Project Research

Project 7

PR7 Project Research on the Advanced Utilization of Multi-Element Mössbauer Spectroscopy for the Study on Condensed Matter Science

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OBJECTIVES AND PERFORMED RESEARCH SUBJECTS:

Mössbauer spectroscopy is a powerful and well established method for wide variety areas of researches, such as physical-, chemical-, biological-, and earth-sciences. As the Mössbauer resonance line is extremely narrow, hyperfine interactions are well resolved and give us the information on the surrounding electronic states and magnetism. The element specific information, which is one of the most superior features of the Mössbauer spectroscopy, is important and required for modern precise materials science and complex systems such as biological substances. Moreover, Mössbauer spectroscopy is useful and valuable because it usually does not demand the doping of radioactive sources for the measured samples; the decay of the unstable nucleus sometimes induces the change of local electronic states.

The main objectives of this project research are the investigation of the fundamental properties of new materials and the development of the advanced experimental methods by using multi-element Mössbauer spectroscopy under high-magnetic fields.

However, owing to the shutdown of the research reactor for the long term, some of the planned researches have not been performed.

The research subjects performed are as follows:

P7-1 Mössbauer Spectroscopy in Applied Magnetic Field of Multiferroic Iron Oxides (S. Nakamura *et al*.).

P7-3 Mössbauer γ-ray size focused using MCX measured by Si-PIN semi-conductor detector (K. Shinoda, *et al*.).

P7-4 Mössbauer spectroscopy of $Fe_{65}Ni_{35}$ alloy irradiated by proton with 2 MeV (M. Matsushita, *et al*.).

P7-6 Mössbauer Study of $BaFe_2As_2$ under High Magnetic Fields (S. Kitao, *et al*.).

MAIN RESULTS AND CONTENTS OF THIS REPORT:

The following reports were contributed by research groups in this project research.

In order to clarify the mechanism of the multiferroicity in iron oxides, S. Nakamura *et al*. (P7-1) studied h-$ErFeO_3$, which has ferroelectric (T_c > 900 K) and antiferromagnetic (T_N = 120 K) properties, by using ^{57}Fe Mössbauer spectroscopy. The Mössbauer spectra were measured at 4.2 K in an applied magnetic field of 5 T parallel to the c-axis. The ^{57}Fe Mössbauer measurements and the magnetization measurements suggest that the magnetic moment of Fe^{3+} has canted antiferromagnetic nature.

K. Shinoda *et al*. (P7-3) have measured the size of focused 14.4keV Mössbauer γ rays from a ^{57}Co source obtained by a multi-capillary x-ray lens (MCX) to evaluate the performance of Mössbauer micro-spectrometer which has been developed. They also measured the size of focused 6 keV Fe K-α x rays from the ^{57}Co source. To identify the energies, on the contrary to previous measurement, they used a Si-PIN semi-conducting detector to distinguish the each energy.

Irradiation of the energetic particles, such as ions, neutrons and electrons, enlarges the ferromagnetic property in Fe-Ni alloys of concentration ranges near 35 at% Ni with face centered cubic structure (FCC) to high temperatures although the detailed mechanism is not understood. M. Matsushita, *et al*. (P7-4) performed Mössbauer spectroscopic measurement of the proton irradiated $Fe_{65}Ni_{35}$ alloy in order to investigate the variation of the magnetic microstructure caused by the irradiation. The obtained spectra of non-irradiated and irradiated $Fe_{65}Ni_{35}$ alloys at 473 K show the difference, and this indicates the change of the local magnetic structures by the irradiation.

