁵⁶Mnの核種が検出ができた。一方、PGAではB, S, Cl, Kの元素

JRR-3 PN-3, PN-2 放射化分析 農作物の元素分析

が検出ができた。



得られた結果について、主成分解析を行いグルー ピングのモデリングを行ったところ、Figure 2 に示 されるように、北海道産と佐賀産の区別がつくこと が判明した。既に、ICP-AES や ICP-MS による元素 分析データからこの 2 つについては区分されること が示されていたが、放射化分析もしくは PGA で得ら れるデータのみでも、産地の判別を行うことが可能 であることが判明した。さらに、放射化分析と PGA のデータをあわせると、より明確に区別ができるこ とも示された(Figure 3)。図では黄色字が北海道産、 赤字が佐賀産のタマネギを示す。

さらによいモデリングを探るために、モデルへの 寄与の少ないデータについては、削除し、残りの主



Figure 2: PCA by with data set of INAA (a) or k_0 -PGA (b).

| Easter? \$=33 | Moo | deling Power |
|--|------------------------------|--------------|
| * sheet 2 | ≴ B/K | 0.350 |
| °H-2 | ⊢ s∕κ | 0.503 |
| °H-7 | _ א⊂ CI∕K | 0.764 |
| °H-9°H-8 | ²⁴ Na | 0.415 |
| H 13 S S S S S S S S S S S S S S S S S S | ²⁷ Mg | 0.512 |
| °H-4 H-12 H-1 ° _{S-6 °_{S-0}} | 28AI | 0.094 |
| °H-11 °S-8_ ^{°S-10} | ≩ ²⁸ CI | 0.594 |
| S-24 | ⁼ ⁴² Κ | 0.377 |
| ¢c_20 | ⁴⁹ Ca | 0.294 |
| °S-7 °S-27 | ⁵⁶ Mn | 0.210 |
| 5 27 | | |



成分解析を行うことにした。つまり、得られた Al や Mn のデータを除いてグルーピングを行った結果 が、Figure 3B であり、より明確な判別が可能である ことが示された。

これらのデータ解析から判明したことの一つに、 モデリングパワーから読み取れる、産地判別に寄与 の大きい元素として、塩素があることである。モデ リングパワーとは、そのモデルに対する寄与度を、 最大値を1として算出した数値である。今回注目さ れる塩素は酸分解を必要とする分析方法では揮発し たり、試料を可溶化させる際に加える酸に含まれて いたりなど、検出することが困難な元素である。し かし、非破壊分析である放射化分析を用いることに より、塩素の測定は容易に行うことができ、かつ今 まで知られていなかった塩素の産地判別への寄与が 大きいことが判明した。

このように、放射化分析は非破壊分析が可能であ りその点が大きな利点である。そして放射化分析法 を産地判別の手段として用いて元素定量分析を行う ことは、これまでは見過ごされてきた元素が判別に 重要な役割を演じていることを明らかにできる可能 性が示された。塩素は農産物に広く存在する元素で あることから他の農産物に対しても広く応用できる のではないかと思っている。

今回用いたタマネギについて、さらに、佐賀産、 北海道産、それぞれの地域におけるいろいろな品種 を入手して実験を行った(Figure 1)。その結果、タ マネギの品種が多岐に渡っているのにもかかわらず、 北海道産と佐賀産を区別することができたというこ との意義は大きい。つまり元素による産地判別方法 は、品種間差を考慮しなくても可能であることが示 されているからである。言い換えれば農作物中に含 まれる元素の濃度のパターンは生育する土壌に含ま れる元素濃度を大きく反映しているからである。

継続する場合は、今後の方針

本課題は H19 年以降も継続する予定である。今度 は、農作物の中でも偽装の多いものや、野菜以外の 農産物への本手法の適用を目指して実験を行ってい く予定である。また今回は時間の関係で行えなかっ たが、長期の放射化を行うことで、長い半減期を持 つ核種、微量重金属元素にも着目した産地判別の可 能性の検討についても今後の課題としたい。

成果の公表

本成果については、H19 年 8 月に行われた「The 12th International Conference on Modern Trends in Activation Analysis (MTAA12)」において、ポスター 発表を行った。

ポスターナンバー:P019

題目: Studies of Elements in Onions, Specific to Producing Districts through Instrumental Neutron Activation Analysis and Prompt Gamma-Ray Analysis

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尚、本成果については、現在、 Journal of Radioanalytical and Nuclear Chemistry に投稿し、審査 を受けているところである。

大気試料の主成分および海洋試料の放射化分析

Activation analysis of major element in overland and marine aerosols

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1. はじめに

本研究は宇宙線生成核種⁷Be (T_{1/2}=53.3 d), ¹⁰Be(T_{1/2}=1.5×10⁶ y), ³⁶C1 (T_{1/2}=3.0×10⁵ y)の大 気中における移動についての情報を得るために,中 性子放射化分析(NAA)を用いて土壌起源の指標とな るA1,海塩の指標となるNa, C1の測定を行うことを 目的としている。

1) 再浮遊¹⁰Beの見積もり

宇宙線生成核種⁷Be,¹⁰Beは高層大気において宇宙 線と窒素、酸素の相互作用によって生成する。生成 後はエアロゾルに吸着し移動するため、高層大気の エアロゾルのトレーサーとして用いることが出来る と考えられる。また'Be, ¹⁰Beは同位体であるため大 気中での挙動は同じであり、¹⁰Be/⁷Be同位体比は滞留 時間のみによって変化するため、エアロゾルの滞留 時間の指標として用いることが出来る。エアロゾル の平均滞留時間が大気の混合に対し短いために大気 中の⁷Be, ¹⁰Be濃度は時間的, 空間的に不均一な分布 を示す。そのため、緯度分布等の空間的な変化を観 測することに加え、定点観測により季節変動を観測 することが必要となる。しかし陸上において観測を 行うと、¹⁰Beは土壌における滞留時間に対し非常に 長い半減期を持つために、一度地表に降下した後、 再浮遊する成分によって大気中の¹⁰Be濃度が過大評 価されている可能性が指摘されている。そこで本研 究では再浮遊による影響を土壌粒子の指標であるAl の濃度から定量的に見積もることを試みた。 2) エアロゾル状³⁶C1の測定法の開発

宇宙線生成核種³⁶C1は高層大気において宇宙線と アルゴンとの相互作用によって生成する。大気中で はC1の安定同位体と混合し、大気中にNaC1などのエ アロゾル状、HC1、C1₂などの無機ガス状、CH₃C1、CFCs などの有機ガス状で存在していると考えられている

が、³⁶C1の大気中の挙動についてはっきりとしたこ とはまだわかっていない。本研究では³⁶C1を高層大 気からのC1のトレーサーとして用いる可能性を探る ために、2006年4月から雨水、エアロゾルの回収し、 ³⁶C1の測定を行ってきた。エアロゾル状³⁶C1の測定は 水抽出を行い水溶性エアロゾルの³⁶C1を測定する方 法を用いたが、エアロゾル状全C1量を把握すること は非常に重要なことである。そこで全C1量を中性子 放射化分析で水溶性C1をイオンクロマトグラフィー (IC)で測定し、水溶性エアロゾルの割合を調べるこ とを行った。

2. 実験

1) 試料

東京都世田谷区の日本大学文理学部5号館屋上に おいてハイボリュームエアサンプラー(紀本電子製 AS-1400)を用いてペーパーフィルター(whatman No. 41)にエアロゾルを回収し試料とした。回収期間は約 1-2 週間、積算流量は 4500-10000m³であった。回収 した試料はハツ折りにし、非破壊ガンマ線スペクト ロメトリーによって⁷Be(E_x=477.6 keV)の定量を行 った。その後、ろ紙の 1/2 を³⁶C1測定用、1/4 を¹⁰Be 測定用、2×2 cmを中性子放射化分析用とした。³⁶C1 測定用試料は細かくちぎり、50mLのイオン交換水で 15分間超音波洗浄を3回行った。試料はそれぞれイ オンクロマトグラフィーを用いてCl⁻の定量を行っ た。その後HNO3とAgNO3を添加し、AgC1として東京大 学MALTのAMSシステムにおいて³⁶C1/C1の分析を行っ た。大気中のエアロゾル状³⁶C1濃度はAMSによって求 められた³⁶C1/C1と安定同位体C1から求めた。¹⁰Be測 定用試料はBe担体 1mgを加え、硝酸を用いて湿式灰 化を行い、分解溶液の一部について誘導結合プラズ マ発光分光分析法(ICP-AES)によって組成分析を行 った。その後陽イオン交換でBeの単離を行い東京大 学MALTにおいて¹⁰Be/Beの分析を行った。大気中¹⁰Be 濃度は¹⁰Be/Beと加えた担体量から求めた。

2) 中性子放射化分析

2×2 cmに切断したろ紙をHNO₃、エタノール、イオン交換水を用いて洗浄したポリ袋に2 重封入し、ろ

JRR-4 気送管、地球化学試料放射化分析

紙の大きさを測定した。2×2 cmに切断した場合、試 料が不均一であると、定量結果に大きな誤差を含む ことになる。そのため試料の均一性の確認のため 1 つの試料について試料採取面を 4×5 ブロックの片 に分割し、同様の測定を行った。また 2×2 cmに切断 したろ紙 (ADVANTEC No. 5C)に標準溶液を滴下し、A1 標準試料 (A1 70 μ g), NaCl標準試料 (Na 110 μ g、Cl 170 μ g)を作成した。作成した試料は 10 グループに 分割しAuフラックスモニター (Au 17 μ g)とともにカ プセルに封入しJRR-4 気送管において 100 kW、1 分 間の照射を行った。照射した試料は直ちに取り出し、 2 台のGe半導体検出器を用いた非破壊ガンマ線スペ クトロメトリーを 50 秒 間 の 測定を行い ²⁸A1 (1779keV)の定量を行った後、300 秒間の測定を 行い²⁴Na (1369 keV)、³⁸Cl (1643 keV)の定量を行った。

3. 結果と考察

1)気送管中性子フラックスの安定性

Au フラックスモニターの測定結果から算出した 気送管中性子フラックスの安定性を表1に示す。照 射は2006年12月25日12時17分から開始した。合 計10回の照射を行ったが、気送管中性子フラックス は実験中において標準偏差1σで2%と安定していた。 2)試料の均一性

試料の均一性を示した図を図 1 に示す。x軸、y 軸はそれぞれろ紙の中心からの距離、z軸はろ紙のブ ランクを差し引いた 1 cm²あたりの元素量を表す。

| 表 1 | IRR-4気送管における中性子フラックスの変動 |
|------|-------------------------|
| 11 1 | |

| 照射番号 | 照射開始 | | 相対中性子 | フラックス |
|------|---------------|------|-------------|-------|
| 1 | 2002/12/24 12 | 2:17 | 0.997 \pm | 0.023 |
| 2 | 2002/12/24 12 | 2:41 | $0.981~\pm$ | 0.023 |
| 3 | 2002/12/24 13 | 3:04 | 1.006 \pm | 0.023 |
| 4 | 2002/12/24 13 | 3:24 | $1.036~\pm$ | 0.024 |
| 5 | 2002/12/24 13 | 3:47 | 1.015 \pm | 0.023 |
| 6 | 2002/12/24 14 | 4:05 | $0.977~\pm$ | 0.023 |
| 7 | 2002/12/24 14 | 4:28 | $0.976~\pm$ | 0.023 |
| 8 | 2002/12/24 14 | 4:52 | $1.008~\pm$ | 0.024 |
| 9 | 2002/12/24 15 | 5:15 | $0.985~\pm$ | 0.023 |
| 10 | 2002/12/24 15 | 5:40 | 1.019 \pm | 0.024 |
| | | 平均 | 1.000 ± | 0.020 |

中心部のA1を除き、ほぼ一様であることが確認された。Na/C1比は全試料において一定であったが、A1/C1 比、A1/Na比は中心部が高くなっていた。中心部のA1 については、⁷Beのガンマ線スペクトロメトリーを行 うため、ろ紙を折り畳んだ際に中心部に粗大な土壌 粒子が集まっていることが目視により確認されてい ることから、中心部に集まった粗大土壌粒子を観測 してしまい、A1量が多くなったと考えられる。この ことから折り畳んだ試料の中心部を用いて測定する ことは避けるべきであることが確認された。

3) 土壌粒子の影響

2006年4月から12月までの中性子放射化分析から求めた大気中A1濃度と¹⁰Be分析用に酸抽出した試料から求めたA1濃度、³⁶C1測定用にイオン交換水で超音波洗浄した水溶性エアロゾルの大気中A1濃度の季節変動を図2に示す。東京におけるA1濃度は4、6月に4µgm⁻³と高い値を示した他は1-2µgm⁻³程度であった。4月の後半に黄砂が観測されたことを除くと大規模なダストイベントは無く、東京におけるA1濃度はグローバルな供給より近隣土壌からのローカルな供給の影響を強く受けていると考えることが出来る。中性子放射化分析により求めたA1が全量だとすると、酸抽出によって43.4-58.5%、水溶性エアロゾル中には0.9-14.6%のA1が存在することがわかった。

土壌中の¹⁰Beは土壌表面に吸着して存在している ため、比較的容易に酸で抽出されることが確認され ている。しかしAlは緑泥石などの酸に可溶なAlとア ルミノケイ酸塩などの酸に不溶なAlが存在する。 ICP-AESを用いた測定はNAAより簡便であるが、土壌 全量推定のためには全Al量が必要であるため、NAA で求めたAl量を用いることが適当であると考えられ る。以下の式から土壌からの¹⁰Be量を見積もり、 ¹⁰Be/⁷Beを求めた結果を表2に示す。

$C_{10} = (C_{A1}/S_{A1}) \times S_{10}$

式中の C_{10} は補正した大気中¹⁰Be濃度、 C_{A1} は大気中全 A1濃度、 S_{A1} は土壌中A1濃度(8.93%)、 S_{10} は土壌中の ¹⁰Be濃度を表す。土壌中¹⁰Be濃度は採取値付近で採取 した土壌中¹⁰Be濃度と中国レスの¹⁰Be濃度の結果か ら 5×10⁸ atoms g⁻¹とした。この式から求められた 大気中¹⁰Be濃度に対する再浮遊した¹⁰Beの割合は

| | 表 2 | 表 2 大気中Al濃度から再浮遊成分の補正を行った ¹⁰ Be濃度と ¹⁰ Be/ ⁷ Be | | | | |
|---------|-----------------|---|------------------|-----------|-------------------|------------------|
| 試料名 | Al濃度/µg m⁻³ | ¹⁰ Be濃度/10 ⁴ atoms m ⁻³ | | | ¹⁰ Be/ | ^{/7} Be |
| | | | 補正 | (再浮遊) | | 補正 |
| 06NH-01 | $3.95~\pm~0.21$ | 12.21 ± 0.44 | $9.99~\pm~0.46$ | (18.1%) | $2.04~\pm~0.10$ | $1.67~\pm~0.09$ |
| 06NH-02 | $2.24~\pm~0.13$ | $12.30~\pm~0.48$ | 11.04 ± 0.49 | (10.2%) | 2.16 ± 0.11 | $1.94~\pm~0.11$ |
| 06NH-03 | $0.88~\pm~0.03$ | $7.64~\pm~0.27$ | $7.15~\pm~0.27$ | (6.5%) | 1.83 ± 0.09 | $1.71~\pm~0.09$ |
| 06NH-04 | $1.27~\pm~0.04$ | 11.85 ± 0.45 | 11.14 ± 0.45 | (6.0%) | $2.29~\pm~0.10$ | $2.15~\pm~0.10$ |

6-18%となった。

4) 大気中のエアロゾル Cl 濃度

大気中全エアロゾル Na 濃度、水溶性エアロゾル Na 濃度、また全エアロゾル、水溶性エアロゾル Cl 濃度を表 3 に示す。酸抽出した Na は水溶性 Na と非 常に良く一致した。全エアロゾル中から抽出される Na は 57.6-90.1%であった。抽出残渣中の Al/Na 比は 1.9-6.0 で関東土壌の Al/Na 比(9.7)より低く、花崗 岩(2-3)や玄武岩(3-5)と同等であった。このことか らも抽出残渣は酸不溶な鉱物であると考えられる。

全エアロゾル中、水溶性エアロゾル中のNaとC1の 関係を図3に示す。図中の実線は海水中のNa/C1比を 示す。水溶性エアロゾルについては海水中Na/C1比と 一致したが、全Na/C1比は海水と同等かNaが過剰にな っていた。このことは、水溶性エアロゾルは海塩の 影響を非常に強く受けていることに対し、全エアロ ゾルは水溶性エアロゾルに難溶性の土壌鉱物が付加 されていると考えることが出来る。水溶性エアロゾ ルに含まれる³⁶C1のAMS測定を行ったところ、³⁶C1/C1 は海水から作成したブランク試料に対し有意に高い 値を示した。このことから、水溶性エアロゾルは海 塩の影響を強く受けているものの、大気中に存在す る間にC1が交換している可能性が示唆された。

4. まとめ

研究炉 JRR-4 の気送管を用いた中性子放射化分析 で大気エアロゾル中の A1、Na、C1 濃度を測定した。 測定中の中性子フラックスは標準偏差が 2%と安定 していた。フィルター上の元素分布の均一性を確認 したところ、放射化分析の前段階においてろ紙を折 り畳んだ際、粗大な土壌粒子が中心に集まった影響 により A1 のみ中心に偏った分布を示したため、ろ紙 の中心部を使った測定は避けるべきであることがわ かった。

中性子放射化分析を用いて測定したA1濃度を用い て大気中¹⁰Be濃度の再浮遊成分の補正を行ったとこ ろ、東京において大気中の¹⁰Be濃度は 6-18%過大評価 されていると算出された。

大気中全エアロゾルNa/C1比と水溶性エアロゾル Na/C1比を比較すると水溶性エアロゾルNa/C1比は海 水中Na/C1比と一致することに対し、全エアロゾル Na/C1比は海水よりNaが過剰に存在していた。また全 エアロゾルから水溶性を差し引いた残渣中A1/Na比 が土壌成分より岩石成分に近かった。このことから 水溶性エアロゾルは海塩粒子の影響を強く受けてい ると考えられた。しかし、水溶性エアロゾル中 ³⁶C1/C1は海水より有意に高く、大気に存在する間に C1が交換している可能性が示唆された。

[成果の公表]

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| 衣 5 八风中Na侲及CCI侲及 | | | | | | |
|------------------|-----------------|--------------------|-----------|-------------------|----------|-----------|
| 試料名 | Na濃度 / µ | ıg m ^{−3} | | Cl濃度 / µg | m^{-3} | |
| | NAA | ICP-AES | (水溶性) | NAA | IC | (水溶性) |
| 06NH-01 | $2.37~\pm~0.14$ | 1.527 | (64.3%) | 3.82 ± 0.12 | 2.615 | (68.5%) |
| 06NH-02 | 1.81 ± 0.11 | 1.697 | (93.6%) | $2.71 ~\pm~ 0.09$ | 2.825 | (104%) |
| 06NH-03 | $1.27~\pm~0.07$ | 0.744 | (58.6%) | $2.64 ~\pm~ 0.08$ | 1.531 | (57.9%) |
| 06NH-04 | $1.66~\pm~0.10$ | 0.960 | (57.8%) | 3.01 ± 0.10 | 1.767 | (58.8%) |

表 3 大気中Na濃度とCl濃度





z y x

> 図1 ろ紙上の各元素の分布. 左端がろ紙の中心となり, x軸, y軸はそれぞれろ紙の中心からの距離, z軸はろ紙のブ ランクを差し引いた1 cm²あたりのa) Al b) Na c) Cl量を表す.



中性子放射化分析法による鉄隕石中の⁵³Mnの定量

Determination of ⁵³Mn in Iron Meteorites by Neutron Activation Analysis 首都大学東京 大学院理工学研究科 分子物質化学専攻

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1. はじめに

隕石は宇宙空間を飛行している間に高エネルギー な宇宙線の照射を受け,核反応,主に核破砕反応に よりさまざまな核種が生成する.この中で,半減期 が長い放射性核種(¹⁰Be, ²⁶A1, ³⁶C1, ⁵³Mnなど)や希ガ ス安定核種を宇宙線生成核種として隕石中で検出す ることが可能である.これらの宇宙線生成核種を利 用して,宇宙線照射年代や,地球に落下した年代を 得ることができる.また,複数の核種の濃度から, その隕石の落下前の大きさや,宇宙線照射環境を推 定することも可能である.

主な宇宙線生成放射性核種は,その半減期が数10 万年〜数100万年と非常に長く,また,存在量がわ ずかなこともあり,その放射能は非常に小さく,放 射線測定による定量は難しい.また,測定が容易な ガンマ線を放出しない核種も多く,さらに放射線測 定の困難さを増している.そのため,近年は,加速 器質量分析(AMS)法を用いた測定が主流である.日本 においても、¹⁰Be,¹⁴C,²⁶A1,³⁶C1の測定はAMS法に可 能である.しかしながら,宇宙線生成放射性核種の 一つである⁵³Mnは,我が国ではAMS法による測定は不 可能で,海外においても、⁵³Mnを測定可能なAMS施設 は非常に限られている. ⁵³Mnは,主として鉄の核破砕反応により生成する 宇宙線生成核種で,半減期3.7×10⁶年でEC壊変する 核種である.EC壊変に伴うガンマ線を放出しないの で,Crの特性X線(5.4 keV)を測定しなければならな い.しかし,X線エネルギーが低く正確な定量は難し いし,測定に長時間を要する.そのため,実用的に は中性子放射化分析法にて定量が行われる.すなわ ち,中性子照射により⁵³Mnを半減期312日の⁵⁴Mnに変 換することにより,放射能強度を桁違いに増すこと ができ,さらにガンマ線測定が可能となる.しかし, 照射前と照射後に化学操作によりMnを濃縮ならびに 精製しなければならず,その操作が煩雑なためか, 最近は⁵³Mnに関する報告はほとんどない.

1836年にナミビア共和国で発見された鉄隕石ギ ベオンは、総重量が26,000kg以上あり、この隕石 は宇宙空間で大きかったと予想できる.この隕石中 の宇宙線生成核種、¹⁰Be,²⁶A1,³⁶C1ならびに^{3,4}Heが 系統的に隕石表面から深部まで測定されているが、 ⁵³Mnのデータは少ない.最近,非常に表面から深い と思われる試料が見つかったが、高感度である希ガ ス同位体測定も限界に近く、核破砕標的である鉄の 質量数に近く、より生成率の高い⁵³Mnの測定に期待 がもたれる.また、鉄隕石中には不均質にFeS鉱物や ケイ酸相が含まれていることが知られている.¹⁰Be や^{3,4}Heなどはこれらからも生成するが、これらの相 の分析に供する試料中での存在をあらかじめ知るこ とは不可能であり, 過剰評価した結果が得られるこ ととなる. 一方, ⁵³Mnは鉄またはニッケルからしか 生成しないため、このような過剰評価は生じないた め、⁵³Mn濃度を得ておくことは重要である.この隕 石で現在報告されている最も低い¹⁰Be 濃度は 6× 10⁻⁵ dpm/kg であり、これに相当する⁵³Mn 濃度は 0.05 dpm/kg と推定され、当研究室の瀬戸口の方法 による定量限界値 0.4 dpm/kg の約 1/10 である. 本課題申請時は、最深部と思われる試料中の⁵³Mnの 定量を計画していたが、ここしばらく本定量実験を 行っていなかったため、いきなりこれまでの定量限 界にせまる、あるいはそれ以下と推定される試料の 分析は無謀であると考えた. そこで, これまでにま だ⁵³Mnの定量が行われていない深度の試料を分析す ることにより,現在の方法の定量限界を再確認し, ギベオン隕石のより深部における低濃度の ⁵³Mn を 測定するために必要な改良方針を得る事を目的とし て実験を行った.

2. 実験方法

試料として3つの鉄隕石ギベオン #204, #1122, #99 を 0.5 g ∽ 1 g用いた. これらの¹⁰Be 濃度は 測定されており, ¹⁰Be 濃度と ⁵³Mn 濃度の相関より, これらの試料の ⁵³Mn 濃度は,約 1/10 づつ小さく なると推定される.

試料は表面を洗浄後, 秤量し, 100 μ gのMn担体と 2mgのCl担体を添加後, 1:2 HNO₃で加熱溶解した. 塩 素をAgClとして分離した後, 7M HCl溶液とし, ジイ ソプロピルエーテルで鉄を抽出除去した. 水層を加 熱濃縮し,ジイソプロピルアルコール-HC1溶液に溶 解し,陰イオン交換樹脂に通し,0.5M HC1にてMnを 溶離した.溶離液は,加熱濃縮し,H₂0にて溶解後, 陽イオン交換樹脂に通した.Mnを 2M HC1にて溶離し, 加熱濃縮した.残渣をH₂0にて溶解後,A1箔に滴下乾 燥させて,照射用試料とした.

照射は, JRR-3M DR 孔にて 1 サイクル (25 日間)行 った.

照射1ヶ月後に、A1箔とともにガンマ線を測定し たところ、Ir、Ag、Coがまだ十分に除去されていな かったことがわかった.そこで、放射性トレーサ、 ⁵⁴Mn,⁶⁰Co,¹¹⁰ Ag,¹⁹²Irを用いて、従来行っていた照 射後のMn精製操作を行い、これらの元素の除去率と Mnの回収率を調べた.除去率は十分であったが、Mn の回収率が悪かった.AgをAgC1として除去した際の ろ過方法が適当でないことがわかったため、ろ過方 法を回収率が低下しない方法に改めた.

照射後、A1箔表面に添着させたMnのみ溶解し、Ag をAgC1として除去した後、照射前の濃縮操作と同様 の陰イオン交換と陽イオン交換によりMnの精製を行 った.Mnフラクションは濾紙上に滴下・乾燥し、⁵⁴Mn 測定試料とした.

Mnの化学収率は、⁵⁴Mn測定終了後,再放射化法 (JRR-4 PNにて 30秒間照射)により求めた.回収率は, 13~83%であった.

