

I. Project Research

Project 5

PR5 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:

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. Combination use of the high-magnetic-field superconducting magnet was also essential to study the magnetism of the materials. 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. Thus, the Mössbauer spectroscopy is applied to widely various areas of researches, such as physical, chemical, biological, and earth sciences. Moreover, element-specific or isotope-specific information is one of the most irreplaceable features of the Mössbauer spectroscopy. Therefore, promotion of the variety of Mössbauer isotope provides more useful and valuable methods for modern precise materials science of complex systems, such as biological substances, multi-layer films, and complicated-structured matter.

In this term of the year, some of the planned researches have not been performed because of the shutdown of the research reactor. The research subjects performed are as follows:

- P5-2 Mössbauer microspectrometer using Si-PIN semi-conductor detector and its application to mineral science (K. Shinoda *et al.*)
- P5-3 ^{57}Fe Mössbauer spectra of $\text{Sr}_2\text{VFeAsO}_{3-d}$ ($d=0.232, 0.267, \text{ and } 0.509$) (Y. Kamihara *et al.*)
- P5-4 Relationship between Heme Electronic Structure and Oxygen Affinity of Myoglobin (Y. Yamamoto *et al.*)
- P5-8 Development of Mössbauer spectroscopy system on ^{67}Zn (M. Saito *et al.*)
- P5-9 Mössbauer Study of $\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2$ 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.

K. Shinoda *et al.* (P5-2) have developed Mössbauer microspectrometer using Si-PIN semiconductor detector and applied to studies of crystallographically-oriented single crystals of thin sections of augite from different occurrences. Obtained three sets of quadrupole doublets were well identified with Fe^{2+} in M1 and M2 sites, and Fe^{3+} in M1 site in pyroxene structure. From the intensity ratio of each doublets, the orientation of the electric field gradient vector was discussed. As a result, good concentration of orientation in Fe^{2+} in M2 site was found, although Fe^{2+} in M1 site did not show concentration.

Y. Kamihara *et al.* (P5-3) studied $\text{Sr}_2\text{VFeAsO}_{3-d}$, which are related compounds of FeAs-based superconductor with blocking layer and some of which show superconductivity and antiferromagnetic ordering of Vanadium. Mössbauer spectroscopy was applied to investigate magnetism of Fe in these compounds. For the samples with $d = 0.232, 0.267, \text{ and } 0.509$, the spin density wave phase was observed, while magnetically-ordered Fe was not observed for superconducting $\text{Sr}_2\text{VFeAsO}_{3-d}$. The result indicates that Fe has two different magnetic phase, depending on the oxygen deficiency.

Y. Yamamoto *et al.* (P5-4) investigated the Mössbauer spectroscopy to elucidate the relationship between electronic structure of heme Fe atom and oxygen affinity of myoglobin(Mb). Through the studies of chemically-modified heme cofactors, obtained isomer shifts could not be simply interpreted as the electronic nature of the hemes. On the other hand, quadrupole splitting values decreased with decreasing the electron density of the hemes. These facts are useful to elucidate the electronic structure of the oxy form of Mb, to understand the oxygenation and autoxidation processes of Mb.

M. Saito *et al.* (P5-8) attempted to observe the ^{67}Zn Mössbauer absorption spectrum, which could be useful for experiments requiring extremely high energy resolution. To obtain the ^{67}Cu Mössbauer source, ZnO crystals were irradiated by KURRI-LINAC through photonuclear reaction. Although measurement of the Mössbauer spectrum was tried, expected absorption was not observed. It is considered to be due to the vibrational noise of the vacuum chamber. Further development of the ^{67}Zn Mössbauer spectroscopic system is in progress.

S. Kitao *et al.* (P5-9) measured detailed temperature dependences of Mössbauer spectra under high magnetic fields to reveal the magnetic properties of the Fe-based superconductor $\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2$. From the temperature dependence of Mössbauer spectra, small broadening of the line width were observed at the temperature a little above the superconducting transition temperature. The measurements under high magnetic fields revealed the line broadenings are due to quadrupole splittings, which is consistent to the fact that the electronic nematic states has the small asymmetry in the structure.