After the discovery of Fe-oxipnictide superconductors, several series of Fe-based superconductors have been successively discovered and extensively investigated to elucidate the mechanism of their superconductivity. Recently, in the isovalent doped $BaFe_2(As_{1-x}P_x)_2$, the electronic nematic phase was found near above the magnetic transition temperature. Since the electronic nematic phase is considered to have some relationship in mechanism of superconductivity, the investigation of this phase has a great importance. S. Kitao *et al*. (P7-6) measured detailed temperature dependences of Mössbauer spectra under high magnetic fields to reveal the magnetic properties of the parent compound, $BaFe_2As_2$. The measured temperature dependent spectra under magnetic fields imply that the nature of the nematic phase is not due to magnetic order but asymmetry in the structure, which is consistent with the initial finding.

PR7-1

Mössbauer Spectroscopy in Applied Magnetic Field of Multiferroic Iron Oxides

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INTRODUCTION: Recently multiferroic properties of iron oxides have been extensively investigated. In addition to the macroscopic investigation such as dielectric and magnetic measurements, the microscopic and dynamic investigations are required in order to clarify the mechanism of the multiferroicity. The ^{57}Fe Mössbauer spectroscopy is one of the appropriate probes. The authors have already conducted Mössbauer spectroscopy on the multiferroics $GaFeO_3$ [1, 2] and $CuFeO_2$ [3, 4], and found the changes in the quadrupole splitting related to the multiferroicity. In the present investigation, we deal with other multiferroic iron oxides by Mössbauer spectroscopy in applied magnetic field. Here in this report, we describe the result of h-$ErFeO_3$. The material is ferroelectric (T_c > 900 K) and at the same time antiferromagnetic (T_N = 120 K). The magnetization measurements and the ^{57}Fe Mössbauer measurements suggest that the magnetic moment of Fe^{3+} has canted antiferromagnetic nature [5, 6].

EXPERIMENTS: The single crystal of ^{57}Fe-enriched h-$ErFeO_3$ thin film deposited on Al_2O_3 (0001) substrate was used as an absorber. The ^{57}Fe Mössbauer spectroscopy was conducted in conventional transmission geometry by using ^{57}Co-in-Rh (50 mCi) as the γ ray source. The incident γ ray direction was parallel to the *c*-axis. The spectra were measured at 4.2 K in applied magnetic field of 5 T parallel to the *c*-axis. The Doppler velocity was calibrated by using Fe metal foil. Lorentzian line shapes were assumed for the analysis.

RESULTS: In Fig.1, Mössbauer spectra of h-$ErFeO_3$ at 4.2 K in applied magnetic field of 5 T is shown. Strong 2-5th line intensity indicates that the Fe^{3+} magnetic moments lie almost in the *c*-plane. Compared with the spectra without magnetic field, the spectral shape dose not change so much. This indicates that the canted antiferromagnetic structure is well retained even in applied magnetic field of 5 T. The outermost lines slightly split into two lines, and thus the spectrum can be analyzed as superposition of two subspectra. The observed field H_{obs} are 41.0 and 42.6 T, slightly smaller and larger than H_{hf} of 41.4 T obtained without magnetic field. Since H_{obs} is a vector sum of H_{hf} and the applied magnetic filed H_{ex}, the two subspectra correspond to the up- and down-domain magnetic moments, respectively. This feature seems to be consistent with the fact that the magnetization curve at 5 K dose not shows hysteresis up to 5 T. The Euler angle (θ, φ) of the hyperfine field (H_{hf}) with respect to the EFG *z*-axis reveals that the Fe^{3+}magnetic moments form a 120º structure in the *c*-plane but incline several degrees toward the *c*-axis. This configuration well depicts a canted antiferromagnetic structure. Noted that $e^2qQ/2$ is -2.432 mm/s, which is larger than that without magnetic field, -2.156 mm/s. This suggests that the local structure around Fe^{3+} ion becomes further distorted by H_{ex}. Such distortion may be caused by a displacement of Fe^{3+} ion toward the *c*-axis, which can be an origin of the magnetoelectric effect of this material.