3. 結果と考察

現在, 信頼できる 53Mn標準溶液がないため, ⁵³Mn 濃度が報告されている#99 試料を比較標準試料とし て定量を行った. その結果を表 1 に示す. #1122, #204 ともにこれまでの⁵³Mn濃度の深度分布と矛盾しない 値が得られた.

| 表 1 ⁵³ Mnの定量結果 | | | |
|---------------------------|-----------------|----------|--|
| 試料 No. | 濃度 [dpm/kg] | Mn 収率[%] | |
| #99 | 196 ± 12 | 12.5 | |
| #1122 | 73.0 ± 5.1 | 82.9 | |
| #204 | 8.29 ± 0.59 | 57.9 | |

ガンマ線スペクトルから本定量法での⁵³Mnの定量

限界を求めた.鉄隕石を1g用いて,収率80%でMnが 回収できたと仮定すると、0.2 dpm/kgが定量限界で ある. 定量を予定している試料の53Mn濃度の推定値 は、0.05 dpm/kgであるから、現状では定量が困難で ある.計数率を向上されることが、定量限界を下げ るには手っ取り早いが、現状ではさらに相対効率の よいGe検出器を準備することは難しい. 次に有効な のは、バックグランド計数を減少させることである. 照射後のMn精製操作は非常に有効で、測定試料中に 存在する鉄隕石由来の放射性核種は⁵²Crのみである. ⁵²Crのガンマ線(320 keV)は⁵⁴Mnからのガンマ線(835 keV)の測定の妨害にはならない. そのため, 現在, 定量限界を左右する大きな要因は天然放射性核種に 由来するコンプトン散乱による計数であると考えら れる. そのため、検出限界を下げるには、より低バ ックグランドな環境で測定することが必要である. この低バックグランドな測定施設として、金沢大学 の尾小屋地下測定室が考えられる. この施設でのガ ンマ線バックグランドレベルは当大学施設の約 1/160 であるため、単純に比較すると、地下測定室 にて測定すれば検出限界は0.03 dpm/kgとなる.

中性子放射化分析法にて正確に⁵³Mnを定量するに は,妨害反応の補正が必要である.すなわち,⁵⁴Fe(n, p)反応と,⁵⁵Mn(n, 2n)反応により生成する⁵⁴Mnを補 正しなければならない.本実験でのFeならびにMnか らの妨害はそれぞれ 0.1 dpm ⁵³Mn/ μ gFeと 3.4 dpm ⁵³Mn/100 μ gMnであった. 照射前分離操作では,まだ 約 1 μ gの鉄が残っており,また,Mn担体を 100 μ g 使用したため,0.05 dpm/kgの⁵³Mnを含む試料を想定 すると,FeならびMnからの⁵⁴Mnの寄与は,⁵³Mnからの ⁵⁴Mnに対して,それぞれ約2倍と約70倍となる.50% までの寄与率を許容できるとすると,照射前の濃縮 操作において,鉄の除去率をさらに1/2にすること, また,用いるMn担体の量を1 μ g程度にまで減らす必 要がある.しかしながら,このMn担体量では,回収 率測定の際に鉄隕石にもともと含まれているMn量を 無視しえないこととなる.そのため,あらかじめ鉄 隕石試料に含まれているMn量を評価する必要がある. また,化学操作中のMnの汚染についても評価する必 要がある.

現在の ⁵³Mn 定量方法においての定量限界は、収 率 80% のとき 0.2 dpm/kg であり,目標とする 0.05 dpm/kg の 4 倍である.定量限界を下げるには低バッ クグランドな環境にてガンマ線を測定することが必 要である.また,正確に 0.05 dpm/kg の試料を測定 するには試料量を 7g 以上,収率 80% 以上, Mn 担 体量は 1 μ g,照射前化学分離において Fe を 0.1 μ g まで除去することが必要である.

今後は、この条件をみたす化学分離操作に改良す るとともに、鉄隕石中のMn元素濃度定量法の開発、 ⁵³Mn標準溶液の調製を行いながら、より深部の⁵³Mn濃 度の定量を目指す.

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- 4. 成果の公表
 - なし

地圏環境における元素分布・循環の研究 — ヒ素とクロム —

Geoenvironmental assessment by INAA analysis of chromium and arsenic for a large number of stream sediments

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Abstract

Geochemical map was studied in many institutes for the specific purpose of environmental assessment. Especially in late years, this map is used to discriminate anthropogenic elemental pollution among primary geoenvironmental factors. Where arsenic shows high concentration gold and antimony also shows similar behavior as arsenic in geothermally affected area. High arsenic concentration was found in Mesozoic and Paleozoic area in western part of Tajimi city, Gifu prefecture but gold abundance is not so high on the geothermal area. This study was intented to clarify the behavior of arsenic and gold in the Mesozoic and Paleozoic area, and to clarify controlling factors of arsenic and gold in this area. Ninety-one stream sediments are analyzed by instrumental neutron activation analysis and X-ray fluorescence spectrometry. The results are expressed in geochemical map. Analytical data are treated by factor analysis to find controlling factors of arsenic and gold distribution in the Mesozoic and Paleozoic area.

Analytical data in the study area examined in referring to three distinctive geology, i.e., clastics area in Mino belt, chert area in Mino belt and Tertiary and Quaternary formation area. Although several sites clastics area in Mino belt have high arsenic concentration between 60ppm and 177ppm, the area generally shows low arsenic concentration. Tertiary and Quaternary formation area has not much notable difference.

Factor analysis shows elemental distribution in this area is controlled by monazite, biotite, zircon, pyroxene, feldspar and material including cobalt and arsenic. Monazite, pyroxene and potassium feldspar control the elemental distribution in Mesozoic and Paleozoic area. Arsenic and gold in the study area doesn't show similar correlation each other as is Tsugu region. This indicates that the factor controlling arsenic and gold distribution in the area is different from the factor of Tsugu region. Minerals that show high arsenic concentrations in the Mesozoic and Paleozoic formation area are prospected a kind of pyrite with red or black features. These minerals analyzed by INAA, show high arsenic concentration but not for gold.

These fact indicate that arsenic concentration in this Mesozoic and Paleozoic area have relatively low concentration, but high arsenic concentration leastways in the area is shown including arsenic minerals in sedimentary rocks. Arsenic and gold are indicated have different carrier, arsenic have high concentration although arsenic shows low concentration in this study area.

装置:JRR-3気送管、JRR-4気送管・T・Sパイプ、 分野:中性子利用・放射化分析、地球化学、環境化学

1. はじめに

地球化学図は、古くから鉱床の探査に使用され てきた(西山、1991)。近年になり、分析機器の進歩 により、多試料中の多元素が迅速に分析できるよう になった。そのために、迅速な対処が必要な土壌汚 染の評価などの基礎資料となる環境評価を目的とし た地球化学図の作成が進んだ。地球化学図は、人為 汚染による元素濃集とバックグラウンドである本来 の地質的要因を区別することを期待されており、環 境基盤図として使用されている。

ヨーロッパでも、全土での地球化学図が作成されている(例えばWebb et al., 1978、Fauth et al., 1985、Haslam et al., 2000など)。また、日本では、 産業技術総合研究所(今井ほか, 2004)を始めとして 様々な機関で広範囲の地球化学図が作成されてい る。(例えば、椎川ほか, 1984、太田ほか, 2002)

る。(例えば, 椎川ほか, 1984、太田ほか, 2002) 愛知県での地球化学図は, 東部や北東部, 瀬戸 市のものが局地的に作成されている。その中でも, 戸上ほか(1997)は愛知県北東部・津具地方の地球化 学図を作成している。戸上らは,地球化学図のデー タに因子分析を適用し, 熱水活動に関わる金・ヒ 素・アンチモン・亜鉛・セシウム, 銅などの元素が 金鉱床周辺で高濃度を持つことを示した。

ヒ素が他の地点より高い濃度の場合,金も同様の傾向を示すことはよく知られている。しかしながら、名古屋大学地球化学講座で作成された地球化学図(2003)では、岐阜県多治見市西方でヒ素が他の地点より高濃度にも関わらず、金はほとんど検出されなかった。そこは、中・古生層分布地域であり、これまで研究された地域とは異なった元素の挙動があることが推測される。

地殻にヒ素は、平均約1.7mg/kg含まれている(文 献)。日本の表層地殻の平均は1.3~10.1ppmであり (Togashi et al., 2000), アメリカ合衆国の河床堆積 物・土壤中では約5~8mg/kgで, 平均7.4mg/kgである(Gilpin et al., 2006)。また, ヒ素の濃集は母岩の鉱 物の形態や、風化環境により大きく異なる。硫化物 や硫砒化合物、特に硫砒鉄鉱に含まれていることが 多い。珪酸塩では、As³⁺によってFe³⁺とAl³⁺が置換 され、マグマから生じた初生の造山鉱物に組み込ま れる。 AsQ_4^{-3} は PQ_4^{-3} などの陰イオンに類似している ために、 As^{5+} はアパタイトなどのような燐酸石の中 のP⁵⁺と置換し、燐酸塩に濃集する (Haslam et al., 2000)。ヒ素は火成岩の中に特に豊富に含まれてい るというわけではない(Haslam et al., 2000)。しか し、熱水活動の結果、豊富になる傾向が見られる。 また、高いヒ素の異常は、浅熱水・中熱水金鉱床の 特色と共通している (戸上ほか, 1997)。堆積岩にお いてヒ素は、泥・沈殿物・硫化物・有機物や2次鉱 物である鉄酸化物の存在する所に濃集している。ヒ 素は粘土部分や含水した酸化鉄や酸化マンガン・硫 化化合物や燐酸塩に強く吸着されているので

鉄マンガンノジュールや類似した堆積物に濃集 している。また、 As_2O_2 や As_2O_5 は酸性の水に穏やか に溶ける。しかし、硫化物・砒酸塩からはヒ素が遊 離しにくい(Haslam et al., 2000)。また、ヒ素は、粗 粒堆積物に比べ、細粒堆積物に濃集することが知ら れている(寺島ほか, 1993)。

本研究では、本調査地域におけるヒ素と金の濃 度を規定する要因を考察するとともに、中・古生層 におけるヒ素と金を中心とした元素の挙動を知るこ とを目的とした。

2. 調査地域

2.1 調査範囲

これまでに名古屋大学地球化学講座で調査され た地域に隣接し、中・古生層の分布する愛知県北部 から岐阜県南部にかけての東西約15km,南北約 10kmを調査地域とした。本研究地域は、庄内川の 上流域である土岐川に流れ込む河川と、人工池であ る入鹿池に流れ込む五条川の集水域である。五条川 流域にはキャンプ場、そのほかの地域には住宅地・ 建造物・ゴルフ場が多く点在する。特に、第三紀・ 第四紀層分布地域には住宅地・工場が多い。また、 入鹿池東と春日井市南部にそれぞれ土砂採掘所が存 在する。また、多治見市北部から可児市南部には工 業団地があり、その他の場所にも工場が点在してい る。本調査地域及び試料採取地点をFig.1に示す。



Fig. 1 Study area and sampling sites of stream sediments. Ninety-one samples were collected in the area of 15km×10km.

2.2 地質

調査地域の西部と北部の一部に、中・古生層で ある美濃帯砕屑岩・チャートが分布している。それ 以外の地域には海成層である中新世の瑞浪層群及び 湖成層である第三紀鮮新世の瀬戸層群およびが分布 している。瑞浪層群は砂岩・泥岩、瀬戸層群は砂礫 層を主体とし、少量の粘土や火山灰を含む(日本地 質学会、2005)。また、多治見市では陶土の採掘が行 われている。また、第四紀完新世・更新世の沖積層 や砕屑岩層が多治見市・土岐市の中心部周辺に分布 している。本調査地域の地質図をFig.2に示す。



Fig. 2 Geology in this study area. Compiled after geological map by Geological Survey of Japan.

3. 試料と分析法

3.1 試料

3.1.1 試料の採取

地球化学図を作成するための分析試料には、土 壤(Kadunas et al., 1999,), 湖沼堆積物(Kadunas et al., 1999,), 氷河堆積物(Bolviken et al., 1986), 更には 地下水(Slowansk, M.Sc., 1997), 雪塵・雪解け水 (Kadunas et al., 1999)などが用いられている。しかし ながら、これらの試料にはそれぞれ問題がある。岩 石や土壌は場所に依存する不均質性が大きいと考え られる。また、地下水・湖沼堆積物・氷河堆積物 は、本研究地域では採取することが困難である。 7 で、土地所有権の問題が無く、地域代表性が良 く、均質的である河床堆積物を用いた。河床堆積物 の均質性については、3.3.2で詳しく述べる。試料採 取は伊藤ほか(1991)と同様の手法で行った。河床堆 積物は、現地の流水を使い、80メッシュの篩に通し、粒径180μm以下の粒子を集めた。流れの速い ころには重鉱物、遅いところには軽鉱物がたまり ト やすい。また、流速により、酸化還元状態が異な る。そのために、極端に流れの早いところや、よど んでいる地点は避けて、試料採取した。

また,地球化学図の描写のためには,試料を地 理的にできるだけ均等な分布になるよう採取するこ とが望ましい。本研究での試料採取は,できるだけ 均等に採取したが,2.1に述べたように住宅や工場 が多い。それらの近隣では,三面工事の行われてい る地点が多数あった。そのような地点では,工事の なされていない上流に遡って採取した。しかしなが ら,それでも工事がなされている場合は,堆積物が 多く堆積しているところで採取した。また,河川の 合流点では、隣の河川からの汚染がないように,数 +m遡った地点で採取した。また,河川横の崖崩れ が起こっており,特定の土砂が河川に流れ込んでい る地点は避けた。約150km²の範囲内で,91地点で 試料を採取した。

3.1.2 分析試料

採取した試料は、実験室に持ち帰り揮発しやすい元素を失わないように40℃で乾燥させた。また、均質性を高めるためにメノウ製のボールミルで30分程度粉砕し、これを分析試料とした。

河床堆積物を構成する鉱物の分析を目的とした 鉱物分離用の試料として、やや粗い粒子を含む350 μm以下の河床堆積物を採取した。上記の試料と同 様に40℃で乾燥させたのち,250µm,180µm,150µ m,125 µ m,75 µ m,38 µ m,25 µ mのふるいを使って8つ の粒度別フラクションに分離した。そのうち,340 ~250μm,250~180μmに分画された量の多い7試料 は、アイソダイナミックセパレータを用いて強磁性 のものを取り除いた。それらの試料と、UI46地点 で採取した1mm~180µmの試料について,ヨウ化 メチレンで比重が3.211以上の鉱物を分離した。各 フラクションは実体顕微鏡下で、ヒ素を含む可能性 の高い非珪酸塩質の不透明鉱物3種類,①黒光りし ている鉱物②赤い鉱物③黒い鉱物をハンドピックに よりそれぞれ数十個~数百個集めた。これらの鉱物 は①黄鉄鉱②黄鉄鉱に鉄がコーティングされた鉱物 ③黄鉄鉱を含む様々な鉱物と鑑定された。

3.2 分析

測定は、中性子放射化分析(上岡・田中, 1989、 柴田ほか, 2001)と蛍光X線分析(杉崎ほか, 1977,山 本ほか, 2000)によって行った。

中性子放射化分析(INAA)では、河川堆積物約 125mgをポリエチレン袋に2重に封入し、日本原子力 開発機構のJRR-3気送管で中性子を5分間照射した。 標準物質には地質調査所のJB-1aを使用した。ヒ素 や金などの、JB-1a中に乏しい元素は、濾紙に含ま せた試薬を標準物質として用いた。また、ハンドピ ックした鉱物試料は、石英管に封入し、JRR-4 Sパ イプで中性子を6時間照射した。照射後の試料のγ 線を、名古屋大学アイソトープ総合センターのGe半 導体検出器で6日後と約1ヵ月後の2回定量した。測 定結果が2回得られた時は、荷重平均データを用い た。半減期より、ナトリウム・カリウム・ヒ素・ル ビジウム・バリウム・ランタン・サマリウム・ジス プロシウム・イッテルビウム・ルテチウム・タング ステン・レニウム・金・ウランは一回目、クロム・ 鉄・コバルト・亜鉛・セレン・ストロンチウム・ジ ルコニウム・アンチモン・セシウム・セリウム・ユ ーロピウム・テルビウム・ツリウム・ハフニウム・ タンタル・トリウムは2回目の測定結果が好ましい と考えられる。しかしながら、金・レニウムは、2 回目に真の値ではない架空の測定値が出てくるの で、これらの元素は1回目の分析結果のみを用い た。

蛍光X線分析 (XRF) では,主成分元素10元素を定 量した。有機物などを取り除くために1000℃で強熱 減量した河川堆積物0.7gに,四ホウ酸リチウムを 6.0gの割合で混ぜ合わせた。その混合粉末を, 1050℃で熱し,ガラスビードを作成した。それを, 島津蛍光X線分析装置SXF-1200を用いて分析を行っ た。但し,試料量の少ないVI10については,必要量 に足りなかったことから,XRFによる分析は行わな かった。

分析値は、別途公表をおこなう。

3.3 分析値の吟味

3.3.1 中性子放射化分析(INAA)と蛍光X線分析 (XRF)による分析結果の比較

鉄・ナトリウム・カリウムの3元素は、INAAと XRFの両手法で測定されている。どちらがより確か な濃度分布を示すか考察した。3元素についてINAA とXRFによる分析データの比較図をFig.3(a)~(c)に 示す。この2つの方法による分析値を比較すると, 鉄・ナトリウムは2つの手法間での違いが少ない。 測定結果が,鉄の含有量の10%程度までは, INAA、XRFともに、ほぼ一致。鉄は、XRFにおい て、高濃度になるにつれて検量線作成域を超えるた め、確度が低くなると考えられる。しかし、そのよ うな試料の数は少なく、こでは、試料量の多いXRF のデータを採用するのが考えられる。同様に、河床 堆積物中のナトリウムは、岩石試料や海洋試料と比 較して含有量が少ないため(0.03~1%)に, XRFで は確度が低くなる傾向が見られる。INAAでは, 0.03~1%の含有量でも,一回目の測定で,²⁴Naの 十分な強度が得られるので,精度が高い。逆に,カ リウムはINAAでは強度が小さく、ピークを見るこ とが難しい。そのために、INAAではデータが大き くばらつく。そこで、今回は、双方の測定値を参考 に, ナトリウムはINAA, 鉄・カリウムはXRFによ り得られたデータを採用した。



Fig. 3 Comparison of analytical data for Fe, Na and K with INAA and XRF.

3.3.2 試料の均質性・分析の確度

地球化学図のデータを使用する上で,分析誤差 とともに考慮しなくてはいけないのが試料の地域代 表性である。それには①同一地点で採取した試料の 組成変動②保存瓶中の不均質性による組成変動があ る。

柴田ほか(2001)は、INAAによって、BCR-1を標 準試料としてJB-1aを多数回分析した。柴田らは、 その結果を推奨値と比較したところ、ナトリウム・ スカンジウム・鉄・コバルト・ランタン・セリウ ム・サマリウム・ユーロピウム・イッテルビウム・ ルテチウム・ハフニウム・タンタル・トリウムは± 5%以内、クロム・亜鉛・セシウム・バリウム・ネ オジム・テルビウム・ウランは±10%以内の精度・ 確度で分析可能であると述べている。これが、分析 誤差を表す。

また,田中ほか(1995)は同じ地点で,多数回河 床堆積物試料を採取,分析した。その結果,同じ地 点での変動は,チタンは±100%,ナトリウム・カ リウム・ニッケルは±20%,その他の元素において は±50%程度であった。したがって,その変動幅を 超える違いについては真の違いであると言えると述 べている。Minami et al. (2005)は,同一地点におい て1994年から2004年まで各年度で複数回採取した試 料をXRFにおいて再測定した。その結果,チタンや リンも同様に±20%の範囲でばらつきがあることを 示した。

本研究での試料は1地点1試料であることから, 保存瓶中の不均質性を見ることを目的とした。加え て,測定結果には測定誤差も含まれていることか ら,このデータは,保存瓶中の不均質性と測定誤差 を合わせたばらつきを見ていると考えられる。同一 サンプル瓶中から5回はかりとり,分析したデータ の平均値と分析値に対する変動をFig.4に示す。 亜鉛・セレン・ルビジウム・アンチモン・セシ

亜鉛・セレン・ルビンリム・アンテモン・セン ウム・ネオジム・サマリウム・ジスプロシウム・ツ リウム・トリウム・タンタル・タングステン・レニ ウム・金は試料によって大きくばらつく。特にルビ ジウムは、±50%の変動があった。これは、不均質 性と、試料に含まれている各元素の少なさが大きな 変動の原因と考えられる。放射化されにくい元素 は、含有量が低ければ、さらに変動が大きくなる。 しかしながら、そのほかの元素は±10%以内の誤差 であった。したがって、これらの変動と誤差を明確 にし、化学組成の違いを解釈する必要があると考え られる。



Fig. 4 Concentrate fluctuation of repetition analyses in a single sample bottle.

x: elements, y:concentration except Na(ppm), Na(%). This figure shows average values and variations.

4. 結果・考察

4.1 地球化学図及び地質に伴う元素濃度の相違 地球化学図の描画には,稲吉(2005)の地球化学 図プログラムを用いた。本研究地域でのヒ素・金・ 主成分元素の地球化学図を,Fig.5に示す。

本研究では、調査地域の地質を美濃帯砕屑岩分 布地域、美濃帯チャート分布地域、第三紀・第四紀 層分布地域の3地域に分け、議論を進める。また、 その議論では、絶対値ではなく相対的に比較を行っ た。

美濃帯砕屑岩地域では、美濃帯チャート地域と 比較するとナトリウム・コバルト・亜鉛・タングス テン・金・ケイ素が低く、チタン・マグネシウムは 高い濃度を示す。また、第三紀・第四紀層地域と比 較すると、ナトリウム・クロム・アンチモン・ルテ チウム・ヒ素・カルシウム・リンは低い濃度を示 す。特に金は、0.006~0.014ppmであり、第三紀・第 四紀層地域のように、0.1ppm以上の高い値は見られ なかった。ヒ素は第三紀・第四紀層分布地域と比 ベ、比較的低濃度の地点が多いが、顕著な違いは見 られない。美濃帯チャート地域では、第三紀・第四 紀層地域に比べ、コバルト・タングステン・マンガ ン・ケイ素が高い濃度を示す。

これら3つの地質分布地域のうち,美濃帯チャート地域では,他の地域に比べ濃度が比較的大きくばらついている。また,希土類元素は,地質による違いはあまり見い出されない。

中・古生層は、第三紀・第四紀層に比べ、より 古い地層であるために、風化により溶脱しやすい元 素は、年月をかけて既に河川中に流出していると考 えられる。その結果、溶脱しやすい元素は濃度がよ り低くなったと考えられる。同様に、溶脱しにくい 元素は、河川堆積物中により多く残留している可能 性があると考えられる。しかしながら、これらのデ ータからは、定量的な議論を行うことができなかっ た。

4.2 因子分析

Gilpin R. et al. (2006)は、約4000試料のデータを non-parametric法を用い補正を行い,地球化学図の 濃度分布を決定した。またSiegel-Tukey Testを用 い、全サンプルのうち、濃度が、主にどの範囲に分 布しているかを記号で表し、解釈を行っている。し かしながら、本研究ではそれらに比べて、検討に加 え得る試料数が少なく、これらの数値解析はできな かった。本研究では,因子分析を用い,解釈を行っ た。因子分析は多変量のデータによって表される変 動をより少数の、基本的、仮説的変動によって指標 の単純化を図るものである。本研究では、北関東の 地球化学図(上岡ほか, 1991)や津具地方(戸上ほか, 1997)で用いられたものと同様に因子数は6と し、バリマックス法で軸を直交回転させ、補正を行 った。因子は、因子負荷量・因子得点分布を元に解 釈した。しかしながら、本研究では試料数が少ない ので, 寄与率の小さい第五因子以下は, 信頼度が低 いと考えられる。各因子の因子負荷量をFig.6に、 因子得点分布をFig.7に示す。



Fig.6 Factor loadings of analysis data in all sampling site.





【第一因子】

第一因子は、ランタン・セリウム・サマリウム・ユーロピウムなどの軽希土類元素・スカンジウム・トリウム・カリウム・マグネシウム・アルミニウム・セシウム等への寄与が大きい。寄与率は、 23.4%である。因子得点は、中・古生層分布地域に 高得点域があり、この地域におけるそれらの元素の 規定要因であると考えられる。第一因子は、モナザ イトと黒雲母だと考えられる。また、ヒ素の因子負 荷量はやや高いが、金は無いと考えられる。

【第二因子】

第二因子はハフニウム・テルビウム・ルテチウム・トリウムの寄与が大きい。寄与率は12.9%で、ほとんどが第三紀・第四紀層で高い因子得点を示す。これは、ジルコンを表す因子だと考えられる。また、ヒ素と金の因子負荷量はともに非常に少ない。



Fig.5 Geochemical map in this study areas.

【第三因子】

第三因子は、マンガン・コバルト・ヒ素の寄与 が大きい。寄与率は11.6%である。因子得点は、 中・古生層分布地域に高得点域が集中している。そ のため、この第三因子も本研究地域の主な規定要因 であると考えられる。また、鉱物であると特定する のは難しい。そのため、これはコバルトとヒ素を含 む物質であると考えられる。また、第一因子と同様 に、ヒ素の因子負荷量はやや高いが、金は無いと考 えられる。

【第四因子】

第四因子は、ナトリウム・カルシウム・カリウム・マグネシウムの寄与が大きい。寄与率は10.2% である。因子得点の分布は、中・古生層と第三紀・ 第四紀層の間では違いが見られない。この因子は長 石類を表す因子だと考えられる。金の因子負荷量は 高いが、ヒ素はほぼ無いと考えられる。

中・古生層は、堆積層であり、変成作用を受けない限り、その堆積層中に存在する鉱物そのものが河床堆積物の濃度に影響を及ぼすと考えられる。因子分析の結果より、本研究地域においてはヒ素と金の規定要因は異なることが示された。また、ヒ素は第一因子と第三因子を構成する元素、金は第四因子を構成する元素と同様の挙動をする可能性が示唆された。

4.3 河川堆積物における粒径別の化学組成変化

今井(1986)は、粒径別に分けた河川堆積物試料 中の化学組成がどのように変化するか調べた。 ICP-AESを用いた分析の結果、細粒の試料になるほ ど銅・鉛・亜鉛・クロムで明確な濃縮傾向を示すこ とがわかった。またコバルトは各粒度であまり変化 が無いと述べている。

本研究ではINAAを用いて粒度別の元素分析を行った。分析結果をFig.8に示す。

その結果、ほとんどの微量元素で細粒になるほ ど濃集する傾向が見られた。これは、SiやAlなどの 主要化学成分は石英や長石などの粗流な鉱物を形成 し、粗粒部分に濃集しているが、ここで分析された 微量元素は微小な不透明鉱物や鉱物粒界の細粒部分 に濃集しており、細粒フラクションほど細粒部分が 多くなることによると考えられる。この分析データ に粒径ごとの重量の割合をかけると、この鉱物試料 の全体の濃度を知ることができる。その結果、ボー ルミルで粉砕し分析した試料に比べ低い濃度であっ た。実際に地球化学図として分析している試料は, 比較的細かな粒子まで十分に沈めた試料が採集され たことによると推測される。また、重鉱物・軽鉱物 以外にも、細粒フラクションの多い地点で試料を採 取すると,濃度が相対的に高くなると考えられる。 しかしながら、試料全体の重量に対しもっとも細粒 な部分の重量は全体の1%以下であるため、それほ ど分析結果への影響は少ない。

ハフニウムは、最も細粒の25 μ m以下の粒径で はなく、38~25 μ mの粒径部分に高い濃集が見られ た(Fig.8)。ハフニウムはジルコンなどの鉱物に含ま れるので、この地域のジルコンは38~25 μ mの粒径 が卓越しており、河床堆積物として堆積したと考え られる。







Fig.8 Concentration on comparing minerals.