PR5-1 Mössbauer Microspectrometer Using Si-PIN Semi-conductor Detector and its Application to Mineral Sciences

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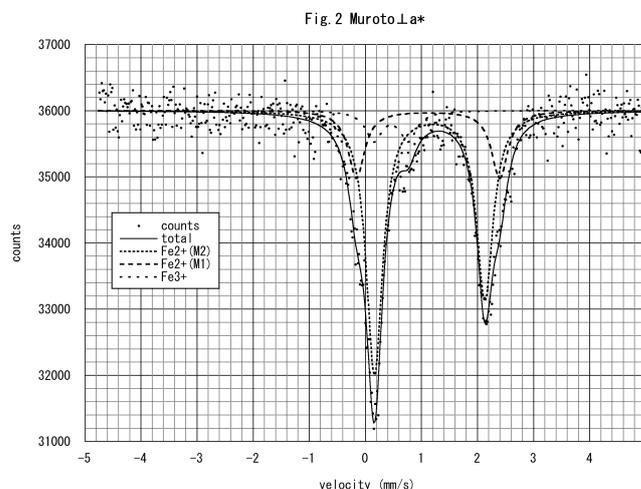
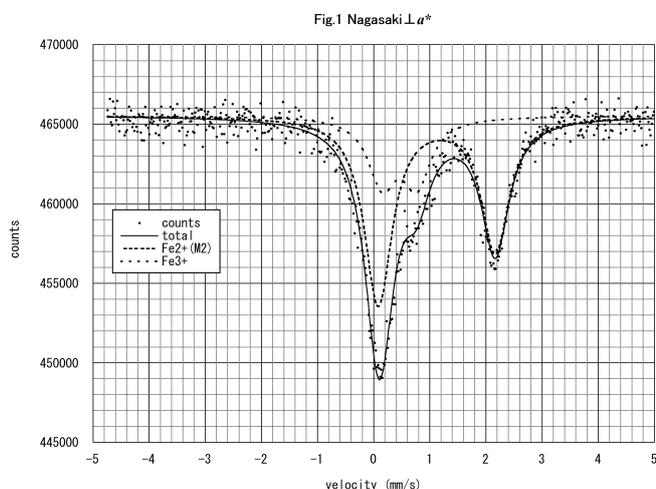
INTRODUCTION: Mössbauer microspectrometer using Si-PIN semi-conductor detector was used to measure Mössbauer spectra of single crystals of mineral thin sections. A Pb pin-hole (1mm ϕ) was used to limit measuring region in a thin section. A Si-PIN semi-conductor of which energy resolution is better than a proportional counter is suitable for micro-measurements. Whereas two peaks' intensity of Q-splitting doublets is equal for powder sample, intensity ratio of Q-splitting doublet of single crystal varies between 0.6 and 3 depending on the angle between γ -ray and electric field gradient vector. Augite is a major rock-forming mineral including Fe²⁺ and Fe³⁺, and they distribute at M1 and M2 sites in pyroxene structure. To fitting out M1Fe²⁺, M2Fe²⁺ and M1Fe³⁺ Q-splitting doublets from raw Mössbauer data of single crystal thin section of augite, orientations of electric field gradient vector of M1 and M2 sites for Fe²⁺ and Fe³⁺ is important. In this study, the orientation of electric field gradient vector of M1Fe²⁺ and M2Fe²⁺ were estimated by measuring thin sections of augite of which crystal graphic orientation were determined by X-ray precession camera.

EXPERIMENTS and RESULTS: Crystal graphically oriented thin sections perpendicular to a^* - b^* - and c^* -axes of augite from two different occurrences (Muroto and Nagasaki) were prepared for Mössbauer microspectrometer. Fig.1 shows Mössbauer spectrum of augite thin section perpendicular to a^* axis from Na-