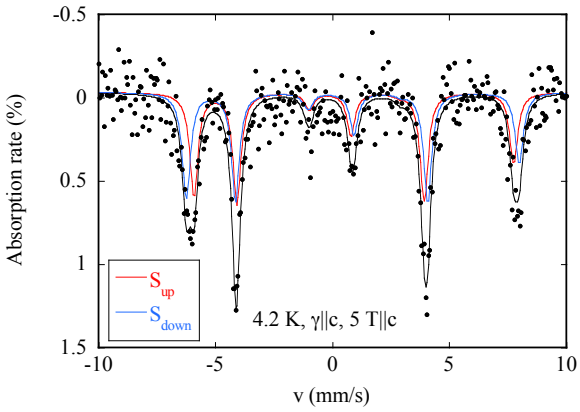

Fig. 1. Môssbauer spectra of h-$ErFeO_3$ at 4.2K in applied magnetic field.

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Mössbauer γ-ray Size Focused Using MCX Measured by Si-PIN Semi-conductor Detector

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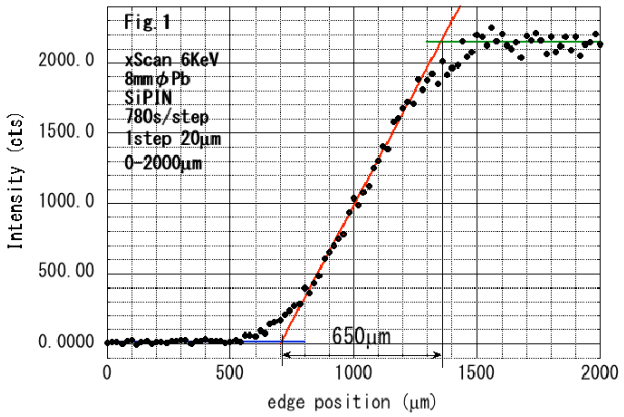
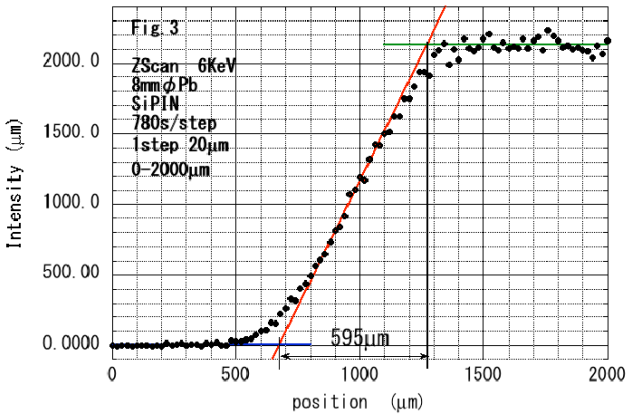
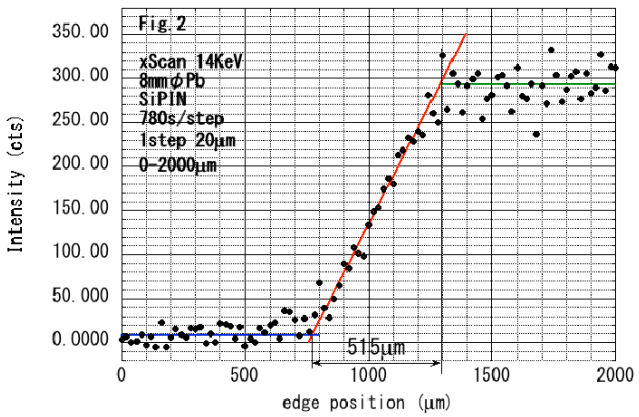
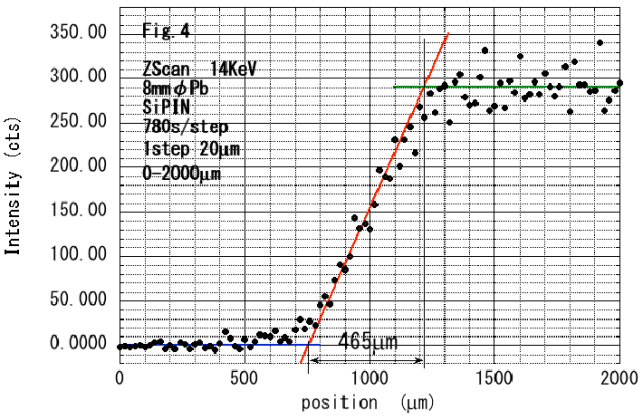
INTRODUCTION: In the 2014 KURRI Progress Report, we estimated focus size of 14.4keV γ-ray of Mössbauer microspectorometer using a multi-capillary X-ray lens (MCX). In that report, a proportional counter was used as γ-ray detector. In this report, a Si-PIN semi-conductor, of which energy resolution is better than a proportional counter, is used to fix the spot size of focused γ -ray by MCX. The spot size is estimated by scanning tungsten edges along horizontal and vertical directions using auto mapping stages (2014 KURRI Progress Report). 6keV FeK X-ray is also emitted from ^{57}Co γ-ray source and focused as 14.4keV. FWHM of 6keV X-ray is also estimated.