4.4 ヒ素を含む鉱物について

中・古生層のバックグラウンドを明確に表すと 考えられる五条川流域の地点の中でヒ素が比較的高 い濃度を示す地点で試料を採取した。3.1.2に示した 手法でヒ素を含む可能性が高い鉱物を分離・分析し た。鉱物別の分析結果をFig.9に示した。

(a)光沢を持つ黒色鉱物:鉱物の外見から黄鉄鉱 と鑑定されたものに準じ、同じ外観をもつ鉱物をハ ンドピックしたもの

ヒ素はさほど多くなく、100pm以内にあり、最 も高いヒ素の濃度は78.4ppmである。金は2地点で検 出された。しかしながら、そのほかの試料では検出 限界0.39ppm以下であった。また、鉄が26.3~40.8% を示した。このことから、この鉱物は黄鉄鉱及び輝 石などの不純物が付着したものと推測される。

(b)赤褐色鉱物:(a)の黄鉄鉱に類するが、表面が 赤褐色を示すもの

ヒ素は、92.8ppm~540ppmの高い濃度を示して いる。また、金も4地点で検出されており、0.09~ 1.69ppmと比較的高い。また、鉄は26.6~45.3%を示 した。1地点を除く4地点の鉄濃度は、(a)の鉱物に 比べ高くなっている。これは、黄鉄鉱にヒ素と鉄が 吸着された鉱物だと考えられる。

(c)黒色鉱物

ヒ素は1地点で901ppmという高濃度を示した。 しかしながら,他の4地点では32.7~123ppmと比較 的低い濃度であった。また、ヒ素の濃度が最も高い 地点では,金が2.1ppm検出された。金はこの地点を 入れた2地点を入れた2地点を除き、そのほかの鉱物 では検出限界以下であった。鉄濃度は13.6~44.8% とばらつきが大きいことから,様々な鉱物が採取さ れたと考えられる。

粉砕した河床堆積物の分析結果でヒ素が高濃度 を示す地点ではヒ素を高濃度で含む黄鉄鉱などの不 透明鉱物が存在することが確認できた。このことか ら、ヒ素は、本来の地質的要因に加え、ヒ素を含む 特定の鉱物の存在の多少がヒ素の規定要因になって いると考えられる。また、多くは高濃度のFe・Crを 伴う。そのために、黄鉄鉱、もしくは鉄酸化物が生 成し、その表面に固着・沈殿している可能性も示唆 される。

しかしながら、これらの鉱物は、全体の重量の 1%以下である。そのために、As全体の濃度は、標 準的な濃度、もしくは少し高い程度にしかならな い。また、鉱物により、全体の濃度が高くなるため には、非常に多量の鉱物、もしくは細粒になった鉱 物が多量に入っていることが原因だと考えられる。



Fig.9 Concentrate fluctuation of repetition analyses in these minerals.

5. まとめ

近年,地球化学図は環境基盤図として用いられ つつあり,土壌汚染など環境問題の評価に大きな役 割を担っている。本研究では,愛知県北部・岐阜県 南部の中・古生層分布地域における化学的バックグ ラウンドを知り,ヒ素と金をはじめとする元素の挙 動を調査し,考察した。その結果、風化に強いと考 えられる元素が河床堆積物中に残留し,弱い元素 は,河川水中に溶出したことが,河川堆積物中の主 要化学成分濃度が変化する一因だと考えられる。

また、因子分析を行い、元素存在度を規定する 因子を推定した。抽出された因子は、モナザイト、 黒雲母、ジルコン、コバルトとヒ素を含む物質、長 石類に対応すると考えられる。また、本研究地域の ヒ素と金の規定要因は異なることがわかった。その 規定要因を特定するために、粒径別分析及び鉱物分 離して分析を行った。その結果、細粒になるほどほ とんどの微量元素で濃集傾向が見られた。これは、 主成分元素が粗粒部分に含まれるため、細粒部分に

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ヒ素が多く含まれている地点の不透明鉱物をハ ンドピックし、①黒光りしている鉱物②赤い鉱物③ 黒い鉱物を見ることができた。また、これらを中性 子放射化分析で定量したところ、特に②には高濃度 のヒ素を含むことがわかった。

以上より、本研究地方の中・古生層におけるヒ 素は、比較的低濃度な地点が多く、第三紀・第四紀 層と比べ、大きな違いは見ることができなかった。 本研究地域においてヒ素が高濃度であるのは河川堆 積物中に含まれる上記の3鉱物を含むことによっ て、高濃度のヒ素を伴うようになったと考えられ る。また、ヒ素と金の規定要因は異なると考えられ るため、本調査地域では、ヒ素が低濃度であっても 金が高濃度を示すことがわかった。

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Ko 放射化分析法を用いた河川の水質階級と指標生物の重金属濃度に関する研究

Investigation on elemental concentrations of aquatic insect larvae in river in relation to water quality by INAA

with k₀ standardization method

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1. はじめに

環境指標生物としてこれまで様々な生物が利用さ れてきている。環境水中の重金属や農薬などの環境 汚染を評価するために利用する場合は、多くの生物 が環境水中のこれらの汚染物質を生物濃縮する性質 を利用している。水中の汚染物質濃度を直接定量す ることが困難な場合でも、生物濃縮により濃度が高 められている生物を分析すると検出が容易になる。

一般に重金属は生物により濃縮されることが多い。 したがって生物中の重金属を分析することは、水中 に存在する重金属を高感度で分析することに等しい といえる。水中の重金属濃度が変動しているような 場合でも、ある程度の時間平均として濃度を評価で きる利点もある。生物は重金属を代謝するとき、代 謝に要する時間に関連した体内濃度を持つので、河 川水の重金属濃度が変動していてもある程度時間平 均された体内濃度になる。河川の水質を月平均ある いは季節平均として評価したい場合、指標生物の利 用は有効な方法である。

本研究では水生昆虫を河川水における金属汚染の 環境指標として利用するための基礎的なデータを得 ることを目的として行った。一般的には水生昆虫は きれいな河川に生息しているので、生息する水生昆 虫の種類や数自体を用いて環境を評価することも行 われている。しかし、水生昆虫の金属濃度と環境水 やそれらの餌との関係についての詳細な研究は少な く、水生昆虫に含まれる重金属濃度を環境評価に利 用するための基礎的な知見についての情報は多いと はいえない。水生昆虫は、孵化して年を越えて成長 し夏前に羽化して水から離れる。このような特徴を 持つ水生昆虫の重金属濃度の季節変化や河川の上流 から下流に沿った金属濃度の変化に関して基礎的な 情報を得ておくことは指標生物として利用する際に は不可欠である。

環境試料の分析には様々な分析法が用いられるが、 生物を環境指標として用いる場合、より多くの元素 を定量することが望ましい。 k₀放射化分析法は、目 的元素ごとの比較標準試料を必要とせず多元素を同 時に分析できるという利点を持っており、環境試料 の分析には魅力的な手法である。本研究は、k₀放射 化分析法で行なった。

2. 実験

2.1. サンプリングと試料処理

水生昆虫は熊本県内を流れる白川で採取した。白 川は阿蘇カルデラに源を発し全長 74kmで流域面積 480km²を有し、有明海に流れ込む河川である。定点 のサンプリングポイントとして河口から 14km上流 の熊本大学に近い場所として黒髪ポイントを選定し た(図1参照)。白川流域は、水田や野菜などをも

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っぱら生産している田園地帯であり、黒髪ポイント は熊本市内の人口密集地帯より上流側に位置し、黒 髪ポイントより上流には大きな工場などの汚染源は ない。



図1 サンプリング地点

黒髪ポイントでは2004年1月~2005年12月の期 間について水生昆虫の採取を行った。ただし、水生 昆虫が確認されるのは、10月から翌年の6月頃まで であり、10月は個体サイズも小さく生息数も少ない。 また、5月頃からは羽化により個体数は減少する。 黒髪ポイントで採取した水生昆虫を表1に示す。

表1 黒髪ポイントで採取した水生昆虫

| エルモンヒラタカゲロウ | ' Epeorus latifolium |
|-------------|------------------------|
| シロタニガワカゲロウ | Ecdyonurus yoshidae |
| コカゲロウ | <i>Baetis</i> sp. |
| ヤマトフタツメカワゲラ | Neoperla niponensis |
| オオシマトビケラ M | acrostemum radiatum |
| ヒラタドロムシ M | ataeopsephus japonicus |

水生昆虫は、河川敷の流れに洗われている石の表 面に見られた。石の表面には短い褐色の藻が成長し ているが、たとえ石が水中にあっても藻が成長して いない石には、水生昆虫は確認されなかった。従っ て、水生昆虫は藻を餌にしていると思われる。藻に 含まれる重金属と水生昆虫に含まれる重金属の関係 を調べるために、2005 年 12 月に黒髪ポイントで藻 と水生昆虫の採取を行った。また、場所による違い を調べるために、2005 年 12 月に、黒髪ポイントの 上流に位置する菊陽と大津で藻と水生昆虫の採取を 行った。菊陽は黒髪の 10km 上流、大津は 21km 上流 にある(図1)。

採取した水生昆虫は、実験室に持ち帰り種類別に 分類した後、デシケーター中で乾燥させた。藻は河 川水で洗った後、水生昆虫と同様にデシケーター中 で乾燥させた。水中の重金属濃度を明らかにするた めに、河川水を蒸発乾固させて残渣を回収した。

2.2. 照射と測定

水生昆虫と藻の乾燥試料及び河川水の残渣は、石 英管及びポリエチレン袋に封入して照射試料とした。 照射は日本原子力研究所の原子炉JRR-4で10分と3 時間を行った。10分照射試料は、照射6時間後にガ ンマ線スペクトルを測定した。3時間照射試料は、 照射1週間後と2-3週間後の2回ガンマ線スペクト ルの測定を行った。ガンマ線スペクトルは、東京大 学原子力研究総合センター大学開放研究室の高純度 ゲルマニウム半導体測定システムで測定した。解析 には解析支援ソフト「SAMPO90」と「KAYZERO/SOLCOI」 を用いた。

3. 結果と考察

3.1 藻、河川水、水生昆虫の金属濃度

石の表面に成長していた藻に含まれる金属濃度と 河川水中の金属濃度を表2に示す。Ca、Fe、KとNa は藻に%オーダーで含まれているが、他の金属は微 量であった。サンプリングポイント間で大きな差は 観察されず、最大でも大津と菊陽のMnの2.4倍であ った。黒髪で2005年10月と12月に採取した藻に含 まれる金属濃度の違いは少なく、最大でもBrの3 倍であった。以上の結果は、藻に含まれる金属濃度 は、採取地点や採取時期で大きな変化がなかったこ とを示している。一方、河川水中の金属で主要なも のは、Ca、KとNaで藻と同じであった。しかし、Fe は藻に比べると河川水では少ない。BrやRbは河川 水と藻は同じ程度であり、Co、La、Mn、Scの水中濃 度は低い。河川水に検出されたZnとSeは藻では検 出限界以下であった。
| | | River water | | | |
|----|------------------|----------------|-----------------|------------------|----------|
| | Ōzu | Kikuyō | Kurokami | Kurokami | Kurokami |
| | Dec. 2005 | Dec. 2005 | Dec.2005 | Oct. 2005 | May 2004 |
| As | 20 ± 9 | 34 ± 6 | 27 ± 5 | 15 ± 2 | |
| Br | 60 ± 3 | 55 ± 5 | 57 ± 3 | 19 ± 10 | 35 |
| Ca | 37500 ± 4700 | 37400 ± 5600 | 39200 ± 7200 | 57600 ± 9200 | 21500 |
| Co | 23 | 26 ± 2 | 23 ± 3 | 26 ± 1 | 0.13 |
| Cr | 23 ± 5 | 21 ± 3 | 29 ± 9 | 26 ± 6 | |
| Cs | 3.6 ± 0.7 | 4.5 ± 0.4 | 3.8 ± 0.3 | 4.0 ± 0.3 | |
| Eu | 1.3 ± 0.1 | 1.4 ± 0.1 | 1.0 ± 0.1 | 1.3 ± 0.1 | |
| Fe | 71800 ± 2000 | 90400 ± 6800 | 78400 ± 6200 | 73400 ± 9300 | 480 |
| Κ | 13200 ± 200 | 11500 | 11500 ± 800 | 17100 ± 3400 | 59000 |
| La | 19 ± 3 | 23 ± 1 | 21 ± 2 | 23 ± 6 | 0.11 |
| Mn | 2200 | 5200 | 2900 | 3200 | 35 |
| Na | 14800 ± 200 | 13800 | 12700 ± 1200 | 20600 ± 4700 | 20700 |
| Rb | 51 ± 10 | 45 ± 5 | 50 ± 20 | 71 ± 21 | 18.5 |
| Sc | 12 ± 1 | 12 ± 1 | 11 ± 1 | 13 ± 2 | 0.04 |
| Se | | | | | 0.72 |
| Zn | | | | | 4.8 |

表2 石表面に成長した藻および河川水中の金属濃度

藻と同時に大津、菊陽、黒髪で採取した水生昆虫 のシロタニガワカゲロウに含まれている金属濃度を 図2に示す。シロタニガワカゲロウは白川で見られ る代表的な水生昆虫である。KとNa濃度は高く、Mn、 Zn と Br 濃度は中程度であり、採取地点による濃度



された傾向と同じである。しかし、大きな違いとし て、Zn はシロタニガワカゲロウでは検出されたが、 藻では検出されていない。2005 年 12 月に大津、菊 陽、黒髪で採取した他の種類の水生昆虫でもZn は検 出されていることから、シロタニガワカゲロウのZn が、この種に特徴的なものとは考えられない。

の違いは見られていない。採取地点で金属濃度に違

いがないシロタニガワカゲロウの傾向は、藻に観察

黒髪ポイントで 2004-2005 年に採取したシロ タニガワカゲロウの金属濃度の季節変化を図 3 に示す。年が変わっても金属濃度には大きな違い はない。金属濃度の平均と範囲は次の通りである。 Br:51±26 μ g/g (24-105)、Fe:2790±1350 μ g/g (1060-5700)、K:9450±3940 μ g/g (3300-18100)、 Na:4120±1370 μ g/g (1650-6380)、Rb:33±14 μ g/g (16-69)、Sc:0.5±0.2 μ g/g (0.2-0.9)、Zn: 370±120 μ g/g (250-720). 最も大きな差は K の 5.5 倍である。水生昆虫は毎年羽化することから、 濃度はその年に生息していた個体の金属濃度を 示していることになる。採取時期による大きな濃 度変化が観察されていないことから、白川水系の 水生昆虫の金属濃度に関して 2004-2005 年は安 定していたといえる。



図 3 黒髪のシロタニガワカゲロウの金属濃度 の季節変化

3.2 水生昆虫と藻及び水生昆虫と河川水の金属の関係

水生昆虫は、藻が成長していた石の表面に生息 していたことから、藻は餌になっていると考えら れる。また、水生昆虫は流れてくる懸濁物やある いは水中の金属も取り込むと考えられるので、ど れが水生昆虫の金属濃度により影響を与えてい るかを濃度比解析から行なった。

藻、河川水及び水生昆虫の各試料に検出された

金属濃度を、それぞれの試料について金属ごとの 比を計算し濃度比マトリックスを計算する。ここ で、X は試料であり、a は試料 X の各金属濃度で ある。

$$X_{ij} = \begin{bmatrix} (a_1/a_1) & & \\ (a_2/a_1) & (a_2/a_2) & \\ (a_3/a_1) & (a_3/a_2) & (a_3/a_3) & \\ - & - & - & - & - \end{bmatrix}$$

得られた試料Aの濃度比マトリックスXと試料 Bの濃度比マトリックスを用い、それぞれの金属 濃度の比についてマトリックス比Yを計算する。



ここでは、マトリックス比Yとして、水生昆虫 /藻と水生昆虫/河川水を求めた。水生昆虫と藻あ るいは水中の金属濃度の分布及び濃度は異なっ ているのが普通であるが、仮に濃度は異なってい るが、その分布が同じであった場合、すなわち、 例えば、水生昆虫が水中のすべての金属を等しく 生物濃縮していたとしたら、マトリックス比Yの すべて成分は1となる。従って、水生昆虫/藻と水



図4 マトリックス比の分布、上段(水生昆虫/藻)、下段(水生昆虫/河川水)

生昆虫/河川水のマトリックス比 Y を比較したと き、より1に近い成分を多く含む方が、より水生 生物と金属の分布が近くいと言える。すなわち、 水生昆虫はより大きな影響を受けていると考え ることができる。これにより餌として藻の影響と 生息環境としての河川水の影響を比較すること ができる。図4に黒髪で採取した水生昆虫につい て求めたマトリックス比を示す。図4では、上段 に水生昆虫/藻の分布を、下段に水生昆虫/河川水 の分布を水生昆虫の種類ごとに示している。分布 がより1に集まっているほど水生昆虫の金属濃 度に影響を与えていると判断される。ヤマトフタ ツメカワゲラ以外の水生昆虫では、明らかに上段 に示している水生昆虫/藻の分布がより1に集中 した分布を示していることがわかる。多くの水生 昆虫は草食性であることが知られているので、図 4は水生昆虫は餌と考えられる藻の金属により 近い金属分布をしていると言える。カワゲラの一 部の種類は雑食性であることが知られている。ヤ マトフタツメカワゲラが雑食性であるかどうか は不明であるが、ヤマトフタツメカワゲラ/藻のマ トリックス比の分布が他の水生昆虫よりばらつ きが大きいのは食性の違いを反映している可能 性がある。

4. まとめ

水生昆虫は、河川水に含まれる金属より、生息 している石に成長していた藻の金属の分布に、よ り近い金属分布を持つことが明らかになった。こ れは藻が水生昆虫の餌であることと関係してい ることを示唆しているが、雑食性と思われる水生 昆虫では異なっていた。藻のZn濃度は検出限界 以下であったにも関わらず、いずれの水生昆虫に も高い濃度でZnが検出された。このことは、必 須元素については、餌以外からの金属の取り込み があることを意味している。白川の上流から下流 までの20km 程度の範囲では、水生昆虫及び藻の 金属濃度に、場所による違いは観察されなかった。 また、2004-2005年に測定した限りでは、黒髪 では季節による差は見れていないことから、白川 の水質環境にその間変化はなかったといえる。

水生昆虫の金属濃度は、河川水よりも餌からの 影響をより大きく受けていることから、水質環境 の指標として利用する場合には、このことを考慮 して利用することが必要である。

成果公表

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5. その他

5. Others

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5-1

研究テーマ:フィッショントラック法による環境試料中の核物質検出

表 題:フィッショントラック法の保障措置環境試料パーティクル分析への応用

フィッショントラック法の保障措置環境試料パーティクル分析への応用

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フィッショントラック(FT) -表面電離質 量分析 (TIMS) 法によるパーティクル分析法は、 2次イオン質量分析器 (SIMS) では測定が難しい 粒径1 µm以下の核分裂性物質を含む微小粒子に 対しても同位体比分析が可能であることから、保 障措置上有効な分析手法とされている。フィッシ ョントラック法では熱中性子照射により起こる 核分裂の痕跡(フィッショントラック、飛跡)か ら核分裂性物質を高感度に検出できる。我々がこ れまでに開発したFT-TIMS法では、核分裂性物質 を含む粒子をFT検出器の中に閉じこめるので(1 層式FT 試料調製法)、高い検出効率、試料調製 の簡便さなどの長所がある。しかし、検出器のエ ッチングの際、ウラン粒子の一部が溶解すること がある。そこで、粒子保持層とFT検出器部を分 離した2 層式FT 試料調製法の開発を行った。こ の方法では粒子層と検出器の一端を固定するこ とにより、粒子溶解の問題だけではなく、従来の 2層式 FT試料で見られた検出器でのFTと粒子層 での目的粒子との位置ずれを解決し、目的粒子の 検出効率を向上させた。今回は、本法の長所であ る、検出器の繰り返しエッチング後でも目的粒子 の同定が正確で簡便であることを利用して、保障 措置上重要な高濃縮度のウラン粒子を優先的に 検出できる方法の開発状況について報告する。1)

ウランの同位体において熱中性子照射により核分裂が起きるのは²³⁵Uであるので、FTの数は

粒子の濃縮度だけではなく粒径にも依存する。熱 中性子の数と粒径が同じである場合、FTのエッ チング速度はその数が多い高濃縮度のウラン粒 子ほど早くなる。これは、高濃縮度のウラン粒子 ほど短い時間でエッチングされることを意味し、 エッチング時間の制御によってウラン粒子の濃 縮度別検出が可能であることを示唆する。²⁾

検出器のエッチング時間の制御によりウラ ン粒子を濃縮度別に検出するためには、濃縮度ご とに検出されるエッチング時間を求める必要が ある。その結果を図1に示す。実験では、粒径の 違いによる影響をできるだけ小さくするために、 2段式粒子吸引法によりウラン粒子の粒径を1~ 3µmにした。図1は、熱中性子照射後、エッチン グによりFTが検出されるまでのエッチング時間 のウラン粒子の濃縮度依存性を示しており、濃縮 度が高くなるほどFT検出までのエッチング時間 が短いことが分かる。この関係を利用して、ウラ ン粒子の濃縮度別検出の実証実験を行った。試料 は天然組成のウラン(NU)と 35%濃縮ウラン (U350)を混ぜて作製した濃縮度混合試料を用

いた。濃縮度別検出のためのエッチング時間は、 U350のみが検出される時間である 2.5 分と、NU が十分検出される時間である 7 分を用いた。それ ぞれのエッチング時間で検出した粒子のTIMSに よる同位体比測定の結果を図 2 (a) と (b) に示 す。図 2 (a) に示すように、エッチング時間 2.5

原子炉: JRR-4

装置:気送管

分野:その他(フィッショントラック法)

分で検出した粒子はすべてU350の認証値(²³⁵U/ ²³⁸U:0.5465)に一致している。一方、エッチン グ時間7分で検出された粒子は、図2(b)に示 すように、NUとU350の双方が検出された。7分 のエッチング後でU350 が検出されたのは、2.5分 のエッチングで検出されなかった粒径の小さい U350 粒子の出現に起因することであり、これは 7 分のエッチングにより現れたFTの形状から確 認できる。図3(a)と(b)にエッチング時間2.5 分と7分で現れたFTの典型的な形状を示す。写 真の番号は、図2の粒子番号に対応している。7 分のエッチングにより現れたNU(10,11)とU350 (16.17) はFTの形状から、両者は明確に区別で きる。図3(b)の写真16と17のFT形状(トラ ックの本数)は、同じエッチング時間で出現した NU(10,11)の形状よりも、2.5分のエッチング により現れたU350のFTと同様な形状をしている。

このように、エッチング時間の制御だけでは 完全な濃縮度別検出に至らなかったが、FTの形 状を比較することにより高い割合で濃縮度別検 出が可能であることが示された。

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図1 種々の濃縮度のウラン粒子における、FT が検出されるまでのエッチング時間の濃縮度依存性。



図 2 濃縮度混合試料 (NU+U350) において、エ ッチング時間 2.5 分 (a) と 7 分 (b) で検出され た粒子の TIMS による同位体比。





図3 濃縮度混合試料 (NU+U350) において、エ ッチング時間 2.5 分(a) と7分(b) で検出され た粒子の FT 形状の例。写真の番号は、図2の粒 子番号と対応する。

5-2

研究テーマ:フィッション・トラック年代測定 表 題:FT 年代測定のためのディテクターの開発

> フィッション・トラック法に用いるDAPプラスティックディテクターの改良(その3) 岩野英樹¹・檀原 徹¹・小林啓一²・鶴田隆雄³ ¹: (株)京都フィッション・トラック ²:山本光学(株) ³:近畿大学原子力研究所

熱中性子によって生じたウラン-235 の誘導核 分裂片(重荷電粒子)を検出するプラスチック材料 として、ジアリルフタレート (diallyl phthalate : DAP) 樹脂がある^{1,2,3,4,5,6}。この DAP 樹脂の特 徴の一つは、熱中性子照射による誘導放射能が比 較的小さく⁷⁾、放射線障害防止の観点上優れてい る点にある。

DAP 樹脂の主原料(DAP モノマー)の製法には、 ①アリルクロライドをフタル酸ソーダと反応させる、②アリルアルコールを無水フタル酸と反応 させる、の2つがある。これまで①の製法のモノ マーで作られた DAP 樹脂(Q-DAP)には Br が不純 物として含まれ、照射直後から数日間は比較的高 い放射能をもつことが放射化分析から明らかに された⁷⁾。一方、②の製法のモノマーで作られた DAP 樹脂(S-DAP)については、Br の定量的な分析 結果は報告されていない⁸⁾。そこで本研究では、 S-DAP の y 線スペクトル測定から微量元素に関 する検討を行った。