gasaki. Two sets of Q-splitting doublets were identified. The wider Q doublet of 2.08mm/s was assigned to M2Fe²⁺ and the narrower doublet of 0.60 mm/s was M1Fe³⁺. On the fitting of raw data of Fig.1, the ratio of intensity of the narrower doublet was fixed to 1:1, and that of the wider doublet was not fixed and calculated to 0.716. Fig.2 shows Mössbauer spectrum of augite thin section perpendicular to a^* axis from Muroto. three sets of Q-splitting doublets were identified. The first is strong doublet of 1.97 mm/s Q-splitting which is due to M2Fe²⁺, the second is middle doublet of 2.55 mm/s due to M1Fe²⁺ and weak doublet of 0.61 mm/s due to M1Fe³⁺. On the fitting of raw data of Fig.2, the ratio of intensity of the weak doublet was fixed to 1:1, the strong doublet due to M2Fe²⁺ was fixed to 0.716 from Fig.1 and intensity ratio of middle doublet was not fixed and finally calculated to 1.00. From the relation between the intensity ratio of doublet (x) and the angle between γ -ray and electric field gradient vector of augite (θ),

$$x = \frac{1 + \cos^2 \theta}{2/3 + \sin^2 \theta}$$

θ of six thin sections were calculated. From the two sets of θ s, orientations of electric field gradient vector of M1Fe²⁺ and M2Fe²⁺ of augite were plotted on stereographic projections. As the results, M2Fe²⁺ shows good concentration of orientation, but M1Fe²⁺ was not show concentration. To improve data fitting, the proper doublet parameter of M1Fe³⁺ must be used.



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INTRODUCTION: Layered oxypnictide Ae₂T_MFePnO_{3-d} (Ae = Alkaline earth metal, T_M = Transition metal) (21113) consists of carrier conducting FePn (Pn = P and As) layer and carrier blocking Ae₂T_MO₃ layer. Several 21113 compounds show superconducting phase at low temperatures. Hyperfine fields (B_{hf}) measurements experienced by nuclei of atoms at crystallographic sites in magnetic and/or antiferromagnetic metals are of interest in view point of hyperfine interactions and important for their use in the determinations of nuclear magnetic dipole moments by a variety of methods including those based on low-temperature nuclear orientation. Guang-Han Cao et al reported that Sr₂VFeAsO_{3-d} is an FeAs-based layered oxypnictide superconductor, which exhibits antiferromagnetic ordering under 150 K originating in local d-electron moments of vanadium, and the superconducting transition temperature T_c is 24 K.[1,2] In this study, we focus on magnetic phase of Sr₂VFeAsO_{3-d} as a complex magnetic compounds. [1-8]

Element-specific magnetism and electronic phase of Fe sublattice in Sr₂VFeAsO_{3-d} are elucidated using ⁵⁷Fe Mössbauer spectroscopy. Studies on hyperfine fields B_{hf} experienced by nuclei are of interest in view point of hyperfine interactions and important for their use in the determinations of nuclear magnetic dipole moments.

EXPERIMENTS: Polycrystalline samples of Sr₂VFeAsO_{3-d} were prepared by the solid-state reactions in a sealed silica tube using dehydrated SrO, FeAs, Vanadium oxides, and V as starting materials. Then, a mixture of the three powders was pressed into pellet and heated in doubly sealed silica tubes at 1050-1300 °C for 40 h. All procedures were carried out in an Ar-filled glove box (MIWA Mfg; O₂, H₂O < 1 ppm). The crystal phase of the obtained product was examined by powder X-ray diffraction (XRD; RigakuRINT-2500) using CuK α radiation. Almost all the diffraction peaks are assigned to the Sr₂VFeAsO_{3-d} phase. Electrical resistivity measurements were performed at 2–300 K by a dc four-probe technique using silver paste as electrodes. Magnetization measurements were performed for polycrystalline samples using a Quantum Design magnetic properties measurement system (MPMS). The ⁵⁷Fe Mössbauer (MS) experiment on the two series of compounds, Sr₂VFeAsO_{3-d} (x = 0.232, 0.267, and 0.509) was performed with conventional ⁵⁷Fe MS equipment using 14.4 keV γ -rays from a ⁵⁷Co source in an Rh matrix.