EXPERIMENTS and RESULTS: 14.4keV γ-ray and 6keV X-ray intensity distributions are measured with a Si-PIN semi-conductor detector by scanning tungsten edges with 20μm step, 780s exposure per a step, over 2000μm ranges (101steps). Fig.1 and 2 show horizontal intensity distributions of 6keV X-ray and 14.4 keV γ-ray, respectively. Fig.3 and 4 show vertical intensity distributions of 6keV X-ray and 14.4 keV γ-ray, respectively. In KURRI Progress Report 2014, FWHM of 14.4keV was estimated to 400μm. FWHM of 6keV was 650μm. In this study, FWHM of 14.4 keV γ-ray is 515 μm along horizontal and 465 μm vertical orientations. FWHM of focused γ-ray measured with proportional counter is not different from that of a semi-conductor detector.









PR7-3 Mössbauer Spectroscopy of $Fe_{65}Ni_{35}$ Alloy Irradiated by Proton with 2 MeV

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INTRODUCTION: The ferromagnetic range in Fe-Ni alloys of concentration ranges near 35 at% Ni with face centered cubic structure (FCC) was expand to high temperature range due to the irradiation of energetic particles, such as, ions, neutron and electron [1-3]. However it have not been understood that the detail of irradiation-induced ferromagnetism. Therefore we have realized Mössbauer spectra of proton irradiated $Fe_{65}Ni_{35}$ alloy in order to investigate the variation of the magnetic microstructure caused irradiation.

EXPERIMENT: A $Fe_{65}Ni_{35}$ alloy ingot was made by Ar arc-melting. The ingot was homogenized at 1273 K for one week in evacuated silica tube, and then quenched. The $Fe_{65}Ni_{35}$ foils with the thickness of 8 μm were made from the ingot by the mean of rolling. After rolling the alloy was annealed at 1273 K for 3 hours to remove the residual strain. The foils were irradiated at proton with 2 MeV. Mössbauer spectra of $Fe_{65}Ni_{35}$ alloy and that irradiated by proton were been measured at various temperatures.

RESULTS: The obtained Mössbauer spectra of $Fe_{65}Ni_{35}$ alloy and that irradiated by proton were shown in Figure 1. The shape of spectra confirmed above that obtained in 473 K is difference between non-irradiated and irradiated $Fe_{65}Ni_{35}$ alloy, which means that the local magnetic structure was changed by the irradiation.