試料は S-DAP 樹脂 (1.20g) と、比較試料とし て Q-DAP 樹脂 (1.32g) を用意した。これらを原 子力科学研究所 JRR-4 号炉気送管 (3.5MW 出力 時)において熱中性子を照射した。熱中性子束は 最大で $3.2 \times 10^{17} (\text{m}^2 \cdot \text{s}^{-1})$ で、180 秒間行った。照 射終了後、3 日後と 30 日後にゲルマニウム半導 体検出器を用いて γ 線スペクトル測定を行った。 また S-DAP および Q-DAP の照射後の表面線量の 変化をモニターした。測定器は GM サーベイメー タで、検出限界(BG レベル)は 80cpm であった。

まず表面線量の変化を表1にまとめた。S-DAP の表面線量率は Q-DAP よりやや小さく、また照 射から1ヶ月後には表面線量が完全に BG レベル まで減衰した。これらの結果は既報の予察結果と 調和的である⁹。

表1. DAP 樹脂の表面線量変化

| 日数 | 3日後 | 11 日後 | 30日後 |
|-------|-----------------------------|-----------------------------|------|
| DAP | | | |
| S-DAP | 350 cpm | 200 cpm | BG |
| | (約 0.6 Bq/cm ²) | (約 0.3 Bq/cm ²) | |
| Q-DA | 400 cpm | 250 cpm | BG |
| Р | (約 0.7 Bq/cm ²) | (約 0.4 Bq/cm ²) | |

y線スペクトル測定の結果を図1に示した。照 射後3日目のS-DAPからQ-DAP同様明瞭なBr-82 が検出された。しかしS-DAPでのBr-82のピーク 値はQ-DAPと比較して1/2以下と小さい。照射 後30日目の測定結果から、S-DAPおよびQ-DAP から中・長寿命核種が検出されないことを確認 した。

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原子炉:JRR-4
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装 置:気送管

分 野:その他(放射年代学)



図1. DAP樹脂の γ 線スペクトル. (a) Q-DAP, (b) S-DAP

5-3

「ホウ素中性子捕捉療法におけるSOF検出器とJCDSシステムとの連携」 Collaboration between SOF detector and JCDS system in Boron Neutron Capture Therapy 北海道大学病院 分子追跡放射線医療寄附研究部門 石川 正純

(1) 研究の目的と意義

目的:本研究の目的は、JCDS 治療計画システム によってあらかじめ評価された線量分布に、SOF 検 出器によるリアルタイム熱中性子束測定情報を加え ることによって、リアルタイムで線量評価が行える システムを完成させることである。

意義:リアルタイムで線量評価を行うことにより、 従来のような照射終了後に線量の評価を行うのでは なく、治療中に必要線量が投与されたかどうかを確 認できることは、治療成績に大きく貢献すると考え られる。

(2) 方法

現在、日本原子力研究開発機構(原研)にて行わ れているホウ素中性子捕捉療法(BNCT; Boron Neutron Capture Therapy)では、原研にて開発された JCDS 治療計画システム(JAERI Computational Dosimetry System)を用いて照射の治療計画を作成さ れている。

一方、治療で実際に照射された中性子量は、従来、 金線の放射化法を用いて評価が行われていたが、当 研究グループによって開発された SOF 検出器

(Scintillator with Optical Fiber detector) により、リア ルタイムでの熱中性子束評価が可能となった。

JCDS による治療計画によって計算された詳細な 患者体内における吸収線量分布(高速中性子線量、 ホウ素線量分布、γ線線量分布)と熱中性子束分布 を用い、SOF 検出器をリファレンス検出器として、 リアルタイムで線量分布を計算するソフトウェアを 作成する。

また、水ファントムを用いた検証を行い、測定の 妥当性について検証を行う。

1. はじめに

放射線療法の一つである中性子捕捉療法(Neutron Capture Therapy)は、腫瘍を細胞選択的に破壊でき るため、術後の生活の質(Quality of Life)の優れた 治療法として近年注目されている^(a-d)。中性子捕捉療 法は、中性子捕獲断面積の大きい核種を含み、かつ、 腫瘍に特異的に集まる性質のある薬剤を患者に投与 し、エネルギーの低い熱中性子または熱外中性子を 照射することによって核反応を誘起し、腫瘍細胞を 死滅させる放射線治療法である(図1参照)。腫瘍細 胞に選択的に取り込まれる化合物を用いることによ り、細胞選択的に腫瘍を死滅させることができるた め、脳腫瘍や悪性黒色腫など、正常組織内に侵潤し た場合に切除が困難な腫瘍に特に有効である。

ホウ素中性子捕捉療法における治療照射場では中 性子線とγ線が混在しているので、患部及び正常組 織での吸収線量を正確に評価するために、それぞれ の線量を分離して測定する必要がある。特に熱外中 性子照射では、熱外中性子および高速中性子による



Tumor (¹B enriched) 図 1 ホウ素中性子捕捉療法の概念図 Fig.1 Schematic illustration of BNCT. 線量も考慮する必要がある。

熱中性子はホウ素(¹⁰B)および生体中の窒素(¹⁴N)と 核反応を起こして高LETの重荷電粒子を発生し、狭 い範囲に大きなダメージを与え、熱中性子よりもエ ネルギーの高い熱外中性子及び高速中性子は、生体 中の水素原子と作用して反跳陽子を生成し、その周 辺にダメージを与える。y線は低LET放射線であり、 広い範囲にわたってダメージを与える。したがって、 現在、ホウ素中性子捕捉療法における中性子線とy 線の混在場における生体の吸収線量は、大きく分け て3つの成分に分け、以下の計算式で求めたRBE吸 収線量(RBE・Gy)で評価している。

 $D_{total} = D_{gamma} + D_{fast} + (N \cdot R_N + B \cdot R_B) \cdot \phi_{th}$ D_{fast} :高速中性子線量、 D_{gamma} : γ 線量 R_N : ¹⁴N(*n*, *p*)反応のRBE、 N: 窒素濃度 R_B : ¹⁰B(*n*, *a*)反応のRBE、 B: ¹⁰B濃度 ϕ_{th} :熱中性子フルエンス

線量評価に必要な中性子フルエンスの分布は、ファ ントムを用いた模擬実験とX線CTやMRI画像を考 慮した計算で事前に評価し、患部近辺に埋め込まれ た金線を用いて測定しているのが現状である。熱中 性子束の測定には直径 0.25mm の金線が用いられて いるが、その理由は、①生体と接しても安定である、 ②小型であるので位置の測定精度が高い、③適度な 放射化断面積と半減期を持っている、④崩壊形式が 単純で崩壊γ線が測定しやすい、などの有利な点が 多いためである。しかしながら、金線の放射化法で は、①リアルタイム測定ができない、②熱外中性子 に大きな感度を有するなどの問題点がある。特に、 近年はより深部の腫瘍を治療するために、熱外中性

子による照射が大半を占めており、金線による測定 は計算との比較に使われるのみとなっている。

ホウ素中性子捕捉療法における熱中性子東モニタ として、これまでにもガスカウンターや半導体検出 器等の検出器を用いた熱中性子東評価が試みられて きた。しかしながら、照射室内は高強度の熱中性子 束およびッ線が存在することから、検出器の中性子 耐性が大きな問題となっていた。また、照射室に配 置した検出器からの信号は、遮蔽の関係上 10 m以上 離れた位置で処理する必要があることから、電気ノ イズの混入を避けることができないという問題もあ り、安定した測定を実現することが困難であった。 そこで、名古屋大学の森千鶴雄先生が考案された光 ファイバーを用いた検出器システムに着目し^(e)、中 性子捕捉療法のための熱中性子東モニタとなるSOF 検出器 (Scintillator with Optical Fiber Detector)の開 発に至った^(f)。

本研究課題では、この SOF 検出器を利用した高度 な吸収線量評価を目的として、リアルタイム線量評 価システムの構築を目指す。

2. 装置および方法

(1) SOF 検出器の概要

図2は、SOF検出器の構成図を示している。熱中 性子検出素子として、バイクロン社製プラスチック シンチレータBC-490に⁶LiF(⁶Li:95% enriched)を塗 布したものを、三菱レイヨン社製光ファイバー PM-3241-HD(1 mm × 15 m)に光学的に接続して いる。光ファイバーにより伝達された光信号は、光 電子増倍管により電気信号に変換され、電気信号は 波形整形アンプ回路を用いて増幅した後、ディスク リミネータでノイズを弁別し、カウンタを用いて有



図 2 SOF 検出器システムの概要 Fig. 2 Schematic illustration of SOF detector system. 効シグナルだけを計数する。

本検出器では、バックグラウンドとして存在する 高速中性子およびγ線によるシグナルが主なノイズ の原因となる。そこで、熱中性子増刊剤(⁶LiF)を 含むシンチレータを用いた検出器と含まないシンチ レータを用いた検出器をペアで用いることにより、 高速中性子線およびγ線を補償し、熱中性子束のみを 正確に評価している^(g)。

熱中性子増刊剤を含むシンチレータの計数値を C_+ 、 含まないシンチレータの計数値を C_- とすると、熱中性子 フルエンス F_n 、高速中性子フルエンス F_f 、 γ 線フルエン ス F_a を用いて、それぞれの計数値は、

$$C_{+} = R_{n+} \cdot F_{n} + R_{A+} \cdot F_{f} + R_{g+} \cdot F_{g}$$
(1)
$$C_{-} = R_{f_{c}} \cdot F_{f} + R_{g} \cdot F_{g}$$
(2)

と表すことができる。ここで、 R_n 、 R_g 、 R_f は、熱中性子、 高速中性子、 γ 線に対するレスポンス係数である。

一方、純粋な γ 線場では、 γ 線フルエンス F'_s を用いて、

$$C'_{+} = R_{g_{+}}F'_{g}$$
 (3)
 $C'_{-} = R_{g_{-}}F'_{g}$ (4)

と表現することができる。(3)式と(4)式から、 γ 線レ スポンス係数の比 R_{g+}/R_{g} を求めることができる。こ こで、 γ 線レスポンス係数の比および高速中性子レ スポンス係数の比は、シンチレータの体積のみに依

$$C_{+} = R_{n+}F_{n} + \frac{R_{g+}}{R_{g-}}C_{-} = R_{n+}F_{n} + \frac{C_{+}}{C_{-}}C_{-}$$
(5)

と表せる。(5)式をF_nについて解くことにより、熱 中性子束を評価することができる。

$$F_n = \frac{C_+ - \frac{C_+}{C_-}C_-}{R_{n+-}}$$
(6)

(6)式を用いて熱中性子束(または熱中性子フルエ ンス)を測定するためには、純粋γ線源による計数 値の比および熱中性子に対するレスポンス係数が必 要であるが、これらは容易に求めることができる。

(2) SOF 検出器の基本性能

図3に原研JRR-4研究炉を用いて、炉出力を20W から3.5 MWまで変化させたときのSOF検出器の熱 中性子束評価値を示す。この図からも分かるように、 SOF検出器は、熱中性子束10⁵ n/cm²/sから10⁹ n/cm²/s にわたって、広い範囲でのリニアリティを有してい る。ただし、10⁹ n/cm²/s以上では、高計数率に依存 する数え落としが原因で、リニアリティが失われて いるが、非まひ型モデルを用いて、数え落としの補 正を施すことにより、3×10⁹ n/cm²/sでは14%あった 数え落としを、0.1%にまで補正している。

(3) 治療計画システム JCDS

JCDSは患者のCT画像から頭部などの計算体型モ デルを作成し、治療計画を行うための総合ツールで ある^(h)。患者体内での線量分布計算には、モンテカ ルロ輸送計算コードMCNPを用いているため、CT画 像によるモデルの計算体型や、あらかじめ計算され た炉心からの中性子場条件などを含んだMCNPの入







カファイルを自動で作成する機能を持っている。ま た、MCNPで計算した結果を再びJCDSに読み込み、 頭部モデル上に線量分布を重ねて表示させることが できる。図4にJCDSによる治療計画の流れを示す。 JCDSでは、①医療画像であるCTとMRIの両データを 使用することによって、正確な患者頭部の3次元モ デルを簡便に作成することができる、②開頭術を伴 ったBNCTにも対応することができる、③患者セッ ティングシステムと連携し、患者を迅速かつ正確に セッティングすることができる、などの特徴を有し ている。



(4) リアルタイム3次元線量評価システム

リアルタイムで患者体内の線量評価を行うために は、患者体内での熱中性子束分布や各種線量分布な どを得る必要がある。しかしながら、これらの実測 情報を得ることは事実上不可能である。そこで、 JCDS によって計算されている患者体内での吸収線 量分布(高速中性子線量、ホウ素線量分布、γ線線 量分布)と熱中性子束分布があらかじめ計算されて いるので、図5に示すように患者の体表面に基準と なる SOF 検出器を配置し、SOF 検出器によるリアル タイム熱中性子束をリファレンスとして、リアルタ イムで CT 画像上に治療中の線量分布を表示できる ソフトウェアを作成した(図6)。

任意の点における線量等は次式によって計算され る。



(5) ファントム実験による検証

JRR-4 で使用している直径 18cm の水ファントム (アクリル製、肉厚 5mm)を用いて、リアルタイム 線量評価システムの検証を行った。水ファントム内 の線量分布をリアルタイムで測定することは困難で



因 5 基準 SOF 使山岙の配直 Fig. 5 Arrangement of reference SOF detector



図 6 リアルタイム線量分布表示システム Fig. 6 Real-time dose distribution display system

あることから、SOF 検出器を水ファントム内でスキ ャンすることにより熱中性子束分布を測定し、リア ルタイム熱中性子束分布評価結果との比較を行うこ とによって検証した。

水ファントムのビーム中心軸および中心軸から 30mm、60mm 離れた位置となるように設定されたア クリル板に SOF 検出器プローブを配置し、沿革ポジ ショニング装置を用いて照射中にビーム軸方向にス キャンした (図 7,8 参照)。



図 7 水ファントムをビーム中心軸上に配置 Fig. 7 Water phantom was set at beam axis



図 8 SOF プローブの配置 Fig. 8 Arrangement of SOF probes

リファレンス用の SOF 検出器プローブは、ファン トムの内側表面中央に配置した。

3. 結果および考察

図9にSOF検出器による水ファントム中の熱中性 子束分布測定結果とリアルタイム線量評価システム による熱中性子束分布の評価結果を示す。中心軸上、 60mm 離れた場所のいずれの場所においても測定と 評価結果はよく一致した結果が得られた。

ただし、リファレンスに使用する SOF 検出器の設 定位置が変化すると、計算値が相対的に変化するた め、注意が必要である。特に、水ファントム表面付 近では、急激に熱中性子が変化する場所でもあるの で、リファレンス検出器の配置場所には適さないと 思われる。

4. 結果に対する評価

本研究の成果により、BNCT 治療中におけるリア ルタイムでの線量評価が可能となるため、より正確 な線量制御が可能となると考えられる。





5. 今後の課題

今後は、実際の症例についてリアルタイム線量評 価システムを用いた評価を行い、治療中の評価結果 と事後評価結果の比較から、このシステムの有効性 を検証していきたいと考えている。

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α線トラックエッチング法による各種鉄鋼材料中微量ボロンの観察

Observation of the ultra small amount boron in various steel materials by α particle track etching method

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I.研究の目的と意義

I-1.研究の目的

ボロン(以下 B) は極微量でも鉄鋼の性質を向上させ ることが知られており、非常に多くの鋼で利用されてい る。さらに今後ますます重要となる環境問題、資源・エ ネルギー問題に対処できる鋼としてB添加鋼の重要性の 認識が高まっている。

著者らは日本原子力研究開発機構(JAEA と略称)の医 療用照射設備を用いて熱中性子とボロン 10 の反応を利 用したα線トラックエッチング(以下、ATE と略)法に ついて実験を進めてきたが近年、医療本来の需要、ない しは動物実験のマシンタイムが増しているため、ATE 法 のマシンタイムが減少傾向にあった。この3年間は、ATE 法を利用できる気送管による照射システムを立ち上げ た。またフェライト系耐熱鋼および Cu-Sn 含有鋼 についてBの状態分布について研究を進めてきたので報 告する。

Ⅱ.研究成果

研究1: JRR-3 及び JRR-4 の気送管設備を用いたα線ト ラックエッチング法による鋼中ボロンの状態分布観 察法の確立と問題点

1. 緒言

ボロンを極微量添加することによって鉄鋼の諸性質を 向上させる研究は盛んに進められている^{1)、2)など}。古くは Armi joらの論文があるが、当初はオーステナイト鋼中の ボロンを検出するために使用された³⁾。またボロン添加 鋼における焼入れ性とオーステナイト粒界へのボロンの 非平衡偏析⁴¹や、粒界偏析におけるボロン欠乏域の幅か ら非平衡偏析が説明されている^{4,5)}。さらにボロンはNbの 有無によりそれらの効果が異なることが明らかにされて きた⁶⁾。しかし鋼中のボロンの挙動については不明な点 が多く、さらに高性能な鋼を開発するためには、ボロン の詳細な挙動を明らかにする必要がある。 一方で、ボロンのような軽元素の可視化や、定量分析 を機器分析で行うことは容易ではない。最近は EDS(Energy Dispersive X-ray Spectroscopy)検出器の高 性能化に伴い、X線吸収の少ない有機高分子膜の UTW(Ultra-Thin Window)が開発され、ボロンまでの分析 は原理的には可能であるが、濃度が 0.2mass%以下であ ると定量分析は難しい。他方、EELS(Electron Energy Loss Spectroscopy)で精度よく分析するには試料の最適膜厚 が 50nm以下と制限されるため、薄くした際にバルクとの 組成比の相関性や、バックグランドが高いために微量元 素の分析には適さないなどの問題もある³。

α線トラックエッチング(以下ATEと略称)法は中性子 照射による¹⁰B(n,α)⁷Li反応を利用することにより、 ppmオーダー以下で検出できる高感度を有している唯一 の可視化法である。このための中性子照射源を有した立 教大学原子炉は、2000年3月をもって閉鎖された。この 問題に対応できる機関として、我が国では日本原子力研 究開発機構(JAEAと略称)しかない。著者らはJAEAにおい て、これまで立教炉で行われてきたような便利さで、ATE 法が利用できるシステムを立ち上げることを目指して実 験を行い、医療用照射設備を転用することで、従来とく らべて遜色のない鋼中ボロンのATE像が得られる照射条 件を明らかにしてきた^{4,5}。

しかし近年、JAEA 炉の医療用照射設備は医療本来の需 要、ないしは動物実験のマシンタイムが増しているため、 ATE 法のマシンタイムが減少傾向にある。そこで JAEA 炉 の照射設備として比較的容易に使える JRR-4 の簡易設備 Tパイプ、Nパイプについて検討したが、秒単位で照射束 をコントロールすることができないため、気送管による 照射を試みた。著者らは過去に、気送管照射の短所とし て、①炉心まで輸送している途中に振動(衝撃)が原因 でフィルムのはく離が生じる、②照射線源に対して試料 が平行であった場合、α線の放射化確率が低下する、③ ボロン像を観察するには、非常に正確な照射時間が必要 である。④速中性子束(ファストニュートロン)やガン

JRR-3(気送管照射設備)、JRR-4(医療用照射設備)、鉄鋼材料工学、ボロン状態分布観察

マ線量が高いことなどから気送管による照射を断念して きた経緯があった⁴。

にもかかわらず医療用照射設備は、前述したようにマシンタイムの制限が生じているため、より簡便な気送管を用いた ATE 法について積極的に検討を進めた。

2. 実験方法

2.1 ATE 法によるボロン分布の観察

ATE法を用いるには、核反応により α 線をつくり出す必要がある。¹⁰B(n, α)⁷Li反応は、中性子照射によって 熱中性子と対象とする元素との間で核反応を起こさせ、 α 線の放射を生じさせる。この核反応が生じる頻度は放 射化散乱断面積によって表される。放射化断面積の大き い核種は¹⁰B(4017born)であり、⁶Li(945born)、¹⁷O(0.4born)がこれに続く。Li、0は鋼中の濃度が少ないた め、¹⁰B(n, α)⁷Li反応を生じる同位体の量も小さい。 したがって、他元素の影響を無視して、¹⁰Bのみが、(1) 式の¹⁰B(n, α)⁷Li反応によって α 線が放射されると考 えて良い。

¹⁰B+¹n → T_Li+⁴He(α)+2.4MeV · · · · · (1) 核反応中に放射される α 線の鋼中の飛程は数 μ mであ るため、ボロンの分布および形態情報は試料表面から数 μ m以内に存在したボロンといえる。

ATE像の撮影までの手順をFig.1に示す。試料を0.2~ 1mm厚に切り出し、片面のみをエメリー紙研磨にて粗研磨 を行い、その後、鏡面に仕上げる。鏡面仕上げした面に 酢酸メチル、あるいはアセトンを滴下した後、工業用硝 酸セルロースフィルム(以下フィルムと略)を試料に貼 り付けるが、フィルムと試料表面の間に気泡が入らない ようにする。中性子照射後は、試料の残留放射能が減衰 するのを待ち、試料からフィルムをはく離する。303K、 2.5mol・1⁻¹のNaOH溶液中で約1.2×10³s~2.4×10³s程度 エッチング処理を行う。その後、フィルムを水洗後乾燥 し、光学顕微鏡によってATE像を撮影する。



Fig.1 ATE 像の撮影までの手順

2.2 中性子照射装置

ATE 法のための照射条件を JAEA 炉で見出すには、はじ めに中性子フルエンスおよびカドミニウム比を選定しな ければならない。カドミニウム比は、共鳴中性子が熱中 性子中にどの程度混在するかを知る簡便な方法としてカ ドミウム被膜の有無による中性子検出器における計数の 比が用いられている。共同利用者らが使える気送管とし ては原子炉 JRR-3M(出力 20MW)と JRR-4(出力 3.5MW) がある。しかし JRR-4のカドミニウム比は 3.6 と低い。 JRR-3 の気送管には PN-1、PN-2 の照射路があり、カドミ ニウム比が 23 である。また、同じ気送管でも PN-3 は放 射化分析用照射設備として用いられている照射路である が、カドミニウム比は 290 と高い。

気送管による照射は、Fig.2 に示すキャプセル内に対 象試料(以下試料と略)を入れて窒素ガスで炉心に送り、 任意の時間照射した後、再び窒素ガスを流して試料取出 し口にキャプセルを戻す。気送管照射は短時間で照射が 終了するため、照射料金も安価ですむという利点がある 反面、窒素ガスで炉心まで送気するため、試料からフィ ルムがはく離しやすいという欠点もある。これまでの実 験の経験上から、確率的に 30%程度がはく離すると考え た方が無難である。なお JRR-3 の気送管キャプセルの内 径は PN-1 用(ϕ 23.5×72L)、PN-2 用(ϕ 28.5×82L)、 PN-3 用(ϕ 10×21L)であり、JRR-4 の気送管キャプセ ルが ϕ 20.5×67L である。なお、キャプセルの大きさに 拘わらず試料重量は 10 g以下に制限されている。



Fig.2 JRR-3 及び JRR-4 の気送管キャプセル

2.3 熱中性子照射の準備

2.3.1 化学成分と熱処理条件

用いた供試鋼の化学成分を**Table 1**に示す。熱間圧延 材を施した B10 鋼は、ボロン濃度が 19ppm の極低炭素 1.7Mn 鋼である。B140 鋼はボロン濃度が 140ppm の 0.024C-9Cr-0.14Mo-2.5W-1.9Co-0.08Nb-0.19V-Fe のフ

| Table 1. | | 供試 | 鋼の化 | t (mas | (mass%) | |
|----------|-------|-----|------|--------|---------|--------|
| | С | Cr | Мо | Co | V | В |
| B10 | 0.004 | - | - | - | - | 0.0019 |
| B140 | 0.035 | 9.0 | 0.14 | 1.8 | 0.19 | 0.0143 |

エライト系耐熱鋼である。両鋼はボロン濃度が大きく異なる。熱処理条件はB10 鋼が 1373K、3.6×10³s加熱後、空冷処理を施した。B140 鋼には 1373K、3.6×10³s焼ならし、1053K焼もどし処理を施した。

2.3.2 試料照射と照射時間

JRR-3 の気送管による中性子照射条件は、**Table 2** で 示すように熱中性子束を制御するために照射時間を調整 した。これまで立教炉で行ってきた最適と考えられる中 性子フルエンス 6.5×10^{14} n・cm⁻²を参照にした。以下、 このフルエンスを"参照フルエンス"と呼ぶ。PN-1 とPN-2 の最小照射時間は原子炉の構造上から 30sであるため、 それぞれ 14×10¹⁴n・cm⁻²と 15.6×10¹⁴n・cm⁻²であり、 参照フルエンスの 2 倍以上になっている。PN-3 の熱中性 子束は 4.4×10⁶n・cm⁻²s⁻¹であるため、中性子照射を 30s~53sの間で照射を行ったが、計算上は 43sが参照フ ルエンスにもっとも近い。

| | Irradiation | Neutron fluence | cadmium | | |
|------|-------------|--|---------|--|--|
| | time (sec) | (10 ¹⁴ n•cm ⁻²) | ratio | | |
| PN-1 | 30 | 15.60 | 23 | | |
| PN-2 | 30 | 14.00 | 23 | | |
| | 30~40 | 4.50~6.00 | 290 | | |
| PN-3 | 43 | 6.45 | 290 | | |
| | 46~53 | 6.90~7.95 | 290 | | |
| | | | | | |

Table 2. JRR-3 気送管の中性子照射条件

JRR-4 の気送管による熱中性子照射条件を**Table 3** に 示す。前述したようにカドミニウム比が 3.6 と小さい。 照射時間を 10s~28sとすると中性子フルエンスは (3.2 ~8.96) ×10¹⁴ $n \cdot cm^{-2}$ になる。参照フルエンスにもっと も近い照射時間は 20s (6.4×10¹⁴ $n \cdot cm^{-2}$) である。なお、 フィルムをはく離するまでの冷却時間 (放射能減衰) は、 JRR-3 およびJRR-4 ともに 3.6×10⁵s以上とした。

| | Table 3. | JRR-4気送管の中性子照射条件 |
|--|----------|------------------|
|--|----------|------------------|

| Irradiation time (sec) | Neutron fluence (10 ¹⁴ n∙cm⁻²) | cadmium ratio |
|---------------------------|--|---------------|
| 10~18 | 3.20~5.76 | 3.6 |
| 20 | 6.40 | 3.6 |
| 22~28 | 7.04~8.96 | 3.6 |