RESULTS: ⁵⁷Fe MS to the samples of d=0.232, 0.267, and 0.509 of Sr₂VFeAsO_{3-d} were measured and analyzed

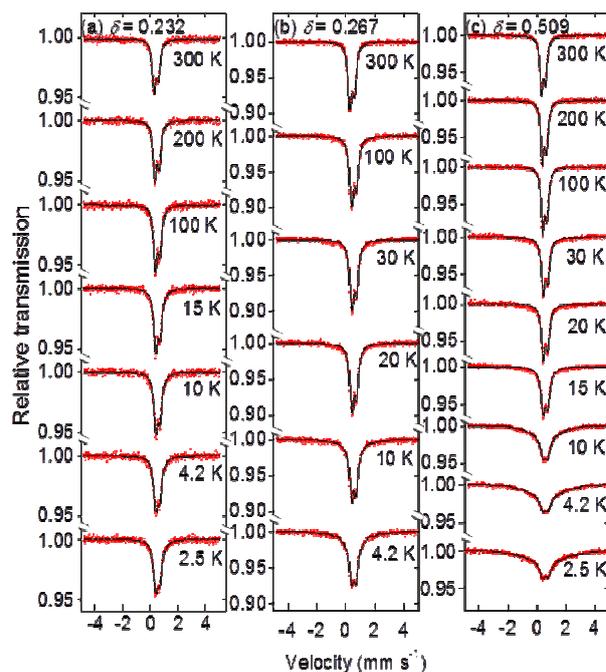


Fig. 1. ⁵⁷Fe Mössbauer spectra (MS) of polycrystalline Sr₂VFeAsO_{3-d} (d = 0.232, 0.267 and 0.508) at several temperatures described in the figure. The solid lines for each samples are fitted patterns provided that internal magnetic fields with wide distribution exist around ⁵⁷Fe. Such internal magnetic field indicate existence of spin density wave in Sr₂VFeAsO_{3-d} (d = 0.232, 0.267 and 0.508).

for obtaining quantitative value of internal magnetic field. As a result, the existence of spin density wave phase are observed for x = 0.232, 0.267, 0.509, while magnetic ordered Fe are not observed for superconducting Sr₂VFeAsO_{3-d} samples.[9] The result indicates that Fe of Sr₂VFeAsO_{3-d} shows two magnetic phase, which stabilities depend on oxygen deficiency.

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PR5-3 Relationship between Heme Electronic Structure and Oxygen Affinity of Myoglobin

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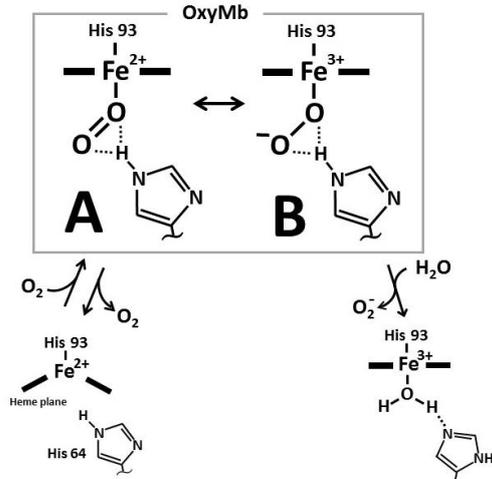
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INTRODUCTION: The function of an oxygen storage hemoprotein, myoglobin (Mb), is regulated through heme electronic structure, in addition to heme environment furnished by nearby amino acid residues. We found that a decrease in the electron density of the heme Fe atom (ρ_{Fe}) leads to lowering oxygen affinity and a decrease in the autoxidation rate of the protein.¹ These findings could be reasonably explained in terms of the effect of a change in the ρ_{Fe} on the resonance $A \leftrightarrow B$ of oxy form of Mb (oxyMb) (scheme 1). In this study, we measured Mössbauer spectra of oxyMbs reconstituted with some chemically-modified heme cofactors (Fig. 1) in order to characterize the relationship between the ρ_{Fe} and the resonance $A \leftrightarrow B$. The formal charges of heme Fe in the canonical structures A and B are +2 and +3, respectively, and hence the effect of a change in the ρ_{Fe} on the resonance $A \leftrightarrow B$ could be analyzed through the resonance hybrid of the formal charge of heme Fe which is sharply reflected in the Mössbauer spectral parameters, i.e., isomer shift (IS) and quadrupole splitting (QS).