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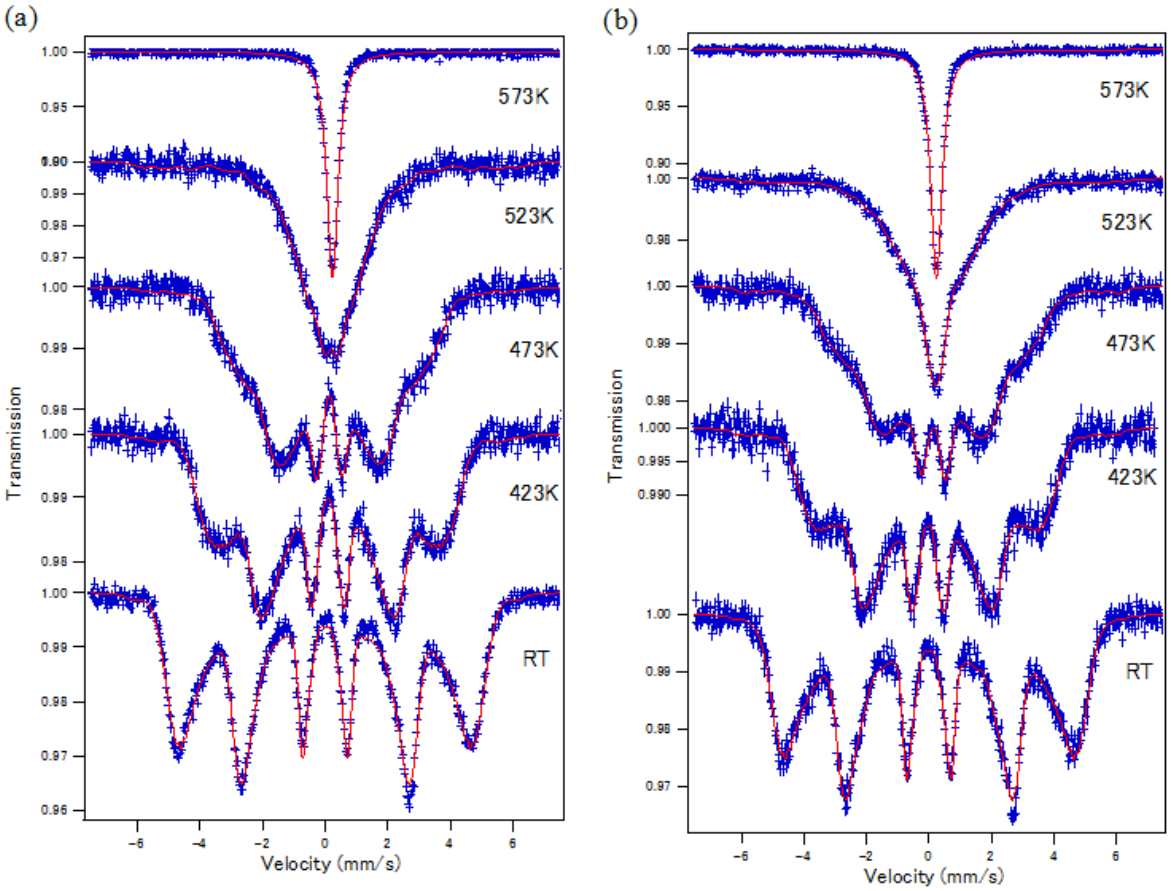

Figure 1. Mössbauer spectra of $Fe_{65}Ni_{35}$ alloy (a) and that irradiated by proton with 2 MeV (b).

PR7-4 Mössbauer Study of $BaFe_2As_2$ under High Magnetic Fields

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INTRODUCTION: After the discovery of the so-called "1111" series of Fe-oxipnictide superconductors, $LaFeAsO_{1-x}F_x$[1], several series of Fe-based superconductors have been successively discovered and extensively investigated to elucidate the mechanism of their superconductivity. Among the related Fe-based superconductors, the so-called "122" series has been found by hole doping (K-doping) of $BaFe_2As_2$[2]. The superconductivity emerges in "122" series by various doping not only with holes or electrons but also by isovalent doping (P-doping). Recently, in the isovalent doped $BaFe_2(As_{1-x}P_x)_2$, the electronic nematic phase was found near above the magnetic transition temperature[3]. Since the electronic nematic phase is considered to have some relationship in mechanism of superconductivity, the investigation of this phase has a great importance.