3. 実験結果

3.1 B10 鋼の ATE 像

PN-1 (JRR-3 気送管照射) における B10 鋼の ATE 像を Fig. 3 に示す。中性子フルエンスは参照フルエンスの 2 倍以上あったので、ATE 像は Fig. 3(a)で示すように、粒 界析出、粒内析出および粒界偏析が不鮮明であった。た だし試料とフィルムが密着していない場合は、Fig. 3(b) に示すように粒界がより不鮮明になるので、ATE 像の良 否については容易に識別できる。もちろんフィルムが試 料からはく離した場合には、ATE 像を観察することはで きない。PN-2 (JRR-3 気送管照射)における ATE 像を Fig. 3(c)に示す。PN-1 に比べて、ほぼ似たような結果を 示したが、鮮明さは PN-1 に比べて良好であった。

PN-3 (JRR-3 気送管照射) におけるATE像を**Fig.4** に 示す。30s照射における中性子フルエンスは 4.5×10¹⁴n ・cm⁻²であり、参照フルエンスに比べて約 70%低い。 Fig.4(a)に示すように粒界析出、粒内析出および粒界偏 析を確認することができたが、わずかにフェライト粒界 は太めで、析出物が大きめに観察された。33s~36sでは 粒界・粒内析出物が比較的鮮明に観察できた。



Fig. 3 JRR-3 気送管 PN-1, PN-2 における B10 鋼の ATE 像



(a) 30sec 照射 (b) 40sec 照射 (c) 43sec 照射 (d) 53sec 照射 Fig. 4 JRR-3 気送管 PN-3 における B10 鋼の ATE 像

またFig. 4(b)に示すように 40s(6.9×10^{14} n・cm⁻²) において、最も鮮明にATE像を観察することができた。また 43s以上になるとフィルム面上に、トラック以外のし み状の影響が顕著になる。

これらの結果は当たり前のように思われるかもしれな いが、これまで JAEA 炉における気送管による ATE データ は皆無であり、参照フルエンスに妥当性があったと言える。

JRR-4 の気送管照射では**Fig.5**に示すように、PN-3 の 結果 (Fig.4) に比べて、10~28sの照射時間(中性子フ ルエンス:3.2~8.96×10¹⁴ $n \cdot cm^{-2}$)の全範囲において ATE像は不鮮明であった。なかでもFig.5(d)~(e)に示し たATE像は、20~24sにおいて不鮮明さが顕著であった。 本来であれば、20s前後の照射時間は参照フルエンスにほ ぼ一致していることから、鮮明に観察されてもよいはず である。他方、Fig.5(f) に示したように 28sでは、ATE 像の鮮明さがわずかに回復している。なお、この不鮮明 に見えたATE像は剥離に起因した像形態ではなかった。こ れらのことから"気送管照射の短所"で述べたように、 照射線源に対して試料が偶然にも平行になったため、 α 線の放射化確率が低下し、像質が不鮮明になったものと 考えられる。



(a)10sec 照射 (b)14sec 照射 (c)18sec 照射 (d)20sec 照射 (e)24sec 照射 (f)28sec 照射

Fig.5 JRR-4 気送管における B10 鋼の ATE 像

3.2 B140 鋼の ATE 像

PN-1 (JRR-3 気送管照射) における B140 鋼の ATE 像を Fig. 6(a) に示す。B140 鋼の ATE 像は B10 鋼に比べて、ボ ロン濃度が 7 倍以上高いことから、また後述するカーボ ン抽出レプリカ像からも推測できるように、多くの析出 物(ほう化物)が観察できる。粒界偏析は、それほど鮮 明ではないが旧オーステナイト(γ と略称)粒界に相当 する領域に沿って ϕ 10 μ m 程度の大きさで観察できる。

これらの結果より、粒内析出と粒界偏析を確認することができた。中性子フルエンスは、前述したように2倍以上であったが ATE 像は比較的良好に観察できた。



Fig. 6 JRR-3 気送管 PN-1 および PN-2 における B140 鋼の ATE 像

PN-2 (JRR-3 気送管照射) における ATE 像を **Fig. 6(b)** に示す。鮮明さについては、B10 鋼と同じように PN-1 に 比べて良好であった。

PN-3 (JRR-3 気送管照射) におけるATE像を**Fig.7**に示 す。参照とした中性子フルエンス(6.5×10^{14} $h \cdot cm^{-2}$) に最も近い照射時間は 43s であるが、36~53s(中性子フ ルエンス: 5.25~7.95×10¹⁴ $h \cdot cm^{-2}$)の範囲においても、 粒界偏析と粒内析出物が比較的良好に観察できた。

他方、JRR-4 による気送管照射においては **Fig.8** に示 すように、B10 鋼と同じように、10~28s の照射時間の全 範囲において ATE 像は不鮮明であった。JRR-3 気送管照 射の PN-1~PN-3 で観察された粒界偏析が、JRR-4 気送管 照射では観察されなかった。



Fig.7 JRR-3 気送管 PN-3 における B140 鋼の ATE 像



(a)10sec 照射 (b)14sec 照射 (c)18sec 照射 (d)20sec 照射 (e)24sec 照射 (f)28sec 照射

Fig. 8 JRR-4 気送管における B10 鋼の ATE 像

4. 考察

ATE像の撮影までの手順はFig.1 に示したように、 2.5mol・1⁻¹のNaOH溶液中で適当な時間エッチング処理し た後に、光学顕微鏡によってATE像を撮影している。観察 倍率としては100~200倍程度が最適である。しかし光顕 の観察倍率から換算した析出物の粒子径や、実測誤差な どについての報告は皆無であり、これまでに、どのよう な像コントラストで結像されているかについての議論は 医療用照射および気送管照射に係わらず、これらを理解 していないことによって生じるいくつかの誤りについて も考察した。

4.1 気送管の照射特性

JRR-3 気送管 (PN-1~PN-3) とJRR-4 気送管を用 いてATE像を比較した。比較した気送管におけるカ ドミニウム比の違いは3.6、23 および290であった。 この結果、Fig.3~Fig.8 に示したように、カドミ ニウム比が高いPN-3 (JRR-3) の像質が最も優れて おり、カドミニウム比の低かったJRR-4 の像質は不 鮮明であった。一つのトラックは(1)式の¹⁰B (n, α)⁷Li 反応に対応しているために、熱中性子の照射条件を最適 化することによって、ppm以下という微量濃度のボロンで も検出可能である。

前述したようにカドミニウム比は、その照射孔における共鳴中性子に対する熱中性子の存在割合を示すので、 カドミニウム比が高いPN-3の照射孔は、熱中性子の相対 的割合が高いといえる。他方、ATE像のバックグランドは Liや0などの元素から生じるα線の影響のほかに、速中性 子によるフィルム中のCやHの反跳があげられる。さらに ¹⁰B(n,α)⁷Li反応は、速中性子よりもエネルギーの低 い熱中性子の照射により生じる反応であるため、カドミ ニウム比は大きい方がよいと言える。

したがってJAEA炉によるATEの像形成としては、カドミ ニウム比が高いPN-3 により最もきれいなATE像が得られ た。この理由を考えるとボロンは熱中性子に対する放射 化断面積が大きいので、ボロンと反応する熱中性子の数 が増えれば、Liに変わってα線を放出する確率があが り、フィルムに損傷を与えるためと考えられる。

さらに重要なことは、原子炉の出力(熱中性子束)は 常に変動している。JRR-3 照射設備は連続運転であるた め、熱中性子束が非常に安定しており、変動率は約1% 程度である。他方、JRR-4 は毎日6時間の定時運転であ るため出力は1回照射当たり±4%、1日の照射中にお いても±10%の出力変動が生じることが JAEA の調査で わかっている。この変動要因は原子炉の臨界を一定に保 つために、絶えず制御棒C1~C5のうちC5を小刻みに動 かしており、これが原因でフラックスが変動する。また C5の稼働範囲を越えるとC1~C4を動かすが、出力変動 はこのときに顕著になる。

このような出力変動があるため照射日によって出力変 動が生じ、熱中性子束にも変動が生じる。このため ATE 像からボロンのマトリックスへの固溶、偏析、それに析 出物の状態分布を議論する場合は同じ照射ロッドで、フ ィルムのエッチング温度、時間を同じにすることが重要 である。

4.2 SEM による ATE 像の観察

基本的には照射条件を最適に選択すれば、微量ボロン

の分布状態をフィルム上で観察できるので、黒点はすべ てボロン由来の分布および形態情報であるといえる。し かし、熱中性子照射によってフィルムにつけられた痕跡 は、このままの状態では光顕レベルの倍率では観察でき ないほど小さい。そこでNaOH エッチング液によって痕跡 を広げることにより、光顕で可視化できる。

B10 鋼を 1323K で加熱後、水冷(冷却速度:230K/s) および空冷(冷却速度:13K/s)処理を行った。PN-3(JRR-3)の参照フルエンスで中性子照射した後、所定の手 順でフィルムにつけられたα線トラック(痕跡)を、ATE 像と SEM 像によって比較した写真を Fig. 9 に示す。なお SEM 像は試料に貼り付けたフィルム面側を、カーボン蒸 着を施してから観察した。



(a), (c): 結晶粒界上への偏析(冷却速度 230K/s)
 (b), (d): 結晶粒界・結晶粒内への析出(冷却速度 13K/s)
 Fig. 9 照射後 B10 鋼の ATE 像と SEM 像

冷却速度 230K/s の ATE 像は、Fig. 9(a) に示すように旧 ッ粒界にボロンの偏析が見られる。また、同じように空 冷した場合は、Fig. 9(b) のように粒界偏析と粒内析出 物(ほう化物)が観察できる。1373K で空冷したときに 見られる粒界偏析の状態は、たとえばFig. 4 とは異なり、 未固溶のほう化物も観察できる。

Fig.9(a)に示したATE像の粒界偏析をSEM観察すると、 Fig.9(c)に示すように、フィルム表面には多くの穴が観 察できる。結晶粒内にも多くの穴が観察できるが、とく に粒界に沿った領域には微細な連続穴が空いており、結 晶粒界への偏析(表記a)と理解できる。また、Fig.9(b)



(a) 偏析 ATE 像 (b) 析出 ATE 像 Fig. 10 B10 鋼における AET 像の拡大 SEM 像

に示したATE像の粒界析出物、あるいは粒内析出物をSEM 観察するとFig.9(d)に示すように、フィルム表面には孤 立した大きな穴(表記bおよび表記c)と、連続した穴(表記d)が観察できる。表記bは粒界析出物、表記cは 粒内析出物、そして表記dは粒界偏析に相当する。 Fig.9(c)および(d)を拡大したSEM像をFig.10に示す。1 μ m程度の大きな析出物ほど、析出物中に固溶している ¹⁰Bが α 線を四方八方に放射するため、大きな穴を形成し ていることがわかる。

このように ATE 像の実体は、フィルムにつけられた α 線トラックを NaOH のエッチング液によって痕跡を広げ ることにより、光顕で可視化している。したがって ATE 像の実体は Fig.10 に示したように「穴」の状態変化か らボロン偏析や、析出状態を間接的に観察している。つ まり金属組織のように試料をエッチングして観察した 直接像ではなく、間接像にすぎない。とはいえ、ボロン の状態分布を 1ppm オーダーで捉えることができる情報 源としては、何ものにも代え難い観察手段である。



 (a), (b), (c): Steel B10 (d), (e), (f): Steel B140
 Fig. 11 B10 鋼と B140 鋼におけるカーボン抽出レプリカ 像と ATE 像の比較

4.3 ATE像による粒子径と誤差

ATE 像から得られた析出物(ほう化物)やボロンを含んだ介在物粒子の大きさ(サイズ)を知ることは、材料の特性や強化メカニズムを議論するには重要な情報となる。ATE 像からはボロンの粒界偏析やほう化物の粒界析出、および粒内偏析や粒内析出などの状態分布などを知ることができる。他方、ほう化物の大きさを正確に知るにはカーボン抽出レプリカ法や透過電顕(薄膜透過像)法がある。しかし ATE 法のようにボロンの固溶やボロンの状態分布を知ることはできない。このように実際のほう化物の粒子径と、ATE 像から求めた粒子径との誤差を求めるには、カーボン抽出レプリカ法と ATE 法による実測が不可欠になる。

B10 鋼とB140 鋼を、1373Kから空冷した後のカーボン抽 出レプリカ像を観察するとFig. 11 のようになる。また ATE像も比較のために掲載した。カーボン抽出レプリカ法 ¹⁰によって観察したB10 鋼の析出状態をFig. 11 (a) および Fig. 11 (b) に示す。B10 鋼の多くの析出物は中央部に見え るフェライト粒界には観察されず、結晶粒内に微細分布 している。しかし倍率を上げて観察すると、わずかでは あるがFig. 11 (b) に示すようにフェライト粒界にも観察 できる。析出物サイズは約25nmと小さい。B10 鋼のATE 像はFig. 11 (c) に示すように結晶粒界には、ボロンの粒界 偏析が観察され、粒内には微細な析出物が多く観察でき る。この微細析出物の大きさを単純に倍率換算すると、 約5~10 µmになる。ATE像による析出物の大きさは、カ ーボン抽出レプリカ像から得られた析出物の大きさと比 較すると、200~400 倍の大きさになっている。

また B140 鋼の析出状態は、カーボン抽出レプリカによ ると Fig. 11 (d) および Fig. 11 (e) に示すようになってい る。微細な析出物は 100nm 以下であるが、粗粒になると 約1 μ m のものが観察できる。Fig. 11 (e) には 250nm サイ ズ (中央部) と、20nm サイズ (右上)の析出物が混在し て観察できる。ATE 像は Fig. 11 (f) に示すように、多くは 微細析出物からなる。ボロンの粒界偏析が観察され、粒 内には微細な析出物が多く観察できる。B10 鋼と同じよ うに析出物の大きさを倍率換算すると 1 μ m の場合は 13 倍、250nm の場合は約 50 倍、25nm の場合は 650 倍と開き が大きくなる。Fig. 11 (f) で観察された粒内の超微細な点 状析出物(母相を黒くしている要因)を 1 μ m として換 算すると、1~65 倍に縮まる。



Fig. 12 ATE 像とカーボン抽出レプリカ像による析出 物サイズの相関性

B10 鋼と B140 鋼のカーボン抽出レプリカ像と ATE 像 の析出物サイズを比較すると、Fig. 12 のように両者は大 きく異なる。また析出物(ほう化物)の大きさや、ボロ ン濃度によっても誤差が生じる。たとえば、ボロン濃度 が高い(放射化確率が高い)B140 鋼の場合、100nm サイ ズのほう化物が、ATE 像では 5~6µm の大きさに観察で きる。しかしボロン濃度が低い B10 鋼の場合には、15µm にもなる。この理由はエッチングによって可視化する際 に、ボロン濃度が低い(放射化確率が低い)と、エッチ ング時間をより長くする傾向にあり、このため見掛けの サイズが大きくなると考えられる。このように Fig. 12 において、B10鋼とB140鋼の曲線の中点から求めた100nm のほう化物はATE 像では10µmになり、おおよそ100倍 程度のサイズ誤差が生じる。

4. 4 ATE 像のコントラスト

ATE 像を観察する際に注意することは、焦点合わせと コントラストの選択である。これまで示した ATE 像の写 真から、ボロンが結晶粒界に偏析している場合は黒い線、 析出物(ほう化物)であると黒点として観察してきた。 しかし、本当に正しい像コントラストであるかを確認す る必要がある。たとえば、B10 鋼を通常コントラスト(ブラックコントラストと略) で観察すると Fig13(a) に示 すようになる。しかし、観察場所を変えないで焦点位置 だけを変化させると、粒界偏析はFig13(b)のように白い 線(ホワイトコントラストと略)として観察できる。ど ちらのコントラストも正しいように思われるかもしれな いが、よく見るとホワイトコントラストには黒点の析出 物が観察されていない。つまり本当は存在するのに、あ たかも存在していないようなコントラストになってしま う。フィルム表面を SEM 観察した結果、多数の穴があい ていたことから、黒線あるいは黒点が ATE 像としては正 しいコントラストであることが理解できる。



 (a)ブラックコントラスト
 (b)ホワイトコントラスト
 Fig. 12 B10 (1373K) におけるATE像のコントラ スト比較

5. 結言

日本原子力研究開発機構において、ATE 法が利用でき る気送管システムを立ち上げるための実験を行った。結 果をまとめると以下のようになる。

- (1) ATE 用照射設備としては JRR-3、PN-3 気送管の像質 が優れており、JRR-4 気送管の像質は不鮮明であっ た。カドミニウム比はそれぞれ 290、3.6 であった。
- (2) カドミニウム比は、その照射孔における共鳴中性子 に対する熱中性子の存在割合を示すので、カドミニウ ム比が高い PN-3 の照射孔は、熱中性子の相対的割合が 高いといえる。
- (3) JRR-4 気送管の 20~28s 間で ATE 像が不鮮明であった原因は、照射線源に対して試料が偶然に平行になっ

たため、α線の放射化確率が低下し、像質が不鮮明に なったものと考えられる。

- (4) カーボン抽出レプリカ像とATE 像からほう化物(析出物)サイズを比較すると、両者で大きく異なる。ATE像によるほう化物の大きさは、真の大きさよりも約100倍のサイズ誤差を生じる。
- (5)ほう化物の大きさはボロン濃度によっても誤差を生じる。これはエッチングによって可視化する際、ボロン濃度が低いあるいは放射化確率が低いとエッチング時間が長くなる傾向にあり、見掛けのサイズが大きくなるためと考えられる。

(6) フィルム表面に観察できるコントラストは黒点が 析出物(ほう化物)、黒線は粒界偏析に相当する。

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研究2:高Cr 耐熱鋼の長時間強度に及ぼすBの影響

1. 緒言

石炭焚き火力発電プラントの高効率化が国内外で推進 されており、超々臨界圧(USC)の蒸気条件も 650~760 ℃の利用に向けて研究が推進されている。欧米では従来、 主として ASME P91 が使用されてきたが温度上昇、経済性 などから現在では ASME P92 が使用されるようになった。 しかし 650℃、35MPa 以上の蒸気条件を達成するには、こ れまでの高 Cr フェライト系耐熱鋼のクリープ破断強度 をしのぐNi 基超耐熱合金の開発が必要とされている。しかし、これらの発電プラントは経済性に課題があることは明らかである。

そこで現在最もすぐれていると考えられるボイラ用9 Cr耐熱鋼の化学成分、熱処理および予想される550℃~ 650℃、10⁶時間のクリープ破断強度を推定した。このボ イラ用9Cr耐熱鋼を使用すれば、主蒸気圧力35MPa/主 蒸気温度650℃/再熱蒸気温度650℃、1000MW級の火力発 電プラントの建設が可能になり、最も安価な電力を得る ことができ、しかも現用の火力プラントより大幅にC0₂を 減少させることができ、環境にすぐれたものを得ること ができると考えられる。

9~12Cr耐熱鋼においてA1、Niを低下させると650℃、 10⁵時間のクリープ破断強度を高めることが明らかになっているが、従来発表されているA1、Niの単独および複 合添加の影響を調べた。一部のフェライト系耐熱鋼については1万時間未満においてクリープ破断曲線の腰折 れ(折れ曲がり)が認められる鋼がある。他方、1万時 間付近でわずかに強度低下を示しながら再びクリープ強 度維持(逆S字クリープ現象)¹⁰を示す鋼がある。ここ では主としてB(ボロン)の挙動と、A1、Ni添加量が及ぼ すZ相析出、それに関連したLaves相の粗粒化抑制と、MX の微細化からクリープ破断強度因子を特定することを目 的とした。

2. 実験方法

2-1 試料の化学成分

高 Cr 耐熱鋼の長時間クリーブ破断強度に及ぼす供試 鋼の化学組成を表1に示す。T11鋼は0.087C-10.9Cr-2.6W -2.6Co-V-Nb(47ppmB)であり、C9 鋼は0.035C-9Cr-2.4W-1.8Co-V-Nb(70ppmB)の組成である。そのほかの主要合金 元素は0.15Mo、0.07Nb、0.20V を添加している。両鋼と も50kgを真空溶解し、Mn とSiによって脱酸した。鍛造 比は約10である。

表1 T11 鋼とC9 鋼の化学成分(mass%)

| | С | Cr | W | Со | Ni | Ν | В | A1 |
|-----|-------|-------|-----|------|-------|-------|--------|-------|
| T11 | 0.087 | 10.87 | 2.6 | 2.61 | 0.10 | 0.046 | 0.0047 | 0.006 |
| C9 | 0.035 | 9.06 | 2.4 | 2.44 | <0.01 | 0.070 | 0.0070 | 0.001 |

2-2 ミクロ組織

T11 鋼と C9 鋼のミクロ組織観察は透過電子顕微鏡(日 立製H-800:加速電圧 200kV)によって行った。析出物の 個々の組成分析は EDS(エネルギー分散型スペクトル分 光器)を用いて行った。マトリックスの影響を除去する ために各種破断材からカーボン抽出レプリカを作製し、 EDSを用いて組成分析を行った。EDS分析はトレイコア・ ノーザン社製のエネルギー分散型X線分析装置を用い、 SMTF(Standardless Metallurgical Thin File)補正プ ログラムにより定量分析を行った。分析時のビーム径は 15~25nm であった。透過電子顕微鏡は日本電子製の JEM-4010 (加速電圧 400kV)を用いて、倍率 20,000~ 100,000 倍で撮影した。

2-3 ATE 法によるボロン状態分布観察

Bの挙動は α 線トラックエッチング (ATE) 法を用いて、 析出形態および分布を調べた。ATE法は熱中性子とボロン との間で核反応を起こさせ、 α 線によって試料の表面に 貼った硝酸セルロースフィルムの表面に痕跡を生じさせ る。 $^{10}B+^{1}n\rightarrow^{7}Li+^{4}He(\alpha)$ の反応によって、Bの分布状 態を観察することができる。この方法はBの観察にもっと も有力な手法のひとつであり、検出感度もB含有量が 1ppm以下の試料でも観察が可能であるなど優れた長所を 有している²⁾。つまりBの存在位置 (たとえば粒界、粒内) や形態 (たとえば偏析、析出)状態を比較的容易に観察 することができる。

ATE 用の試料はクリーブ破断した試験片を輪切りにして観察した。中性子照射は日本原子力研究開発機構の原子炉 JRR-4 (3.5MW)を用いた。

3.研究結果と考察

3-1 クリープ破断曲線の腰折れ挙動

T11 鋼のクリープ破断曲線は図1に示すように、1000h を超えるあたりから腰折れが認められ、100N/mm²におい て破断寿命は4000h程度であった。T11 鋼は、後述する逆 S字クリープ現象が見られたC9 鋼に比較してCr、C量が 高く、NiおよびA1量が高い。



図1 T11 (11Cr-W-Co) 鋼のクリープ破断強度

3-2 逆S字クリープ破断曲線

他方、C9 鋼は図2に示すように1万時間付近でわずか に強度低下を示しながら逆S字クリープ破断現象を示し た。100N/mm²における破断寿命は30,000h以上ある。 朝倉ら³¹ はNi添加量が高いとフレッシュマルテンサイト を生成し、このため焼もどし時における硬さを上昇させ、 短時間側のクリープ破断強度を高めるが、長時間側強度 を低下させることを指摘している。一方、T11 鋼および (9 鋼の初期組織に大きな違いが認められることから、変 態温度の違いが転位密度、マルテンサイトラス幅、析出 挙動など下部組織に与える影響も考えられる。



3-3 クリープ破断曲線のミクロ組織

マトリックスの組織変化については薄膜法、M₂₃C₆、 Laves相、Z相およびMXなどの析出に関しては薄膜法とカ ーボン抽出レプリカ法、そしてATE法を併用して観察する が、ここでは主として薄膜法について簡単に触れ、ATE 法について詳述した。

T11 鋼のミクロ組織

写真1にクリーブ破断強度の腰折れが認められた T11 鋼のTEM 組織を示す。写真1(a)~(f)は撮影倍率5,000 倍の比較的低倍で観察したミクロ組織である。0.6h~17h 破断材において旧オーステナイト(γ)粒界およびマル テンサイトラスの境界には多くの析出物が密集して観察 される。短時間側で破断した試験片であるにもかかわら ずラス内部の転位密度が低い。クリーブ破断強度の著し い低下が認められた1,632h 破断材では、写真1(c)に示 したようにラスの形態が崩れ、ラスの幅にも広がりが見 られる。約3,000h になるとラスの形態は残っているがラ ス幅は広がり、析出物も写真1(d)に示したように粗大化



(a) 0.6h
(b) 16.9h
(c) 1632h
(d) 3030h
(e) 4898h
(f) 7158h
写真1
T11 鋼における 650℃破断材の TEM 組織

している。5,000h以上の破断材では、写真1(e)および写 真1(f)に示したように回復が著しく進んだ亜結晶粒(サ ブグレイン)が観察され、析出物も大きなものでは約1 μ mにもなる。

T11 鋼における 650°C-7,158h破断材平行部の抽出カー ボンレプリカ像からMX型 (NbC)の析出物を同定した。こ こで観察されたMX (NbC)のサイズは 50~70nmであった。 このほかにM₂₃C₆、Laves相およびZ相が同定された。

(2) C9 鋼のミクロ組織

C9 鋼の特徴は写真2に示すように、マルテンサイトラスの形態が破断時間11,000h付近でも鮮明に見られる。 ラス内部の転位密度も2,000h程度ではasNT(焼ならし/焼もどし)まま材に比べ、遜色のない転位密度であった。



(a) as NT
(b) 4.7h
(c) 75.2h
(d) 484.5h
(e) 1,604h
(f) 2,168h
(g) 8,715h
(h) 11,424h
写真 2
C9 鋼における 650℃破断材平行部の TEM 組織

8,700h 破断材では、写真2(g)で示すようにラスの形態 は残っているが、転位密度の低い領域も認められた。こ のまま下部組織の回復が進行すれば腰折れの原因になる と思うが、11,000h 破断材では写真2(h) に示すように、 1 μ m程度の亜結晶粒が多数観察され、微細な析出物に ピンニングされた転位が多数観察される。