EXPERIMENTS: ApoMb was prepared from sperm whale Mb, using the standard procedure, and reconstituted with ⁵⁷Fe-labelled heme cofactors. 2 mM Mbs in 50 mM potassium phosphate buffer, pH = 7.4, were cooled rapidly in liquid nitrogen bath. The Mössbauer measurements were performed at 3-6 K.



Scheme 1. Oxygenation and autoxidation of Mb, and the resonance structures A and B of oxyMb.

Heme	IS(mm/s)	QS(mm/s)
Meso	0.260	2.36
3,8-DMD	0.260	2.32
Proto	0.271	2.29
7-PF	0.264	2.28
2,8-DPF	0.270	2.21

Heme	R ₂	R ₃	R ₇	R ₈
Meso	CH ₃	CH ₂ CH ₃	CH ₃	CH ₂ CH ₃
3,8-DMD	CH ₃	CH ₃	CH ₃	CH ₃
Proto	CH ₃	CH=CH ₂	CH ₃	CH=CH ₂
7-PF	CH ₃	CH ₂ CH ₃	CF ₃	CH ₂ CH ₃
2,8-DPF	CF ₃	CH ₃	CH ₃	CF ₃

Fig. 1. Chemically-modified heme cofactors used in the study, and the obtained Mössbauer spectral parameters.

RESULTS: The Mössbauer spectrum of oxyMb reconstituted with ⁵⁷Fe-labelled proto (Fig. 2) was almost identical to that previously reported.² The IS values of the heme cofactors ranged from 0.260 to 0.271 mm/s and could not be simply interpreted on the basis of the electronic nature of the hemes. On the other hand, the heme cofactors were arranged as 2,8-DPF < 7-PF \approx Proto < 3,8-DMD < Meso, in order of increasing QS (Fig. 1), indicating that the QS decreases with decreasing the ρ_{Fe} . This result confirmed that a decrease in the ρ_{Fe} results in shifting the resonance $A \leftrightarrow B$ toward structure A. Proto and 7-PF exhibited similar QS values, supporting that the ρ_{Fe} values of the two heme cofactors are closely similar to each other. Thus, Mössbauer spectroscopy is a powerful tool to elucidate the electronic structure of oxyMb.

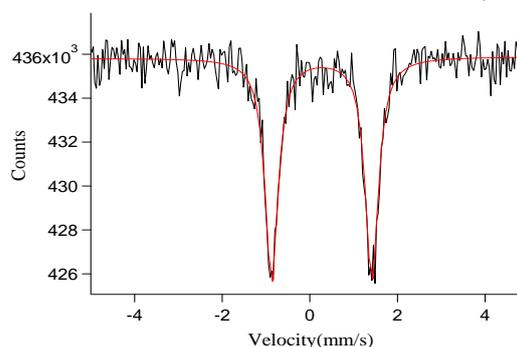


Fig. 2. Mössbauer spectrum of oxyMb (proto) at 3 K.

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PR5-4 Magnetic Property and Local Structures of Functional Irons in Glass by Mössbauer Spectroscopy

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INTRODUCTION and AIM: Glass is used in many applications in our every-day lives and has new applications. Coexisting divalent iron ions (Fe^{2+}) and trivalent iron ions (Fe^{3+}) in glass affect the transmission from the near-ultraviolet (NUV) to the near-infrared (NIR) range (hereinafter denoted as “transmission_{NUV_NIR}”) and coloring (value, chroma, hue) of glass.^[1] The transmission_{NUV_NIR} and coloring determine the utilization purpose of glass in industry. Commercial glass ineluctably contains very low concentrations of irons (about 0.01-0.1 wt.% iron oxide concentration), which are derived from raw materials or industrial processes. Higher iron concentration are added by manufacturing design. The iron concentrations mainly affect the value of coloring. Fe^{2+} and Fe^{3+} mainly affect the chroma and hue of coloring. Fe^{2+} gives absorption mainly in the NIR range, resulting in bluish coloring.^[1] Fe^{3+} gives strong absorption mainly in the visible to NUV range, resulting in yellowish coloring.^[1]

Two macro parameters have been used in industry to control transmission_{NUV_NIR} and coloring: (1) the total iron ion mass concentration in terms of Fe_2O_3 (hereinafter denoted as “iron oxide concentration; $M_{\text{Fe}_2\text{O}_3}$ ”), and (2) the ratio of the number of Fe^{2+} to the number of total irons (hereinafter denoted as “ $\text{Fe}^{2+}/\Sigma_n\text{Fe}$ ”).