Since ^{57}Fe-Mössbauer spectroscopy is an essential method to extract the electronic states of Fe, a number of Mössbauer studies on these Fe-based superconductors have been carried out and revealed many important facts, for example, in $LaFeAsO_{1-x}F_x$[4]. Moreover, Mössbauer spectroscopy under high magnetic fields has advantageous to reveal the nature of magnetism in these compounds[5]. In this study, detailed temperature dependences of Mössbauer spectra under high magnetic fields were measured to investigate the magnetic properties of the parent compound, $BaFe_2As_2$.

EXPERIMENTS: $BaFe_2As_2$ was synthesized by heating of a stoichiometric mixture of ground Ba and FeAs in a crucible of aluminum oxide sealed in a quartz tube, as in the reported method[2]. The obtained polycrystalline powder was characterized by x-ray diffraction and magnetic susceptibility measurements. For $BaFe_2As_2$, the superconducting transition was not observed but the magnetic transition was observed at 140K. ^{57}Fe-Mössbauer spectra were measured using a pellet of powder sample using a ^{57}Co source in Rh matrix with a nominal activity of 1.85 GBq. The velocity scales are referenced to α-Fe. Magnetic fields were applied by a superconducting-magnet cryostat with a direction parallel to the γ-rays.

RESULTS AND DISCUSSION: Mössbauer spectra of $BaFe_2As_2$ under the magnetic transition temperature showed magnetically-split pattern as in Fig 1(a) at 2.5K. When high magnetic fields are applied, the direction of magnetic moments has changed partly towards the direction of applied magnetic fields as in Fig 1(b). The spectra were well understood by a model of antiferromagnetic powder under the magnetic fields. This fact is a good proof that the antiferromagnetic order has occurred at the magnetic transition temperature.

On the other hand, Mössbauer spectra of $BaFe_2As_2$ above the magnetic transition temperature has not magnetically split pattern as shown in Fig. 1(a) above 140K. The spectra showed 4-line patterns under the magnetic fields as shown in Fig. 1(b). This pattern can be well understood as a paramagnetic feature, where the magnetic moments are entirely aligned to the direction of the applied magnetic fields. The spectrum at 160K, which is near above the magnetic transition temperature, showed the wider line width than spectra far above. This broadening of the line width is considered to be due to the electronic nematic phase. However, the line broadening has not appeared in the spectrum under the magnetic field. That is, the broadening may not be originated by internal magnetic fields but by quadrupole splittings. This fact implies the nature of the nematic phase is not due to magnetic order but asymmetry in the structure, which is consistent with the initial finding[3].

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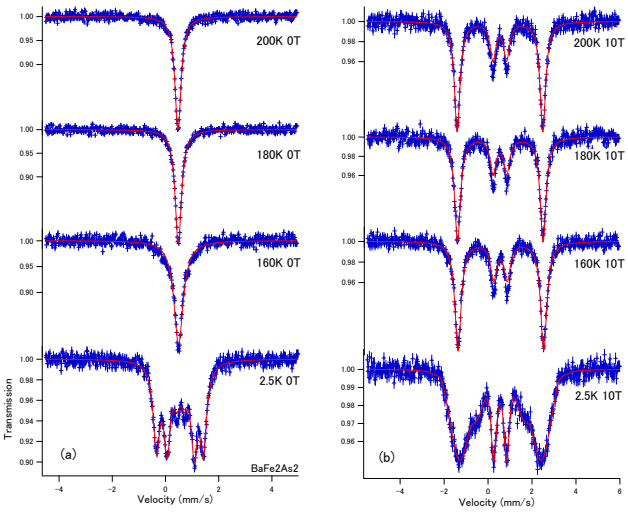

Fig. 1. Typical Mössbauer spectra of $BaFe_2As_2$ (a) without magnetic field and (b) under magnetic fields of 10T.