つまり1万時間加熱でも高い転位密度が観察される。 この領域を高倍率(撮影倍率50,000)に拡大すると写真



写真 3 C9 鋼における 650℃-11,424h 破断材平行部の TEM 組織

3に示すように約200nm、また10~12nm程度の微細析出 物にピンニングされた転位が多数観察される。このよう に下部組織の回復が著しく抑制された下部組織が母相と なり、逆S字クリープ現象を示したものと考えられる。

11,000h付近になると微細析出物の密度が高くなるの に加えて、再び転位密度の上昇が認められる。また、短 時間側で認められなかったFe₂W型金属間化合物Laves相 が観察される。T11 鋼では比較的短時間で析出したのに 比して、C9 鋼では遅れて析出する傾向が認められた。さ らに析出物サイズもここで示したように大きなものでも 300nm程度で、Laves相(Fe₂W)の粗大化が抑制されてい ることが確認された。

3-4 ATE 法による B の挙動

Bの挙動を調べるために主としてATE法によって調べた。ATE法で析出物を観察すると黒いコントラストがついて見える。前述したように、この方法は熱中性子により核反応¹⁰B(n、 α)⁷Li反応をつくり、 α 線を放射させる。この反応が生じる頻度は放射化散乱断面積によって表される。放射化散乱断面積の大きい元素がB(4017barn)であり、Li(945barn)、0(0.4barn)と続く。Li、0は鋼中の含有量が少ないため、B(正確には¹⁰B)だけが¹⁰B(n、 α)⁷Li反応を生じて、 α 線を放射する。したがって、このコントラストはBのみによって形成されたコントラストと考えてよい。

(1) T11 鋼の ATE 像

B添加によって $M_{23}C_6$ やLaves相の粗大化が抑制され、MX が微細化されることは、すでに多くの研究報告がある^{たと} ^{えば4)}。他方で、Bは旧γ粒界上や旧γ粒界近傍の $M_{23}C_6$ 中に 濃化されており、Bの大半が $M_{23}C_6$ 中に含まれると報告され ている⁵⁾。そこでT11 鋼、650°C破断材のB分布状態をATE 法によって調べた。この結果を写真4に示す。



(a) 0. 6h (b) 16. 9h (c) 1, 632h (d) 3, 030h (e) 4, 898h (f) 7, 168h

写真4 T11 鋼における 650℃破断材平行部の ATE 像

塊状の析出物は、0.6h~7,168h破断材のすべてで観察で きる。低倍率では微細析出物の存在はわからないので、 倍率をあげて観察すると写真5になる。写真5は4,898h 破断材であるが、ここでは3種類の形態が観察できる。 棒状、塊状(球状)、点状(黒点)である。

棒状に見えるほう化物は薄膜、カーボン抽出レプリカ 観察から類推すると、MaC₆、Laves相およびZ相の析出



写真5 T11 鋼における 650°C-4, 898h 破断材の ATE 像

物群が旧 γ 粒界を被うように連続析出したことで、棒状の形態様を示したことも考えられるが、カーボン抽出レ プリカによって観察をおこなった結果、写真5の左下に 示すような棒状形態の析出物が観察できた。サイズは直 径 1~1.5 μ m、長さ10 μ mであった。構造については電 子線回折とEDS分析で調べた結果、Fe₃(SiB)あるいはSiB₆ に相当する介在物であった。

塊状および球状の析出物はM2C6、点状(黒点)はMXに 相当する。よってBはM22(CB)。のみに濃化されるのでは なく、すべての析出物に濃化することを示唆している。 またBの析出物(ほう化物)中への固溶、あるいはマトリ ックス中への固溶については、マトリックスのコントラ ストからBはマトリックスにも固溶している。さらに析出 物をよく観察するとBは析出物とマトリックスの界面に 濃化(析出物が黒くフチ取りされている。これがBの偏析 である)していることがわかった。仮にBが析出物中にす べて固溶していれば、黒い棒状あるいは黒点になるので、 この差は歴然である。したがってT11鍋のBはマトリック スにわずか固溶しており、析出物(M2C6、Laves相、Z相) とマトリックス・析出物界面に濃化し、微細析出したMX にも濃化していると考えられる。

なお著者らは 0.05C-3Mn-B鋼を用いて、オーステナイ ト粒界に析出したほう化物(200~250nm)と粒内に微細析 出(100nm)したほう化物について、得られたATE像とカー ボン抽出レプリカ像から大きさの比較を行った⁶⁾。この 結果、1個のほう化物(黒点1個)が5~10 μ mに観察さ れることから、ATE像は10~100倍に拡大されて観察され ることになる。このように処理条件によって1 μ mのほう 化物は、10~100 μ m(0.1mm)の大きさに観察されるので、 単純には析出物(ほう化物)の大きさを議論することは できないことを指摘している。つまり、直径1 μ mのほう 化物においては間隔がおよそ 100 μ mより広く離れてい ないとATE像では2つの析出物としては観察できないこ ともある。

(2) C9 鋼の ATE 像

ATE 法によって C9 鋼の As NT および 650℃-5h~

11,424h 破断材の B 分布状態を調べた。結果の一例を写 真 6 に示す。球状の析出物は As NT~11,424h 破断材の すべてに観察できる。○で囲んだ領域は他の領域に比べ て明らかに析出物の再固溶が認められる。低倍率では微 細析出物の存在はわからないので、倍率をあげて観察し た例を写真7 に示す。ここではT11 鋼に見られたような 棒状や球状のほう化物はみられず、点状(黒点)に微細 析出していることがわかる。つまり B はほとんどの析出 物中に固溶した状態で存在すると考えられる。



(a) 1,604h
 (b) 2,168h
 (c) 8,715h
 (d) 11,424h
 写真6
 C9 鋼における 650℃破断材平行部の ATE 像



写真7 C9 鋼における 650℃-11, 424h 破断材の ATE 像

さらによく観察すると、どの破断材においても旧ッ粒 界に相当する領域にBの偏析(矢印)が観察できる。こ れはBが旧ッ粒界に偏析することにより、結晶粒界エネ ルギーを下げて、粒界析出を抑制(析出物の微細化)す る効果を促進し、あるいはBの拡散速度は比較的速いた めに、結晶粒の成長速度を下げていること(他の溶質原 子とのサイトコンペティション)の傍証とも考えられ る。またBのマトリックス中への固溶については、マト リックスのコントラストから旧ッ粒界だけではなく、マ トリックス中にも固溶していると推定できる。 3-2-5 逆S字クリープ現象とミクロ組織

(9 鋼において、逆S字クリープ破断現象が認められ た。そこで本項では、逆S字クリープ破断現象について ミクロ組織の視点から考察する。(9 鋼のクリープ変形に ともなう組織変化としてはクリープ強度の低下が認めら れた8,715h 付近において転位密度の減少、局所領域での 亜結晶粒の成長と不均一な回復が認められた。しかし、 11,000h 付近において再びミクロ組織にも変化が見られ る。つまり微細析出物の増加と転位密度の上昇が生じた。 このことが (9 鋼の逆S字クリープ現象を生じさせた要 因と考えられる。

C9 鋼のクリープ強度因子をまとめると、①析出物の粗 大化は 75.2h と 8,715h で認められ、それ以降の 485h と 11,424h において析出物の細粒化が認められた。②すべ ての析出物中に濃縮するボロンが認められ、これが析出 物の凝集粗大化を抑制。③旧 y 粒界、フェライト粒界お よびフェライト粒内にも、B の固溶(偏析)が認められ る。④析出強化が重要と考えられているが、C9 鋼では固 溶強化も十分に寄与していると考えられる。

4. 結 言

9~12Cr 耐熱鋼の長時間クリープ破断強度に及ぼす A1、Ni、Pなどの影響について調べた。またA1、Niを低 減した9Cr 耐熱鋼の長時間クリープ破断強度の強化機構 を検討し、以下の結果を得た。

- A1、Niを低減すれば析出物の成長、粗大化を抑制 でき、クリープ強度が維持できる。このことによりCr、 Mo、W、V、Nb およびBなどマトリックス中の固溶量が 増し、マトリックスが強化される。
- (2) 析出物中への A1、Ni 濃化は当然、その制御量によって異なる。T11 鋼(11Cr)では、ほとんどの析出物中に A1、Ni の濃化が認められたが、一部の Z 相で Niの無濃化が認められた。C9 鋼(9Cr)では A1 濃化が少ないのは Laves 相、MX であり、一部の MX(VNbCN)にNiの無濃化が認められた。
- (4) A1、Ni量が比較的高い高Cr耐熱鋼を650℃、数1000
 ~1万時間程度加熱すると、析出物M₂₃(CB)₆、
 Laves相Fe(Mo, W)₂B、Z相などの周囲にA1、Niが拡散して、析出物の成長、粗大化を促進させるため、クリープ強度を低下させるものと考える。
- (5) 固溶度の比較的小さいNb、Vが10~50nm 程度のMX
 型炭窒化物として析出し、クリープ強化する。
- (6) ボロンは主として析出物中、あるいは析出物とマト リックスの界面に偏析して、析出物の凝集粗大化を抑 制(微細化)することによって、析出強化する。

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研究3: 銅すず含有鋼の熱間加工における表面割れ抑制 へのボロン添加効果

1. 緒言

我が国では鉄スクラップ量は年々増加している¹⁾。こ のため廃棄物量の縮小とCO₂ガスの排出抑制という環境 問題の観点から、スクラップをなお一層再利用すること が日本における鉄鋼生産プロセスの中で重要になってい る。鉄スクラップ中にはCuやSnなどのトランプエレメン トが含まれ、その濃度は年々増加している。

しかし、鉄スクラップ中に含まれる銅が熱間圧延時に 表面割れを引き起こすため、鉄スクラップの利用促進に は大きな障害となっている。銅を含有する鋼スラブを熱 間加工するときに酸化雰囲気中で高温加熱され、鉄の選 択酸化により鋼と酸化層界面に銅濃化相が生成する。 1083℃以上になると銅は液相になり、熱間圧延での変形 中にオーステナイト(γ)結晶粒界に浸入し、表面割れを 発生させる。この現象は銅起因表面赤熱脆性と呼ばれて いる²⁾。また、Snは表面赤熱脆性を助長させることが報 告されている³⁾。

これまで鉄スクラップ中から銅を分離する研究や製鋼 プロセスで溶鋼中から銅を除去する研究が試みられてき たが、現在の技術では銅を鉄鋼中から安価に取り除くこ とは非常に困難である。そこで銅を含む鋼の熱間加工に おいて、材料学的方法により銅起因赤熱脆性の抑制法を 探ることは重要で、かつ有益な課題である⁴⁾。

本研究では、大気中およびLNG 燃焼ガス雰囲気において、CuとSnを含有する炭素鋼の銅起因表面赤熱脆性に及ぼすボロン(B)添加の影響について調べた。

2. 実験方法

2.1 供試鋼

供試鋼の組成を Table 1 に示す。Cu を 0.3%、Sn を 0.04%含有 する 0.05%炭素鋼であり、B 量を 50ppm まで変化させた。約 20 kg を真空溶解した後、熱間圧延した厚さ 16mm の板材を供試材とし た。

Table 1 供試鋼の化学成分 (mass%).

| | С | Mn | Cu | Sn | В |
|----|------|------|------|-------|--------|
| B1 | 0.05 | 0.28 | 0.31 | 0.044 | 0.0002 |
| B2 | 0.05 | 0.30 | 0.31 | 0.037 | 0.0011 |
| B3 | 0.05 | 0.28 | 0.31 | 0.044 | 0.0030 |
| B4 | 0.05 | 0.29 | 0.31 | 0.042 | 0.0051 |

2・2 高温引張試験

各鋼の熱間圧延材より、その圧延方向と軸方向が一致 するように平行部長さ30mm、直径6mmの丸棒引張試験 片に加工した。

高温引張試験はArガス、大気中およびLNG燃焼ガス雰囲 気で行った。LNG燃焼ガスに相当する混合ガスの組成は 74‰2-16‰L20-8‰C02-2‰2とした。ガス流量は2 1/ minである。室温から0.33K/sで昇温し、1100℃で1.8 ks 保持後、ひずみ速度1.0×10⁻² s⁻¹で引張変形させた。 高温引張試験の荷重-のび曲線における最大荷重から、 以下の式を用いて脆化感受性パラメータを算出した⁵⁾。

$$Ep=(P_{Ar} -P) / P_{Ar} \cdots (1)$$

 $Ep' = (P_{Ar} - P') / P_{Ar} \cdots (2)$

ここで、P_{Ar}はArガス中での最大荷重、Pは酸化雰囲気中 での最大荷重、P'は酸化による試験片の有効断面積の減 少分を補正したときの最大荷重である。

2・3 光学顕微鏡による組織観察

鋼と酸化層界面に生成する銅濃縮相の量や存在サイト を観察するために光学顕微鏡による組織観察を行った。 熱間圧延材から10 mm×10 mmの立方型試験片を 切り出し、エメリー紙で#1200まで表面を研磨した。

加熱試験は、大気およびLNG 燃焼ガス雰囲気において、 室温から0.33 K/s で昇温し、1100℃で1.8 ks もしくは 5.4 ks 保持した後、炉冷した。酸化させた試料を樹脂に 埋め込み、切断面を観察した。腐食液として4%ナイター ルを用いた。

2・4 ATE 法によるボロン分布の観察

ボロンの分布はα線トラックエッチング法(以下、ATE と略す)により調べた。試料の形状および採取方法は光 学顕微鏡観察と同一である。加熱は、大気およびLNG燃 焼ガス雰囲気において、室温から0.33 K/sで昇温し、1100 ℃で1.8 ks 保持した後、水冷した。試料中央部を1 mm に切断し、切断面をバフ研磨した後、硝酸セルロースフ イルムを貼り付けた。

硝酸セルロースフィルムを貼り付けた試料に中性子照 射を行った。ボロンに中性子を照射すると、 $^{10}B+^{1}n \rightarrow$ $^{7}Li+^{4}He(\alpha)$ の反応により α 線を放射し、セルロース フィルムに痕跡を残す。このセルロースフィルムのみを 回収し、2.5 mol・ 1^{-1} のNaOH溶液中でエッチング処理し た後、フィルム表面を光学顕微鏡により観察した。

2・5 銅インプラント高温引張試験

銅液相の γ 結晶粒界への浸入性を評価するために、Cu 合金インプラント高温引張試験を行った。鋼の熱間圧延 材より、圧延方向と軸方向が一致するように、平行部長 さ 20 mm、その外径 10 mm、内径 4 mmの中空型丸棒引張 試験片を作製した。この中空型試験片の中に径 3.9 mmの Cu-9.3%Sn合金の棒を挿入した。Cu合金は、無酸素銅(純度 99.99%)、高純度すず(純度 99.9%)を用い、真 空溶解炉で溶製した。溶製した試料を熱間鍛造や熱間圧 延により板材にした後、スウェージング加工により丸棒 にした。試験は、Arガス雰囲気において、室温から 0.33 K/sで昇温し、1100℃で 1.8 ks保持後、ひずみ速度 1.0 ×10⁻² s⁻¹で引張変形させた。

3. 実験結果および考察

3·1 表面赤熱脆性

鋼の脆化感受性パラメータに及ぼすB添加の影響を Fig.1に示す。大気中、LNG燃焼ガス雰囲気とも、B量が 増加するにつれて脆化感受性パラメータの値が小さくな っている。LNG燃焼ガス雰囲気では、Bを11ppm添加し たときにEpの値を約10%低下させ、表面赤熱脆性を抑制 するのに有効である。大気中では、B添加量11ppmでは 脆性抑制効果が小さく、50ppmまで添加すると脆性抑制 に有効である。LNG燃焼ガス雰囲気のほうが大気中より 脆化感受性パラメータの値がやや大きくなっている。



Fig.1 脆化感受性パラメータに及ぼすBの影響

3・2 鋼と酸化層の界面付近の組織

LNG 燃焼ガス雰囲気において、1100℃、1.8 ks 保持し たときの鋼と酸化層界面付近の組織を Fig.2 に示す。い ずれの鋼でも鋼と酸化層界面に銅濃縮相がフィルム状に 生成している。B 量が増加しても銅濃縮相の量や形態に 変化は見られなかった。



 (a) B1, (b) B2, (c) B3, (d) B4
 Fig. 2 LNG 燃焼ガス中における鉄/スケール界面の 銅濃縮相

3・3 ボロンの分布挙動

大気中で 1100℃、1.8 ks 加熱後水冷した試料の ATE 像を Fig.3 に示す。B 量が少ない鋼 B1 と鋼 B2 の表面部 にはB の粒界偏析が見られない。一方、B 量が 30ppm 以 上の鋼 B3 と鋼 B4 では表面部に粒界偏析が確認される。

LNG 燃焼ガス雰囲気で 1100℃、1.8 ks 加熱後水冷した 試料の ATE 像を Fig. 4 に示す。B 量が 30ppm 以上の鋼 B3 と鋼B4 では大気中と同様にLNG燃焼ガス雰囲気でも表面 部の粒界にB が偏析している。また B を 11ppm 添加した 鋼 B2 でも表面部にわずかに粒界偏析が見られる。

一方、試料内部では大気中とLNG 燃焼ガス雰囲気による違いは全く見られなかった。B量が増えるとともに粒界偏析量が増加している。また、B量が30ppm以上で粒内析出が顕著になり、B量が50ppmで粒界析出も現れるようになる。



(a) B1, (b) B2, (c) B3, (d) B4 Fig. 3 1100 ℃-1.8 ks(大気中)処理における ATE 像



 (a) B1, (b) B2, (c) B3, (d) B4
 Fig. 4 1100 ℃-1.8 ks (LNG ガス燃焼ガス雰囲気) 処理 における ATE 像

3・4 銅濃縮相の粒界浸入性

各鋼に Cu-9.3%Sn 合金を挿入し、インプラント高温引張 試験をしたときの応力--ひずみ曲線を Fig.5 に示す。ひ ずみを付加すると応力が徐々に増加し、ある臨界点に 達すると応力が急激に低下する。この臨界点で銅液相が 鉄粒界へ急速に侵入したと考えられる。このときの臨界 応力を破断応力とし、臨界ひずみを破断ひずみとする。B を 11ppm 添加した鋼 B2 では、Bが 2ppm の鋼 B1 と破断ひ ずみはほぼ同じである。また、B が 30ppm の鋼 B3 は鋼 B1 や鋼 B2 と破断応力はあまり変わらないものの、破断ひず みは増加している。さらに B 量が 51ppm に増加した鋼 B4 は、破断応力、破断ひずみとも増加している。B 添加量 が増えると、銅液相のγ粒界への侵入性が抑制されるこ とがわかる。



Fig.5 各鋼に Cu-9.3%Sn 合金をインプラントした試験 片の高温引張試験における応力--ひずみ曲線

3・5 表面赤熱脆性に及ぼすボロンの影響

以上の結果より、鋼表面部におけるBの粒界偏析と表 面赤熱脆性の低下が非常に良く対応していることが明ら かとなった。銅すず含有鋼の表面赤熱脆性はBを添加す ると低下し、大気中では一定量以上のBを添加すると表 面赤熱脆性は完全に抑制された。鋼へのB添加により表 面赤熱脆性を低下させているときには、鋼表面部の粒界 にBが偏析していることがATEにより確認された。また、 鋼へのB添加は、Cu-Sn合金を挿入したインプラント引 張試験での破断応力や破断ひずみが上昇させ、粒界浸入 性を抑制させている。

したがって、B添加による脆性抑制効果は、鋼表面部に おいてBが粒界偏析することによりγ粒界エネルギーを 低下させ、銅濃縮相の粒界浸入性を低下させることによ るものと考えられる。このようなB添加による効果はSn 無添加銅含有鋼でも認められていたが⁶⁾、同様に粒界浸 入性の抑制に起因するものであると推察できる。

4. 結言

本研究では、0.3%Cuと0.04%Snを添加した炭素鋼を 用いて、大気中とLNG燃焼ガス雰囲気における1100℃で の銅起因表面赤熱脆性を調べ、赤熱脆性に及ぼす微量 B 添加の影響を調べた。

- (1) 大気中、LNG 燃焼ガス雰囲気とも、B が増加するとともに鋼の表面赤熱脆性は低下していく。大気中では50ppmの添加で表面割れが抑制できる。一方、LNG 燃焼ガス雰囲気では、11ppmのB 添加が有効である。
- (2) Bを添加した鋼では表面部においてもBが粒界に偏 析している。Bは粒界偏析により粒界エネルギーを低 下させ、y粒界への浸入性を抑制するためであると推 察される。

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Ⅳ. 今後の方針

原子力機構炉(医療用および気送管設備)を用いて ATE 法の手法をほぼ確立した。そこで今後については以 下の研究について遂行する。

- (1) 積層鉄鋼材料を用いて、硬質/軟質界面における B の状態分布挙動の調査を行う。
- (2) 溶接構造用鋼の基本成分に C, Nb, B を変化させ、 真空溶解にて試験片を作製する。その後、溶接熱影響 部相当の熱サイクルを付与し acicular フェライトを含 む溶接部組織を再現し、組織観察を行うとともに、ボ ロンの存在位置の調査研究を行う。
- (3) Cu および Cu 合金(Cu-Ni-Si-0.02B)を用いての研究も併せて遂行する。高周波加熱溶解炉で純銅中に B 量を 25ppm、50ppm、100ppm 添加し、種々の熱処 理における B 分布について調査研究を行う。

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ホウ素ナノカプセルを用いた中性子捕捉治療 Development of boron nano capsules for BNCT

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現在まで長期にわたりX線によるがん治療が行われ ているが、X線療法とホウ素中性子捕捉療法の治療効 果を比較すると後者の治療方法の方が治療効果が高い と言うデータも示されている。

ホウ素中性子捕捉療法とはホウ素化合物を予めがん 細胞に集積させ、そこに熱中性子を照射してホウ素(B ¹⁰)と中性子の核反応により局所的にがん細胞だけを死 滅させる治療法である。熱中性子による正常細胞への 影響が少ないこと、核反応から生じるエネルギーが細 胞1つ分だけを破壊することから、極めて副作用の少 ないがん治療法である。したがって高い治療効果を得 るためにはホウ素の癌細胞選択性、蓄積性が求められ ており、がん細胞へ40ppn以上のホウ素濃度、さらに 腫瘍/正常組織のホウ素濃度の比が5以上を蓄積させ る必要がある。この数値を達成することが可能となれ ば現在開発中である病院施設内に設置可能な小型加速 器(中性子源)を用いて、ホウ素中性子捕捉治療が身近 な治療法となり、この治療で治るがん患者が増えるで あろう。

本研究では、目的数値を達成するためにドラッグデリ バリーシステムに用いられているリポソームに注目し た。リポソームとは脂質二分子膜からなるナノキャリ アーであり内部に薬剤などを封入し、患部に送達させ ることで知られている。リポソーム内部にホウ素化合 物を封入することは報告されているが目標数値は達成 出来ていない。脂質二分子膜は分子間相互作用により 自己集合化しているため密度が高い。そこで本研究で はリポソームを構成する脂質二分子膜にホウ素導入を 指向したホウ素イオンクラスター脂質の開発を行った。 この脂質を用いることでキャリアー自身をホウ素薬剤 とし、さらに内部にホウ素化合物を封入出来ることか ら、高濃度でホウ素をデリバリーできる。また、この ホウ素リポソームの内部にホウ素化合物ではなく抗が ん剤を封入し、中性子照射を行うことにより抗がん剤 のリリースを狙い、中性子捕捉療法と化学療法を同時 に行うコンビネーションセラピーの検討を行う。 我々は脂質の親水性部位に親水性ホウ素イオンクラ

スターを導入したホウ素イオンクラスター脂質(6)の

JRR-4、中性子ビーム設備

合成に成功した。



図1 ホウ素リポソーム

した。(図 1)

さらにこのホウ素脂質とコ レステロール、DSPC、PEGを 用いて逆相蒸発法によりト ランスフェリン修飾型ホウ 素リポソームの調整に成功

調整したトランスフェリン修飾ホウ素リポソームを 用いてマウス内での各臓器におけるホウ素分布を測定 した。ヨウ素 125 ラベルしたイヌリンを含むホウ素リ ポソームを左足にColon26細胞を移植したBalb/cマウ ス(6週齢、18~20g)に静脈注射した後、1~72時間に おいてマウスの血液、肺、肝臓、腎臓、脾臓、腫瘍を 各々取り出し、各組織の放射活性を測定した。(図2) 血液中の濃度変化は、ホウ素リポソームおよびトラン スフェリン修飾型ホウ素リポソームとも速やかに低下 した。一方、肝臓、腎臓、脾臓ではトランスフェリン 修飾型ホウ素リポソームの方が高濃度で蓄積している ことが分かった。腫瘍では非修飾型ホウ素リポソーム は時間に伴い濃度が減少しているのに対し、トランス フェリン修飾型ホウ素リポソームでは時間経過と関係 なく蓄積しており、72時間後でも非修飾型ホウ素リポ ソームと比較し約3倍の濃度であることが分かった。 左足にColon26 細胞を移植したBalb/cマウス(6 週歳、 18~20g)にトランスフェリン修飾型ホウ素リポソー

ム (7. 2mg/kg¹⁰B, 14. 4mg/kg¹⁰B) をそれぞれ静脈注射し、 72 時間後に 37 分間中性子照射を行い、照射後の生存 曲線を調べた。



図 2 ホウ素リポソームとトランスフェリン修飾型ホウ素 リポソームのマウス体内分布

ホウ素リポソームを投与していないマウス(コントロ ール)では中性子照射後の平均寿命が22日であったの に対し、トランスフェリン修飾型ホウ素リポソーム (7.2mg/kg¹⁰B)投与したマウスでは、平均寿命が32日 と約1.5倍の延命効果が得られた。しかし投与量を 14.4mg/kg¹⁰Bにしたところ急性毒性が見られた。この ことから毒性を改善した新しいホウ素脂質を分子設計 し、合成することを試みた。

我々は中性子捕捉療法において臨床応用されている BSH(ホウ素イオンクラスター化合物)を親水性部位に 導入した新しい低毒性ホウ素脂質(12)の合成に成功し

た。(Scheme 1)