Three dimensional (3D) local structures and property of iron ions should also contribute to the transmission_{NUV_NIR} and coloring. Although many scientists proposed structures of Fe^{2+} and Fe^{3+} by traditional measuring methods, they could not explain the property of irons in glass completely.

By enriching with ^{57}Fe , we made basic soda-lime glass samples that had 0-0.6 $^{57}\text{Fe}^{2+}/\Sigma_n\text{Fe}$ and $M_{\text{Fe}_2\text{O}_3}$ of 0.1, 0.5, 1.5, and 5.0 wt.%.

We have investigated these samples by nuclear resonant inelastic scattering (NRIS) and XAFS methods at synchrotron radiation, and revealed the 3D local structure around iron atoms in sub-nanometer region (Okada et al, submitted to X-ray Spectrometry). And we found the capability of complex magnetic fields of Fe^{3+} in glass at RT. Then we have proposed Mössbauer measurements to reveal the magnetic states and internal magnetic fields from Fe^{3+} and Fe^{2+} atoms, independently, at various temperatures.

EXPERIMENTS: The measurements were performed using conventional Mössbauer spectrometer. The specimens for Mössbauer measurements were tuned to 10 mm-phi pellet from the ^{57}Fe enriched glass powders. We investigated samples at room temperature (RT), 150 K and 77 K.

RESULTS and DISCUSSION: The three glass samples

with 0.5 wt.% $M_{\text{Fe}_2\text{O}_3}$ were measured at RT. As shown in Fig. 1, there were the differences of continuous components between samples that had different $\text{Fe}^{2+}/\Sigma_n\text{Fe}$. These wide structures indicated the local magnetization around iron atoms. The two Fe^{3+} components with large internal magnetic field and the two Fe^{2+} components with large quadrupole splitting have been determined from their isomer shifts by our fittings shown in Fig. 1. And the results from glass with 0.1-5 wt.% $M_{\text{Fe}_2\text{O}_3}$, indicated that the Fe^{3+} and Fe^{2+} atoms in glass had separate structures. Moreover we measured glass with 0.5 wt.% $M_{\text{Fe}_2\text{O}_3}$ and with 0 $\text{Fe}^{2+}/\Sigma_n\text{Fe}$ at 150 K and 70 K. The internal magnetic field from Fe^{3+} in the sample was about 51 T and had internal distribution. We concluded that about 90 % of the Fe^{3+} in glass had local magnetic order like antiferromagnetic materials. On the other hand, we concluded that Fe^{2+} atoms had no magnetic order.

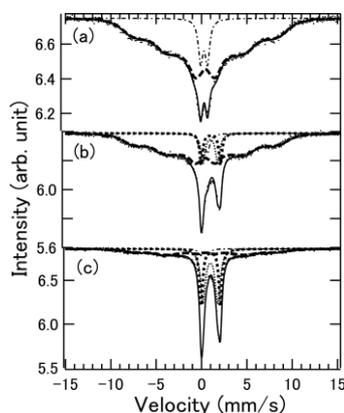


Fig. 1. Mössbauer spectra of glass at RT with 0.5 wt.% $M_{\text{Fe}_2\text{O}_3}$ and with $\text{Fe}^{2+}/\Sigma_n\text{Fe}$ of (a) 0, (b) 0.2, and (c) 0.6. The dot lines and dot-and-dash lines were fitting curves from Fe^{3+} and Fe^{2+} , respectively. The solid line showed the total fit.

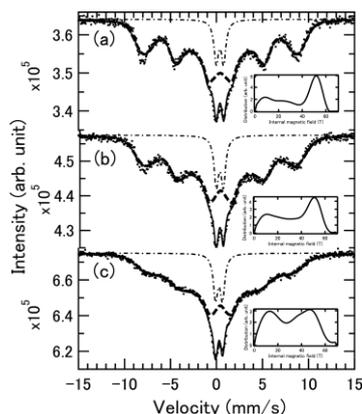


Fig. 2. Mössbauer spectra of sample glass at (a) 70 K, (b) 150 K, and (c) R.T. with 0.5 wt.% $M_{\text{Fe}_2\text{O}_3}$ and with 0 $\text{Fe}^{2+}/\Sigma_n\text{Fe}$. Same lines as Fig. 1. The inset panels showed internal magnetic fields of each temperature.