Scheme 1 BSH を導入した脂質の合成

また、合成した第二世代ホウ素脂質、コレステロール、 DSPC、PEG を用いてホウ素リポソームの調整に成功し た。調整したホウ素リポソームの中性子捕捉療法効果 を細胞レベルにおいて no wash, wash の二つの条件で検 討した。no wash での方法は Colon26 を 20 時間培養し、 ホウ素リポソーム存在下さらに 30 分間培養する。その 後、中性子照射を 30 分行った後 3 日後の MTT assay に より細胞増殖阻害活性を調べた。Wash 条件ではホウ素 リポソーム処理 30 分後に培地を交換し、その後中性子 照射を行った。図 4 には、ハイスループットスクリー ニングのための新しい細胞への中性子照射システムを 示した。この、システムは現在ある「弥七」システム と異なり、一度に 480 サンプルを照射できるため、薬 剤開発の効率化が可能となる。



図4 細胞用照射器具(Cyborg 480)



図5 細胞レベルにおける第二世代ホウ素リポソームの中 性子捕捉療法効果

その結果、no wash の条件ではホウ素リポソームは濃 度依存的な細胞増殖阻害活性が見られた。BSH と比較 しても同程度、もしくはそれ以上の効果を示している。 一方 wash 条件では、BSH は活性が見られないのに対し、 ホウ素リポソームは no wash の条件と活性がほとんど 変わらないことが言える。このことよりホウ素リポソ ームは BSH よりも細胞に多く蓄積していることが示さ れた。今後はこの第二世代ホウ素リポソームにトラン スフェリンを修飾し、マウスに投与した後中性子照射 を行い、腫瘍の完全消失を目指す。
αトラック法による硼素薬剤の細胞内局在計測法の開発

Development of boron drug localization measurement method inside biological cells by neutron-induced alpha track mapping technique

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1. 研究目的

硼素中性子捕捉療法¹⁾ (Boron Neutron Capture Therapy: BNCT)は、硼素を含む化合物に腫瘍集積 性を持たせ、外部から照射される少量の熱中性子と の核反応で生ずる α線・Li反跳核を用いて腫瘍細胞 にダメージを与える新しいタイプの放射線がん治療 法である。BNCTの特徴は生成したα線・Li反跳核の 飛程が細胞1個分程度(~10µm)であり、放射線エ ネルギーの全てを細胞1個の範囲内に落とすため殺 細胞性が極めて高いことである。また硼素薬剤が腫 瘍細胞のみに集積していれば、隣接する正常細胞を 傷つけることなく腫瘍のみを選択的に撃退できるた め、浸潤の激しい腫瘍(悪性脳腫瘍・悪性黒色腫等) を患部の機能を温存したまま根治できる画期的な治 療法である。現在、BSH及びBPAと呼ばれる腫瘍集積 性硼素化合物が見出されており、さらに十分に集積 比・取込量を上げるべく硼素薬剤の化学修飾や新規 硼素薬剤の開発が盛んに行われているが、その取り 込み機構は必ずしも解明されておらず、またそれを 調べるための細胞内微小器官のレベルでの硼素薬剤 の分布測定法自体も開発途上の段階にある。

そこで本研究では硼素分布測定法のひとつである 中性子誘起 α オートラジオグラフィ法²⁻⁵⁾を高度化 し、詳細な細胞構造イメージ中に硼素分布をマッピ ングする手法を開発・要素技術を確立して各種硼素 薬剤によるBNCTの治療効果の評価や硼素薬剤の輸送 メカニズムの解明に資するデータを取得することを 目的とする。具体的にはFig.1 に示すように、硼素 ー中性子反応により発生した α・Liトラックととも に、紫外線暴露により細胞の"影絵"をプラスチッ クポリマー上に記録、同時観察する手法を開発する ことであるが、これを高分解能化し細胞内微小器官 のスケールで観察できるようにすること、また処理 JRR-3M7R 中性子ジオグラフィー装置、医工連携 JRR-4 中性子ビーム設備、医工連携 時に硼素薬剤の分布が変化しないような試料調整法 を確立・データの信頼性を保証することが肝心とな る。

細胞内の放射線感受性は細胞核(感受性高)と核 外(感受性低)とで大きく異なる⁶上、荷電粒子タイ プの放射線はその飛跡に沿って極めて狭い範囲に高 密度な損傷をもたらす性質があるため、細胞内での α・Li粒子の発生分布を知ることは、BNCTの治療効 果を判定する上で薬剤の腫瘍選択性にも増して重要 な情報である。本研究が開発を目指す手法を用いる ことで、BNCTで急務とされる新規硼素薬剤開発のた めの硼素薬剤の詳細な局在情報が得られるものと考 えられる。

細胞内硼素分布測定法としては現在、αオートラ ジオグラフィ法のほか、硼素化合物の抗体を用いた 免疫染色法^{7,8)}および二次イオン質量分析法⁹⁾ (SIMS) や電子線エネルギー損失スペクトル法¹⁰⁾ (EELS) に よる元素分布マッピングが主流である。しかし現状 の方法では細胞内構造まで画像化するには難がある、 固定・染色などの処理を必要とする場合に水溶性硼 素薬剤が溶出する可能性がある、などの問題を抱え ている。本研究で提案する手法は高分解能な上、固 定・染色を施すことなく処理することが可能で、よ り信頼性の高い細胞内硼素分布計測が可能になるも のと期待される。

前年度までの研究で、αオートラジオグラフィの 立場からは細胞内硼素分布計測に向けて一定の成果 を挙げることができたとも言えるが、それでも以下 に挙げる2点についての検討が必ずしも十分ではな かった。ひとつは、Fig.1(b)に示されているような 画像はオルガネラレベルでの硼素薬剤分布計測を必 要としている向きには解像度がいまだ不十分である 点である。確かに細胞核へのヒットの有無について

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は確認できる。しかし BNCT に限らず薬剤の開発や特 性評価に当たっては分子生物学的な視点を避けて通 れない。硼素薬剤も分子標的で設計されるから、細 胞内オルガネラレベルでの分布情報が創薬において 鍵となるのである。

もうひとつは使用している細胞切片試料の調整法 についてである。本手法は細胞試料の切片化が不可 欠で、切片作成にはやわらかい細胞組織を固定・樹 脂包埋して固化してからナイフで薄切する必要があ るのだが、広く一般的に行なわれている化学的固定 法を採用してしまうと、細胞内の硼素薬剤分布が実 際の生体内での分布と変わってしまう可能性がある。 我々は Fig.1 の手法開発後も解像度不足および試料 調整法の信頼性不足を克服するために様々な工夫を してきた。ここでは特にその成果について報告する。



Fig.1:a) 開発した BNCT マイクロドシメトリ用 α オートラジオグラフィ手法の手順。
 b) 本手法で得られた画像の例(硼素薬剤BSHを 16 ppm⁻¹⁰Bの濃度で含む腫瘍細胞切片を使用)。
 c) は b) の画像の説明図。画像サイズは 20 μm x 20 μm。

JRR-3M7R 中性子ラジオグラフィー装置、医工連携 JRR-4 中性子ビーム設備、医工連携

2. 細胞内オルガネラの解像度向上

2.1. 試料厚さが紫外線顕微鏡像に及ぼす影響

紫外線顕微鏡法は、軟X線顕微鏡法^{11,12)}のアナロ ジーで筆者らが新規に開発した手法である。殺菌に 用いられる紫外線灯の波長は254 nmで、生体内の核 酸の吸収ピークに相当するため、殺菌線の透過像は 核酸による吸収コントラストがつく。一方、CR-39 プラスチックは紫外線に対して感度を有しており、 暴露量に比例してエッチング速度が増加する。した がって吸収コントラストがエッチング後のレリーフ として現出するのでこれをAFMで高解像度に観察で きる。軟X線顕微鏡法と比べ、紫外線顕微鏡では安価 に大量処理が可能となるため、硼素薬剤分布計測の ようなスクリーニング目的に向いているといえる。 しかし使用している波長が比較的長いため、100 nm 以下の微細構造を解像するには近接場を用いて回折 限界を打ち破る必要がある。

以前の報告では、エッチングを短時間にすること で試料のごく近傍の像を現出させて読み取れること を示した⁴⁾。その一例として、Fig.2 に直径 100 nm の標準ポリスチレンラテックス粒子の紫外線顕微鏡 像を示す(本図ではラテックス粒子による紫外線吸 収像というよりも、球体の粒子がレンズのように働 き紫外線が屈折され集光されたような像になってい て、粒子のあった場所が掘れた状態になっている)。 100 nmを切る解像度があるため、ラテックス粒子も 十分解像できていることがわかる。一方、エッチン グ時間を短縮したとしても、試料とCR-39 基板との 密着度が不十分な場合には高い解像度が得られない ことがある。近接場とはせいぜい数十nmの領域をさ すためである。Fig.3 でその様子を説明すると、珪 藻のように湾曲した試料はCR-39 基板と完全に密着 させることが難しく、それゆえ解像度にムラが現れ ているのがわかる。







b)で示すように珪藻は湾曲し た構造になっており、CR-39 基板との密着度の良否に差が あるため、紫外線像にも解像 度にムラが生じている。



JRR-3M7R 中性子ラジオグラフィー装置、医工連携 JRR-4 中性子ビーム設備、医工連携

αオートラジオグラフィの際には厚さ 1 μ m 程度 の細胞切片を用いているため、100 nm 解像度を得る ことが困難となっていたものと考えられる。そこで より薄い試料として 300nm 厚の切片について紫外線 顕微鏡法の適用を試みた。Fig. 4(a)にその結果を示 す。1 μ m 厚切片の使用時(Fig. 4(b))と比べて、解 像度が向上したのがわかる。しかし電子顕微鏡像 (Fig. 4(c))に見られるようなオルガネラの解像ま でには残念ながら至っていない。さらなる高解像度 を得るにはより薄い試料の適用が必要と考えられる が、一方でαオートラジオグラフィを同時に行なう ことを考えた場合、試料に含まれる硼素の絶対量が 厚さに比例して減少することになる。硼素濃度数十 ppm程度の治療条件下において、αトラックの統計量 を稼ぐには 1μm程度の試料厚が必要と試算される ので、紫外線像の解像度とはトレードオフの関係に あるといえる。また細胞内オルガネラの解像には膜 構造の可視化が不可欠と考えられるが、生体膜の主 成分である脂質の吸収ピークは紫外線灯の波長とは 異なり、また他の成分との吸収コントラストがつき にくい¹³⁾という特徴を有しており、原理的にも解像 が難しい。この点では軟X線を用いてもコントラスト 確保は難しく、波長による回折ボケ以前の問題であ る。



b) Γμm 厚のエホン樹脂包理細胞の 片の紫外線顕微鏡像。いずれも 2 分エッチング、20μm 角。試料を薄 くすることで解像度は高まってい るが、c)の電子顕微鏡画像内に見ら れるようなオルガネラ構造までは 解像できていない。(右の各図は細 胞構造の説明用)。

JRR-3M7R 中性子ラジオグラフィー装置、医工連携 JRR-4 中性子ビーム設備、医工連携

2.2. 細胞切片自体の AFM 直接観察法の応用

紫外線顕微鏡法の解像度が不足する状況では、別 途なんらかの方法で細胞組織像を高解像度で得る必 要がある。Fig.5 に考えられる手立てを図解する。 一つの手段として、ミラー切片法が考えられる。ま ず測定対象となる細胞切片を作成する際に連続切片 を次々に作成しておく。連続する2枚の切片はほぼ 同じ断面を有しており、片方をFig.1 でも示したα オートラジオグラフィ法に使用し、もう片方は透過 型電子顕微鏡(TEM)観察に回す。それぞれで得られ た画像を照らし合わせ、TEM の高解像イメージ中に αトラックマッピングするという手法である。しか し TEM 用、αオートラジオグラフィ用の切片厚はそ れぞれ 50nm, 1μm であり、一桁以上も厚さの異なる 連続切片を作成して選別するのは技術的にもかなり 難しいため、効率が悪いと考えられる。 αオートラジオグラフィ用にCR-39 上にマウント済 みの切片試料を観察すれば確実に同一の試料につい て議論できるので間違いないのだが、TEMは使えない ため観察法が限られる。最も一般的なのは通常の光 学顕微鏡観察であるが、これは解像度が低いためオ ルガネラ観察には不向きである。近年、こうした細 胞切片をAFMで直接観察してTEM並みの画像を得よう という試みが何件か報告された。切片化した試料で あるため、通常のAFMで観察してもフラットな像が得 られるだけであったが、試料の粘弾性分布が計測で きる特殊なAFMを用いたり¹⁴⁾、試料を薬品¹⁵⁾や電子線 ¹⁶⁾で処理したりすることで細胞内オルガネラの構造 が表出し、TEMに迫る解像度で観察できたというもの である。



Fig.5:詳細な細胞組織 像内での α トラックマ ッピングを達成するた めの手立てを図解した もの。実線の丸で囲ん だ部分が今回採用した 「AFM による細胞切 片の直接観察法」であ る。

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今回、筆者らはαオートラジオグラフィ時に切片 試料の AFM 直接観察法を応用することを試みた。ま ず CR-39 上にマウントした切片試料を、一般的なタ ッピングモード AFM で観察した例を Fig. 6(a) に示す。 未処理の切片はナノメートルレベルでフラットであ り、TEM 並みの解像度には遠く及ばない。しかし、 紫外線顕微鏡法と同じ条件で UV 照射を施した後に 切片を AFM 観察したところ、Fig. 6(b),(c)に示すよ うに細胞内構造まで明確に可視化できることがわか った。紫外線吸収により変質した細胞内成分の一部 が揮発等で除去され、平坦だった切片表

面にこのような細胞内構造が現出したものと考えられる。これにより核内のクロマチン構造や細胞膜の存在が明らかとなったばかりでなく、ミトコンドリ

アや小胞体といったオルガネラ構造までもが十分解 像できており、TEMとほとんど同等の画像が得られた。 αオートラジオグラフィ試料では、このあとでCR-39 基板をエッチングしてαトラック像の分布を計測し ておき、細胞紫外線像をガイドとして先程の細胞組 織AFM像と位置合わせすることで細胞組織像中のα トラックマッピングも可能になる。一例として、細 胞切片直接観察像と同じ位置に生じたCR-39 上の紫 外線像を並べて示したのがFig.7 である。Fig.7 の (b), (c)については、αトラックとの同時観察も実証 するために、²⁴¹Amからのα線を照射してオートラジ オグラフィを模擬した例を示している。ガイドとし て紫外線顕微鏡像を用いているため、同一箇所の探 索や画像のアライメントが容易なばかりで



Fig.6: a)エポキシ包埋切片を AFM で直接観察した像。30µm スキャン。 細胞らしき影も見て取れるが、切片 は通常 nm レベルで平坦であるため、 凹凸像として得られる情報は少な い。



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b) エポキシ包埋切片を
 AFM で直接観察した像
 (撮像前に UV 照射処理
 を施した場合)。30µm ス
 キャン。c)は b)内のカコ
 ミ部分を拡大した像
 (10µm スキャン)。

ミトコンドリアやその他 細胞内オルガネラの膜構 造などが見て取れ、電子 顕微鏡で観察したものと 遜色ない解像度が得られ ている。

※右の画像は説明図(凡 例は Fig.4 を参照のこ と)。 なく、高精度な位置合わせが可能となるという特長 も有している。これにより、真に細胞内オルガネラ レベルでの硼素薬剤分布計測法を確立することがで きた。

本手法は TEM を全く用いずに TEM レベルでの計測 が可能となる特色があり、1µm 程度の比較的厚い切 片が利用できるため、今回のαオートラジオグラフ ィ法との親和性が高い。TEM 試料作成に必要なウラ ンや鉛イオンを用いた電子染色も不要で環境にもや さしい。AFM のスキルのみで作業が可能であるため 測定者の負担も軽減できる点も有利である。



Fig.7: エポキシ包埋切片のAFM直接観察像と(左)、CR-39 プラスチック上に焼き付けられたUV像を現像して得られたレリーフ(中央)。右は細胞内構造の説明図(凡例はFig.4 のものを参照)。b), c) については²⁴¹Amからの α 線を 10⁷/cm²程度照射し、 α トラックとの同時観察も試みた。UV像をガイドに細胞組織像を位置合わせし画像をオーバーラップさせることで、オルガネラレベルで粒子飛跡マッピングが可能となる。

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Fig.8:フォトリソグラフィ用 マスクの UV 透過像を CR-39 表面に焼き付け現像した様子 を AFM 観察したもの (30 µm スキャン)。段差は 70nm 程度。 右は使用したマスクと同じ素 材の光学顕微鏡像 (石英基板に クロム蒸着し、電子線描画でパ ターニングしたもの)。Fig.7 で 示した画像の位置合わせを容 易にするためのガイドとして 利用できる。

スクリーニングのように大量のデータを取得して 統計を稼ぎたい場合は、画像の位置合わせも効率よ く行なう必要がある。Fig.8 に示すように、測定を 始める前にCR-39 上にあらかじめフォトマスクなど を通して紫外線パターニングを施しておくとよい。 区画のナンバリング等も行なうことで、低倍率画像 から所望の箇所へのアクセス・画像拡大が容易にな ると考えられる。以前、CR-39 上にフォトリソグラ フィでアルミパターニングする手法を提案したこと がある¹⁷⁾が、アルミは反応性が高くCR-39 に少なか らず影響を与えるため、Fig.8 のような単に段差を つけるだけのマーキングの方が使い勝手もよいと考 えられる。

高圧凍結固定法による高信頼性試料調整法の 利用

二つ目に検討すべき項目は細胞試料の健全性に関 する問題である。例えば TEM で細胞内オルガネラを 観察する場合、ただ漫然と組織試料を樹脂で固めて 薄く切り、TEM の機械にかければよいというもので はなく、適切な固定処理が必要とされる。固定とは 切片化のための樹脂包埋とは別に、細胞の形を保ち 続けるための処理をさす。細胞は生ものであり、組 織を摘出した瞬間から劣化が始まるため、何らかの 方法でその進行を防がねばならない。通常 TEM 用試 料の場合はグルタールアルデヒドでたんぱく質を変 性固定し、四酸化オスミウムによって脂質が固定さ れる。こうした処理は溶液中で行なわれるため、も し組織中に含まれる成分、たとえば硼素薬剤が溶液 に溶解する性質を有していると、処理中にもとあっ JRR-3M7R 中性子ラジオグラフィー装置、医工連携 JRR-4 中性子ビーム設備、医工連携

た場所から流れ出てしまう懸念がある。このように 溶液処理による試料の信頼性低下が心配される場合 には、組織試料をまるごと急速凍結し、凍結のまま クライオスタット中で切片化する手法が取られる。 ただし、組織試料は必然的に水分を多く含むため、 凍結する際に膨張しながらスパイク状に氷晶が形成 されることよって組織が破壊されることがある。こ れを防ぐには氷を結晶化させずにアモルファス状に 凍結する必要がある。アモルファス氷生成には、大 気圧下では 10000 度/秒もの冷却速度で凍結する必 要があるが、それでも破壊を免れるのは組織表面か らごくわずか分のみである。近年、2000気圧の高圧 下で 1mm ほどの大きさの組織試料全体を健全に急速 凍結できる装置が市販されるようになった。そこで この高圧凍結装置を用いて作成した試料について、 αオートラジオグラフィ法の適用可能性を試験した。 使用したのは BAL-TEC 社の HPM 010 高圧凍結装置で ある。本装置では組織試料を半球状の小さな銅製カ ップで両側から挟み、その外側から対向して液体窒 素の高圧ジェットを吹き付けることによって、2000 気圧もの高圧印加と同時に急速凍結を達成している。 摘出した腫瘍組織を 1mm 角以下の大きさとし、同装 置で急速凍結したのち、水分をアセトンで凍結置換 した。切片化するためにエポン樹脂に包埋した後は、

(1)切片の直接観察と、(2)紫外線顕微鏡像およ び α トラックとの同時観察がこれまでの化学固定試 料を用いた場合と同様に行なえるかどうかを確認し た。Fig.9 にその結果を示す。切片の直接観察像は Fig.6,7 と比べると細胞内オルガネラの解像が一部 不足しているが、これは高圧凍結固定が通常の化学 固定と比べて高い技術を要求されるためで、使用す



Fig.9:a) 高圧凍結固定した組織のエポキシ包埋試料を切片化し、UV 照射後にAFM 直接観察した像。
b),c) 高圧凍結固定・エポキシ包埋試料の切片についてUV顕微鏡を適用した例。
c)については²⁴¹Amからのα線を10⁷/cm²程度照射し、αトラックとの同時観察も試みた。
右は細胞内構造の説明図。

いずれも 20μm スキャン。 細胞内薬剤分布についてよ り現実に近いと考えられる 凍結固定試料を用いても高 解像度でαトラックマッピ ングが実現できる目処がつ いた。

る組織の性質に合わせた固定・後処理の条件出しに 検討の余地があると考えられる。細胞核や細胞膜な どは細かく解像できており、また適切な条件下では オルガネラの解像も可能であるとの報告もある¹⁸⁾。 一方、紫外線顕微鏡像のほうは全く問題なくこれま でと同じ解像度が得られており、α線との同時観察 も達成できている。こうして高圧凍結試料の切片を 用いることで、オルガネラレベルでの解像度を持た せつつ、試料の信頼性も高い条件で硼素薬剤の分布 計測が行なえる見込みが十分得られたと考えられる。

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4. おわりに

BNCT の鍵は、硼素薬剤の分布特性にかかっている ことは序論でも述べた。薬剤自身の設計・開発がそ の大部分を決定付けることになるのだが、実際に開 発された薬剤が細胞内でどのような分布を示すのか、 組織ごとに分布特性がどのように違うのかといった 情報がフィードバックされてこそ、薬剤開発の進展、 そしてひいては BNCT が治療として確立されていく ことにつながる。これまで高解像度の硼素分布計測 技術が不足していたが、αオートラジオグラフィ法 の立場からは今回ついに細胞内オルガネラレベルで の分布計測が可能となる手法を提案・確立できたと 考えている。ただし人命に関わる計測である。ただ 「測れる」だけではなく、計測した結果の信頼性に も責任を持つ必要がある。これについても当初のよ うな試料の信頼性不足を克服できる可能性を示せた。 しかし、これでようやくスタートラインに立てたば かりである。本手法を活用し、さまざまな硼素薬剤 について、組織ごとの分布特性データを蓄積してい くばかりでなく、時間的な分布状況の変化に関する 情報も収集することで硼素薬剤の特性把握を進め、 BNCT の確立に向けて貢献していく必要がある。これ らの研究を通じ BNCT が近い将来、がん患者さんたち の希望となるよう願ってやまない。

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成果の公表

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5-7

「悪性脳腫瘍に対する非開頭硼素中性子捕捉療法」

Boron neutron capture therapy without craniotomy for malignant brain tumors

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(1) 研究の目的と意義

目的:悪性脳腫瘍患者に対し、BSH(Borocaptate)と BPA(Boronophenylalanin)の同時併用投与下に熱外 中性子を非開頭で照射する「硼素中性子捕捉療法」 (Boron Neutron Capture Therapy; BNCT)を行い、頭 部皮膚および正常脳組織に対する安全性を確認する とともに腫瘍制御と生存期間の改善を目指す。

意義:悪性脳腫瘍は、腫瘍細胞のX線感受性が低い ことや周囲脳組織への広範な腫瘍細胞浸潤などから 難治疾患であり、この数十年間治療成績の改善がほ とんど見られていない。BNCT は、腫瘍細胞を選択的 かつ生物学的効果の高い粒子線にて治療するため、 通常のX線分割照射に比べ高い治療効果が期待でき る。BPA 投与量の増加や、BNCT 後にX線分割照射を 追加することにより、腫瘍縮小後の再増大の抑制の 面で更なる改善が見られている。生存期間の延長に ついては今後の追跡調査が待たれるが、少なくとも 腫瘍縮小効果に関しては従来のX線分割照射よりも 反応率が高く、非開頭にもかかわらず頭皮への影響 が少ない。BNCT後の摘出組織の検討では、BNCTの治 療域に一致した necrosisを認めた。共同研究者の松 村は原研東海研究所において、悪性脳腫瘍に対する 開頭下でのBSHを用いたBNCTを多くの症例に行った 経験を有し、最近非開頭によるBNCTを開始した。本 研究は、熱外中性子を利用することにより、非開頭 で深在性腫瘍に対する治療を可能とし、さらにBSH の高い腫瘍選択性とBPAの高い腫瘍細胞集積性を合 わせて利用することにより抗腫瘍効果と 安全性の向上を図る。悪性脳腫瘍に対する効果的か つ実用的な新しい治療法となりうる。

方法:悪性脳腫瘍患者に対し、医学部研究倫理委員 会で承認されたプロトコールにより症例を登録し、 非開頭で硼素中性子捕捉療法を行う。 京都大学研究用原子炉(KUR)で施行されていた臨床 研究プロトコール(2001年6月12日 KUR原子炉医 療委員会承認)を基に、プロトコールを作成し東京 大学医学部附属病院の倫理委員会にて承認を得た。 KUR では、臨床研究プロトール「"熱外中性子"ビー

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ムを用いた悪性神経膠腫に対する非開頭硼素中性子 捕捉療法」が承認施行された。ただし、KUR は平成 18年2月以降点検のため約2年間操業を停止してお り現在では東海村が唯一の治療原子炉となっている。 腫瘍摘出術施行後の病理診断の確定した悪性脳腫瘍 患者を対象に、多施設共同研究として、非開頭の BNCTの開発研究を行う。平成16年度からBNCTの臨 床研究プロトコールを東京大学医学部付属病院の倫 理委員会に申請し、規定様式の同意書を作成した。 平成18年2月21日に倫理委員会にて承認を得た(研 究課題名:脳腫瘍に対する非開頭硼素中性子捕捉療 法、受付番号1312)。

本研究では、KUR での経験に基づいた臨床研究プロ トコールを用い、腫瘍摘出術施行後の病理診断の確 定した悪性脳腫瘍患者を対象に、BSH と BPA の2種 の硼素化合物投与を行った上、熱外中性子モードに よる非開頭での硼素中性子捕捉療法を施行する。

腫瘍は最新のナビゲーションシステム(ステルス) および神経生理学的術中モニタリングを駆使し、新 たな神経障害を生じない範囲で可及的に大きく摘出 する。腫瘍摘出後の病理診断において膠芽腫と診断 され、かつ年齢が10歳から80歳までの症例で、術 後残存腫瘍が確認され、脳表より比較的浅部にある 症例で、本人および家族に対して本治療法の説明を 倫理委員会により承認された説明文により行い、同 意を得られた場合に、研究協力を依頼している筑波 大学医学部附属病院へ転院し、必要な検査および BSH および BPA の点滴を行う。JRR-4 において熱外中 性子ビーム照射時の腫瘍内推定硼素—10 濃度は 50ppm 以上を目標とし、血中濃度を即発ガンマ線分 析によって測定する。照射後線量分析に応じて、東 京大学医学部附属病院にて放射線分割照射を追加す る。神経学的所見と画像の経時的観察により、抗腫 瘍効果と生存期間に対する評価を行い、一方で照射 野内に皮膚および脳組織への影響を調査して安全性 の評価を行う。適応の判断を迷うような症例に対し ては都立老人医療センターにて BPA の PET 検査を追 加し、L/N 比 2 以上をもって適応と考えることとす る。

(2) 研究成果

平成17年度~19年度文部科学省科学研究費補助金 (基盤B)「熱外中性子を用いた悪性脳腫瘍に対する 次世代 BNCT」(研究代表者:松村明、研究分担者: 藤堂具紀、森田明夫ほか)が採択された。平成18 年度に倫理委員会を通過した後に適応症例が3例あ ったが、1 例は BPA-PET で T/N 比が 2 以下であっ た為 BNCT は行わなかった。またもう1例はちょう ど9月半ば頃の症例で原研が点検で使用できず断念 した。平成18年12月19日、膠芽腫再発例の患者 に本プロトコールによる硼素中性子捕捉療法を東海 村の JRR-4 で行った。東大脳神経外科の 4 症例を含 めて、既に多数例の悪性脳腫瘍患者に対し非開頭で の治療を行っており、大多数の症例で2日~7日後 までに腫瘍の縮小を認めている。今回の症例も硼素 中性子捕捉療法後翌日、2日後、6日後に行った頭 部 MRI では腫瘍の縮小を認めた。この間に症状の一 時的な改善を認めた。しかし、本症例はその後髄腔 内播種を合併し1ヵ月後に死亡している。

(3) 成果の公表

I. Publications

 Tanaka M, Ino Y, Nakagawa K, Tago M, Todo T: High-dose conformal radiotherapy for supratentorial malignant glioma: a historical comparison. Lancet Oncology 6(12): 953-960, 2005.