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INTRODUCTION: Among various Mössbauer spectroscopy systems, ^{67}Zn Mössbauer spectroscopy system shows relatively very high energy resolution: the energy width of the gamma rays is narrow $\Delta E \sim 50$ peV comparing with the gamma-ray's energy $E_0 \sim 93$ keV, and the relative energy uncertainty of the gamma rays $\Delta E/E_0$ is the order of $\Delta E/E_0 \sim 10^{-15}$. [1,2]

Therefore, ^{67}Zn Mössbauer spectroscopy system has been used to study the various physics experiments which require high energy resolution such as the detection of the gravitational red shift of the photons as well as to study the solid state physics on materials including ^{67}Zn .

However, in spite of its usefulness, only few group succeeded to develop ^{67}Zn Mössbauer spectroscopy so far owing to its difficulty: the system requires very accurate control of the relative velocity between the source and the absorber. Recently, by trial experiment, the Mössbauer absorption of ^{67}Zn has been observed by authors using the radioactive Mössbauer source produced by the electron linear accelerator (KURRI-LINAC).

The purpose of this study is to establish the ^{67}Zn Mössbauer spectroscopy system by controlling velocity accurately using a piezo driving system.

EXPERIMENTS: In this experiment, the source of ^{67}Zn Mössbauer spectroscopy is ^{67}Zn in ZnO mono-crystal produced by the $^{68}\text{Zn}(\gamma, p)^{67}\text{Cu}$ reaction using high energy gamma-rays from the platinum target of the LINAC. The ZnO mono-crystal was irradiated by the high energy gamma-rays for three days and taken out from the target room one-day later after the irradiation. The source was, then, annealed at 700 °C for 9 hours in Ar atmosphere. Gamma rays and X rays were detected by Ge-semiconductor detector. In Fig. 1, we show the obtained energy spectrum.

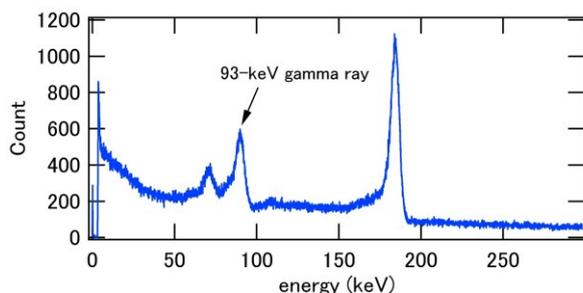


Fig. 1. Energy spectrum of radiations from the source.

The 93-keV gamma-rays from ^{67}Zn source could be nicely observed and selectively used to obtain the Mössbauer spectrum. The source and the ^{67}ZnO mono-crystal

absorber were set to the vacuum chamber and cooled down to around 10 K. The chamber was put on the vibration-isolated table for the isolation from the external vibration and a piezo driving stage (P752, PI Japan Co., Ltd.) was used for a velocity control. Against for the stable absorber, a sinusoidal motion with the amplitude of 12 $\mu\text{m/s}$ was induced to the source.

RESULTS: The obtained ^{67}Zn Mössbauer spectrum is shown in Fig. 2. The velocity calibration was performed by the time dependence of the piezo elongation. The error bar shows the standard deviation of the obtained value.

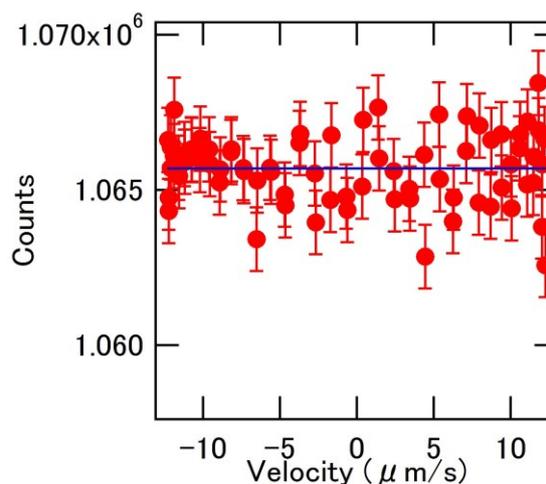


Fig. 2. Obtained ^{67}Zn Mössbauer spectrum.