- II. 学会発表
- 藤堂具紀、田中実、稲生靖、高橋雅道、斎藤延 人:星細胞腫の長期治療成績からみた治療スタ ンダードの検討:130 例の解析。第66回日本脳 神経外科学会総会(東京)、2007年10月3-5日
- 藤堂具紀、稲生靖、田中実、丸山啓介、鎌田 恭輔、斎藤延人:悪性神経膠腫に対する多角的 先端医療の実践。第65回日本脳神経外科学会 総会(京都)、2006年10月18-20日
- 田中実、稲生靖、斉藤延人、藤堂具紀:Recursive partitioning analysisを用いた悪性グリオー マ高線量局所照射の治療解析。第24回日本脳 腫瘍学会(阿寒湖)、2006年10月1-3日
- 4. 田中実、稲生靖、藤堂具紀:テント上悪性グリオーマに対する高線量局所照射の治療成績
 —60G 照射と比較した 184 例の解析—。第 23 回日本脳腫瘍学会(鹿児島)2005 年 10 月 30 日-11月1日
- 5. 田中実、稲生靖、藤堂具紀:Low-grade astrocytomaの放射線治療の意義 119 例の検 討。第 22 回日本脳腫瘍学会(松島)、2004 年 10 月 17-19 日

6. 田中実、稲生靖、藤堂具紀:テント上悪性グリ

オーマに対する高線量局所照射の治療成績 --606 照射と比較した 184 例の解析--。第 64 回 日本脳神経外科学会総会(横浜)、2005 年 10 月 5-7 日

 7. 田中実、稲生靖、藤堂具紀:Low-grade astrocytomaの放射線治療の意義 119 例の検 討。第63回日本脳神経外科学会総会(名古屋)、 2004 年 10 月 6-8 日

おわりに

本報告書は、研究炉(JRR-3、JRR-4)を利用した利用者の協力を基に、研究炉の成果を 提出して頂き、研究炉利用課で編集したものであります。この成果を公表する事で、研究 炉の今後の有効利用並びに利用拡大に役立つ事を期待します。

編集委員

編集委員メンバー

| 和田 | 茂 | (研究炉利用課長) |
|----|-----|-----------|
| 広瀬 | 彰 | (研究炉利用課) |
| 吉永 | 真希夫 | (研究炉利用課) |
| 高橋 | 俊行 | (研究炉利用課) |
| 渡辺 | 広子 | (研究炉利用課) |

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本報告書の発刊にあたり、多くの皆様から多大なご協力を頂きました。

原稿を提出して頂いた利用者の皆様のご協力に感謝するとともに、今後も研究炉が有効 に利用され、種々の研究がさらに進展されることを期待します。

編集に際し、ご協力頂いた、研究炉加速器管理部長山下清信氏、研究炉加速器管理部 JRR-3管理課課長 寺門義文氏に深く感謝致します。



Appendixes

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付 録

原科研研究炉の利用設備一覧

JRR-3
 1)実験設備

| 実験孔 | 実 | 験 | 装 | 置 |
|---------------------|-------------------------|----------------|--|------|
| 1 G | 高分解能粉末中的 | 生子回折装置(| HRPD) | |
| 1 G – A | 生体高分子用中位 | 生子解析装置(| B I X - III) | |
| 1 G – B | 生体高分子用中位 | 生子解析装置(| BIX-IV) | |
| 2 G | 三軸型中性子分类 | 光器(TAS- | 1) | |
| 3 G | 中性子トポグラン | フィ及び精密光 | 学実験装置(| PNO) |
| 4 G | 汎用三軸型中性 | 子分光器(G P | TAS) | |
| 5 G | 偏極中性子散乱影 | 表置(PONT | A) | |
| 6 G | 東北大学中性子 | 散乱分光器(T | OPAN) | |
| 7 R | 中性子ラジオグ | ラフィ装置(T | NRF) | |
| $T \ 1 - 1$ | 中性子偏極回折約 | 表置(HQR) | | |
| T 1 - 2 | 単結晶中性子回 | 新装置(KSD |) | |
| T 1 - 3 | 粉末中性子回折 | 表置 (KPD) | | |
| T 1 - 4 - 1 | 即発ガンマ線分析 | 所装置(PGA |) | |
| T 1 - 4 - 2 | 多重即発ガンマ約 | 暴分析装置(M | PGA) | |
| T 1 - 4 - 3 | TOF型中性子质 | 反射率計(TO | F) | |
| T 1 - 4 - 4 | 中性子ラウエ回打 | 新装置(LAU | E) | |
| T 1 - 4 - 5 | 中性子ベータ崩り | 裹基礎測定装置 | | |
| T 2 - 1 | 残留応力測定中位 | 生子回打装置(| R E S A) | |
| T 2 - 2 | 中性子4軸回折 | 表置(FOND | ER) | ~ \ |
| T 2 - 3 | 多目的単色熱中的 | 生子ビームボー | ► (MUSA | SHI) |
| $T_{2} - 4$ | 高分解能三軸型 | 甲性子分光器(| TAS-2) | \ |
| $C \ 1 - 1$ | 高エネルギー分類 | 解能二軸型甲性 | 子分光器(H | (ER) |
| $C \ 1 - 2$ | 二次元位置測定/ | 小角散乱装置(| SANS-U |) |
| $C \ 1 - 3$ | 超局分解能後方 | 教乱装置(UL | S) | |
| C 2 - 1 | 冷甲性子散乱美题 二。(云) 小山 二二 | 険アバイス開発 | 装置(LTA | S) |
| C 2 - 2 | 局Q領域対応中 | 性子反射率計(| SUIREN |)) |
| C 2 - 3 - 1 | 甲性子スピンエ: | コー分光器(N | SE) | |
| C 2 - 3 - 2 - 1 | 多里即発力ンマれ | 家分析装置(M | PGA | |
| C 2 - 3 - 2 - 2 | 即発力ンマ線分 | |) | |
| C 2 - 3 - 3 - 1 | 伶屮性子フシオ: | | $\mathbf{R}\mathbf{F}$ | |
| C 2 - 3 - 3 - 2 | ハルス甲性子機 | 品用発装置(C | HOP) | |
| C 2 - 3 - 3 - 3 | TOF型甲性子加 | 又射率計(IO | F) | |
| C 2 - 3 - 3 - 4 | 中性子フリエ回 | 介装直(LAUE | $(\mathbf{A} \in \mathbf{N} \in \mathbf{A})$ | λ. |
| C 3 - 1 - 1 | 局分解能ハルス | 令中性于分光器 | (AGNES) |) |
| C 3 - 1 - 2 - 1 | 甲性十光学ンス | アム評価装直(| NOP | |
| $C_{3} - 1 - 2 - 2$ | 多層限中性十十次 | 歩計/ | (MINE) | |
| $C_3 = 2$ | 屮性于小角 散乱 ╣ | 密 直 (SANS | — J) | |
| | | | | |
| | | | | |
| | | | | |

2) 照射設備

| 水 | 力 | 照 | 射 | 設 | 備 | HR-1,2 |
|----|----|----|----|----|----|--|
| 気 | 送 | 照 | 射 | 設 | 備 | PN-1,2 |
| 放身 | 村化 | 分析 | 用照 | 射認 | 於備 | P N - 3 |
| 均 | _ | 照 | 射 | 設 | 備 | S I – 1 |
| 旦 | 転 | 照 | 射 | 設 | 備 | D R – 1 |
| 垂 | 直 | 照 | 射 | 設 | 備 | $V T - 1$, $R G - 1 \sim 4$ $B R - 1 \sim 4$, $S H - 1$ |

- 2. J R R -4
 - 1)実験設備

| プール |
|--------------|
| 中性子ビーム設備 |
| 散 乱 実 験 設 備 |
| 冷却水循環ループ |
| 医療照射設備(BNCT) |
| 即発ガンマ線分析装置 |

2) 照射設備

| 簡 易 照 射 筒 | Tパイプ(水力) |
|-----------|----------|
| | Sパイプ |
| | Dパイプ |
| | Nパイプ |
| 気送管照射設備 | ΡN |

| 表 1. SI 基本単位 | | | | |
|--------------|---------|-----|--|--|
| 甘木昌 | SI 基本単位 | | | |
| 基个里 | 名称 | 記号 | | |
| 長さ | メートル | m | | |
| 質 量 | キログラム | kg | | |
| 時 間 | 秒 | s | | |
| 電 流 | アンペア | Α | | |
| 熱力学温度 | ケルビン | Κ | | |
| 物質量 | モル | mol | | |
| 光度 | カンデラ | cd | | |

| 表2. 基本単位を用いて表されるSI組立単位の例 | | | | | |
|--------------------------------------|------------------------|--|--|--|--|
| an de SI 基本単位 | | | | | |
| 名称 | 記号 | | | | |
| 面 積 平方メートル | m^2 | | | | |
| 体 積 立法メートル | m ³ | | | | |
| 速 さ , 速 度 メートル毎秒 | m/s | | | | |
| 加速 度メートル毎秒毎秒 | m/s^2 | | | | |
| 波 数 毎メートル | $\mathbf{m}^{\cdot 1}$ | | | | |
| 密度 ,質量密度 キログラム毎立方メートル | kg/m^3 | | | | |
| 面 積 密 度 キログラム毎平方メートル | kg/m^2 | | | | |
| 比体積 立方メートル毎キログラム | m ³ /kg | | | | |
| 電 流 密 度 アンペア毎平方メートル | A/m^2 | | | | |
| 磁 界 の 強 さ アンペア毎メートル | A/m | | | | |
| 量 濃 度 ^(a) , 濃 度 モル毎立方メートル | mol/m ³ | | | | |
| 質 量 濃 度 キログラム毎立法メートル | kg/m^3 | | | | |
| 輝 度 カンデラ毎平方メートル | cd/m^2 | | | | |
| 屈折率 ^(b) (数字の) 1 | 1 | | | | |
| 比 透 磁 率 (1) (数字の) 1 | 1 | | | | |

(a) 量濃度(amount concentration)は臨床化学の分野では物質濃度 (a) 量減反 (and to includation) (素加水にビックガリで(ネック資源反 (substance concentration) ともよばれる。
 (b) これらは無次元量あるいは次元1をもつ量であるが、そのこと を表す単位記号である数字の1は通常は表記しない。

表3. 固有の名称と記号で表されるSI組立単位

| | | | SI 組立単位 | |
|----------------|-----------------------|------------------------------|----------------------|------------------------------------|
| 組立量 | 名称 | 記号 | 他のSI単位による | SI基本単位による |
| | 74 W.F | | 表し方 | 表し方 |
| 平 面 角 | ラジアン ^(b) | rad | 1 ^(b) | m/m |
| 立 体 角 | ステラジアン ^(b) | $\mathrm{sr}^{(\mathrm{c})}$ | 1 ^(b) | $m^{2/}m^2$ |
| 周 波 券 | ヘルツ ^(d) | Hz | | s^{-1} |
| 力 | ニュートン | Ν | | m kg s ^{·2} |
| 圧力,応力 | パスカル | Pa | N/m^2 | m ⁻¹ kg s ⁻² |
| エネルギー,仕事,熱量 | ジュール | J | N m | $m^2 kg s^2$ |
| 仕事率, 工率, 放射束 | ワット | W | J/s | $m^2 kg s^{\cdot 3}$ |
| 電荷,電気量 | クーロン | С | | s A |
| 電位差(電圧),起電力 | ボルト | V | W/A | $m^2 kg s^{\cdot 3} A^{\cdot 1}$ |
| 静電容量 | ファラド | F | C/V | $m^{2} kg^{1} s^{4} A^{2}$ |
| 電 気 抵 抗 | オーム | Ω | V/A | $m^2 kg s^{\cdot 3} A^{\cdot 2}$ |
| コンダクタンス | ジーメンス | s | A/V | $m^{2} kg^{1} s^{3} A^{2}$ |
| 磁東 | ウエーバ | Wb | Vs | $m^2 kg s^{\cdot 2} A^{\cdot 1}$ |
| 磁束密度 | テスラ | Т | Wb/m ² | $\text{kg s}^{2} \text{A}^{1}$ |
| インダクタンス | ヘンリー | Η | Wb/A | $m^2 kg s^{2} A^{2}$ |
| セルシウス温度 | セルシウス度 ^(e) | °C | | K |
| 光東 | ルーメン | lm | cd sr ^(c) | cd |
| 照度 | ルクス | lx | lm/m^2 | m^{2} cd |
| 放射性核種の放射能(+) | ベクレル ^(d) | Bq | | s ⁻¹ |
| 吸収線量,比エネルギー分与, | ガレイ | Gv | J/kg | m ² s ^{.2} |
| カーマ | | α, j | oning | m 5 |
| 線量当量,周辺線量当量,方向 | シーベルト (g) | Sv | .I/kg | m ² e ⁻² |
| 性線量当量, 個人線量当量 | 1 | 21 | 3. ng | |
| <u>酸素活性</u> | カタール | kat | | s ⁻¹ mol |

(a)SI接頭語は固有の名称と記号を持つ組立単位と組み合わせても使用できる。しかし接頭語を付した単位はもはや

(a)SI接頭語は固有の名称と記号を持つ組立単位と組み合わせても使用できる。しかし接頭語を付した単位はもはや コレーレントではない。
(b)ラジアンとステラジアンは数字の1に対する単位の特別な名称で、量についての情報をつたえるために使われる。 実際には、使用する時には記号rad及びsrが用いられるが、習慣として組立単位としての記号である数字の1は明 示されない。
(d)剤光学ではステラジアンという名称と記号srを単位の表し方の中に、そのまま維持している。
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(d)ヘルツは周期現象についてのみ、ベクレルは放射性核種の統計的過程についてのみ使用される。
(e)セルシウス度はケルビンの特別な名称で、セルシウス温度を表すために使用される。
(f)をないたがって、温度差や温度間層を表す数値はどちらの単位で表しても同じである。
(f)放射性核種の放射能(activity referred to a radionuclide)は、しばしば誤った用語で"radioactivity"と記される。
(g)単位シーベルト(PV,2002,70,205)についてはCIPM勧告2(CI-2002)を参照。

表4.単位の中に固有の名称と記号を含むSI組立単位の例

| | SI組立単位 | | | |
|-----------------|-------------------|--------------------|---|--|
| 組立量 | 名称 | 記号 | SI 基本単位による 表し方 | |
| 粘度 | パスカル秒 | Pa s | m ⁻¹ kg s ⁻¹ | |
| カのモーメント | ニュートンメートル | N m | $m^2 kg s^2$ | |
| 表 面 張 九 | ニュートン毎メートル | N/m | kg s ^{·2} | |
| 角 速 度 | ラジアン毎秒 | rad/s | $m m^{1} s^{1} = s^{1}$ | |
| 角 加 速 度 | ラジアン毎秒毎秒 | rad/s^2 | $m m^{-1} s^{-2} = s^{-2}$ | |
| 熱流密度,放射照度 | ワット毎平方メートル | W/m^2 | kg s ^{·3} | |
| 熱容量、エントロピー | ジュール毎ケルビン | J/K | $m^2 kg s^{2} K^{1}$ | |
| 比熱容量, 比エントロピー | ジュール毎キログラム毎ケルビン | J/(kg K) | $m^2 s^{-2} K^{-1}$ | |
| 比エネルギー | ジュール毎キログラム | J/kg | $m^{2} s^{-2}$ | |
| 熱 伝 導 率 | ワット毎メートル毎ケルビン | W/(m K) | $m \text{ kg s}^{-3} \text{ K}^{-1}$ | |
| 体積エネルギー | ジュール毎立方メートル | J/m^3 | $m^{1} kg s^{2}$ | |
| 電界の強さ | ボルト毎メートル | V/m | m kg s ⁻³ A ⁻¹ | |
| 電 荷 密 度 | クーロン毎立方メートル | C/m ³ | m ⁻³ sA | |
| 表 面 電 荷 | クーロン毎平方メートル | C/m^2 | m^{-2} sA | |
| 電東密度,電気変位 | クーロン毎平方メートル | C/m^2 | m ⁻² sA | |
| 誘 電 卒 | ファラド毎メートル | F/m | $m^{-3} kg^{-1} s^4 A^2$ | |
| 透 磁 率 | ヘンリー毎メートル | H/m | $m \text{ kg s}^{2} \text{ A}^{2}$ | |
| モルエネルギー | ジュール毎モル | J/mol | $m^2 kg s^2 mol^1$ | |
| モルエントロピー, モル熱容量 | ジュール毎モル毎ケルビン | J/(mol K) | $m^2 kg s^2 K^1 mol^1$ | |
| 照射線量 (X線及びγ線) | クーロン毎キログラム | C/kg | kg ⁻¹ sA | |
| 吸収線量率 | グレイ毎秒 | Gy/s | $m^{2} s^{-3}$ | |
| 放 射 強 度 | ワット毎ステラジアン | W/sr | $m^4 m^{-2} kg s^{-3} = m^2 kg s^{-3}$ | |
| 放 射 輝 度 | ワット毎平方メートル毎ステラジアン | $W/(m^2 sr)$ | m ² m ⁻² kg s ⁻³ =kg s ⁻³ | |
| 酵素活性濃度 | カタール毎立方メートル | kat/m ³ | m ⁻³ s ⁻¹ mol | |

| 表 5. SI 接頭語 | | | | | | |
|-------------|--------|---|----|-----------------|------|----|
| 乗数 | 接頭詞 | 吾 | 記号 | 乗数 | 接頭語 | 記号 |
| 10^{24} | П | Þ | Y | 10^{-1} | デシ | d |
| 10^{21} | ゼ | タ | Z | 10^{-2} | センチ | с |
| 10^{18} | エク | サ | Е | 10^{-3} | ミリ | m |
| 10^{15} | \sim | タ | Р | 10^{-6} | マイクロ | μ |
| 10^{12} | テ | ラ | Т | 10^{-9} | ナノ | n |
| 10^{9} | ギ | ガ | G | $10^{\cdot 12}$ | ピュ | р |
| 10^{6} | メ | ガ | М | $10^{.15}$ | フェムト | f |
| 10^3 | キ | | k | $10^{.18}$ | アト | а |
| 10^2 | ヘク | ŀ | h | $10^{.21}$ | ゼプト | z |
| 10^{1} | デ | 力 | da | $10^{.24}$ | ヨクト | У |

| 表6. SIに属さないが、SIと併用される単位 | | | | |
|-------------------------|------|--|--|--|
| 名称 | 記号 | SI 単位による値 | | |
| 分 | min | 1 min=60s | | |
| 時 | h | 1h =60 min=3600 s | | |
| 日 | d | 1 d=24 h=86 400 s | | |
| 度 | 0 | 1°=(п/180) rad | | |
| 分 | , | 1'=(1/60)°=(п/10800) rad | | |
| 秒 | " | 1"=(1/60)'=(п/648000) rad | | |
| ヘクタール | ha | $1ha=1hm^{2}=10^{4}m^{2}$ | | |
| リットル | L, 1 | $1L=11=1dm^{3}=10^{3}cm^{3}=10^{\cdot 3}m^{3}$ | | |
| トン | t | $1t=10^{3}$ kg | | |

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| 表7. | SIに属さないが、 | SIと併用される単位で、 | SI単位で |
|-----|-----------|-----------------------------|-------|
| | 1. 1. 3 | NAMES AND ADDRESS OF A DECK | |

| 表される奴値が実験的に得られるもの | | | | |
|-------------------|----|--|--|--|
| 名称 | 記号 | SI 単位で表される数値 | | |
| 電子ボルト | eV | 1eV=1.602 176 53(14)×10 ⁻¹⁹ J | | |
| ダルトン | Da | 1Da=1.660 538 86(28)×10 ⁻²⁷ kg | | |
| 統一原子質量単位 | u | 1u=1 Da | | |
| 天 文 単 位 | ua | 1ua=1.495 978 706 91(6)×10 ¹¹ m | | |

| 表8. | SIに属さないが、 | SIと併用されるその他の単位 |
|-----|-----------|----------------|
| | | |

| | 名称 | | 記号 | SI 単位で表される数値 |
|----|----------|-----|------|---|
| バ | <u> </u> | ル | bar | 1 bar=0.1MPa=100kPa=10 ⁵ Pa |
| 水銀 | 柱ミリメー | トル | mmHg | 1mmHg=133.322Pa |
| オン | グストロ | - 4 | Å | 1 Å=0.1nm=100pm=10 ⁻¹⁰ m |
| 海 | | 里 | М | 1 M=1852m |
| バ | | ン | b | $1 \text{ b}=100 \text{fm}^2=(10^{\cdot 12} \text{cm})2=10^{\cdot 28} \text{m}^2$ |
| 1 | ツ | ŀ | kn | 1 kn=(1852/3600)m/s |
| ネ | - | パ | Np ~ | |
| ベ | | ル | в | し 51単位との 数 値 的 な 関係 は、 対数 量の 定 差 に 佐 存 |
| デ | ジベ | N | dB - | |

| 表9. 固有の名称をもつCGS組立単位 | | | | | |
|-----------------------|----------------------|---|--|--|--|
| 名称 | 記号 | SI 単位で表される数値 | | | |
| エルグ | erg | $1 \text{ erg}=10^{-7} \text{ J}$ | | | |
| ダイン | dyn | 1 dyn=10 ⁻⁵ N | | | |
| ポアズ | Р | 1 P=1 dyn s cm ^{·2} =0.1Pa s | | | |
| ストークス | St | $1 \text{ St} = 1 \text{ cm}^2 \text{ s}^{\cdot 1} = 10^{\cdot 4} \text{m}^2 \text{ s}^{\cdot 1}$ | | | |
| スチルブ | $^{\mathrm{sb}}$ | $1 \text{ sb} = 1 \text{ cd} \text{ cm}^{-2} = 10^4 \text{ cd} \text{ m}^{-2}$ | | | |
| フォト | $^{\rm ph}$ | $1 \text{ ph}=1 \text{cd sr cm}^{2} 10^{4} \text{lx}$ | | | |
| ガル | Gal | $1 \text{ Gal} = 1 \text{ cm s}^{-2} = 10^{-2} \text{ ms}^{-2}$ | | | |
| マクスウェル | Mx | $1 \text{ Mx} = 1 \text{G cm}^2 = 10^{-8} \text{Wb}$ | | | |
| ガウス | G | $1 \text{ G} = 1 \text{Mx cm}^{\cdot 2} = 10^{\cdot 4} \text{T}$ | | | |
| エルステッド ^(c) | Oe | 1 Oe 🖁 (10 ³ /4п)А m ⁻¹ | | | |

(c) 3元系のCGS単位系とSIでは直接比較できないため、等号「 🎍 」 は対応関係を示すものである。

| 表10. SIに属さないその他の単位の例 | | | | | |
|----------------------|------|-----|--------|----------------------|---|
| | 名称 | | | | SI 単位で表される数値 |
| キ | ユ | IJ | ĺ | Ci | 1 Ci=3.7×10 ¹⁰ Bq |
| $\scriptstyle u$ | ント | ゲ | ン | R | $1 \text{ R} = 2.58 \times 10^{-4} \text{C/kg}$ |
| ラ | | | F | rad | 1 rad=1cGy=10 ⁻² Gy |
| ν | | | Д | rem | $1 \text{ rem}=1 \text{ cSv}=10^{-2} \text{Sv}$ |
| ガ | ン | | 7 | γ | 1 γ =1 nT=10-9T |
| フ | .T. | N | 1 | | 1フェルミ=1 fm=10-15m |
| メー | ートル系 | カラッ | ット | | 1メートル系カラット=200 mg=2×10-4kg |
| ŀ | | | ル | Torr | 1 Torr = (101 325/760) Pa |
| 標 | 準 大 | 気 | 圧 | atm | 1 atm = 101 325 Pa |
| 力 | П | IJ | - | cal | 1cal=4.1858J(「15℃」カロリー), 4.1868J (「IT」カロリー)4.184J(「熱化学」カロリー) |
| Ξ | ク | | \sim | ц | 1 1 |

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