From the previous studies, absorption with the absorption depth ratio of 0.7 % is expected at zero position of the velocity.[1] However, from the experiment, the absorption depth ratio is, if any, estimated to be less than 0.1 %. This result suggests that the strong reduction of the depth of the absorption occurs.

After the experiment, we checked the vibrational noise of the vacuum chamber by using the laser-Doppler velocimeter. The result suggests that the vibrational noise of our system is larger than our expectation and too large to obtain the ^{67}Zn Mössbauer spectrum.

From the experiment, we could obtain fundamentally important knowledge about the current system such as the gamma-rays count-rate and degree of the external noise. Based on the obtained knowledge, further development of the ^{67}Zn Mössbauer spectrum is in progress.

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INTRODUCTION: After the discovery of so-called “1111” series of Fe-oxipnictide superconductors, $\text{LaFeAsO}_{1-x}\text{F}_x$ [1], several series of Fe-based superconductors have been extensively investigated. Among related Fe-based superconductors, so-called “122” series has been of great interest because the superconductivity emerges with various doping methods. That is, the superconductivity was observed not only with hole doping, $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ [2] or electron doping, $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$, but also with isovalent doping, $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$. Recently, the electronic nematic phase was found in the isovalent-doped $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ [3]. This electronic nematic phase is considered to have an important relationship with superconductivity. The electronic nematic phase was also found in $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$. However, it is not clear in the case of $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$. Therefore, it is important to investigate the electronic nematic phase in $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$.

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 $\text{LaFeAsO}_{1-x}\text{F}_x$ [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 properties of the electronic nematic phase.

EXPERIMENTS: $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ was synthesized by heating of a stoichiometric mixture of ground Ba and FeAs with a little excess of K 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. The doping level of $x = 0.4$ is the optimal doping, that is, the superconducting transition temperature (T_c) has the maximum value of about 38 K. ^{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 $\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2$ showed a singlet pattern down to 4.2 K as in Fig 1(a). This implies the optimally-doped superconductor $\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2$ has no magnetic order down to 4.2 K. However, the line width at a little above T_c , showed a small broadening. This line broadening is considered to be due to the electronic nematic phase at a little

above T_c . On the other hand, the line width broadening was not clearly observed below T_c .

When high magnetic fields were applied, 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. However, Mössbauer spectra under the magnetic fields did not show specific broadened feature even at a little above T_c . Since the spectra did not show broadened magnetically-split spectra, the line broadening due to small internal magnetic fields was excluded. 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 due to asymmetry in the structure. This is consistent with the original finding of the nematic phase due to small structural anisotropy in the magnetic torque measurements[3].

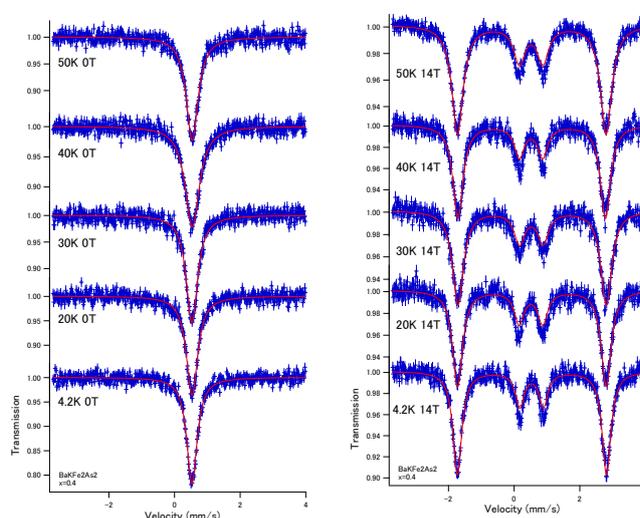


Fig. 1 Typical Mössbauer spectra of $\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2$ (a) without magnetic fields and (b) under magnetic fields of 14T.

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