

PR13 Project Research on the Advanced Utilization of Multi-Element Mössbauer spectroscopy for the Study of Condensed Matter

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OBJECTIVES AND PERFORMED RESEARCH

SUBJECTS: Mössbauer spectroscopy is a powerful and well established method in a wide variety of research areas, 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 unwanted 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 unexpected shutdown of the research reactor and the tracer laboratory for the long term, some of the planned researches have not been performed.

The research subjects performed are as follows:

- P13-2 Magnetism of an iron oxypnictide Cr-doped CeFePO (T. Okano *et al.*).
- P13-3 A study of formation of Au(III) surface complex on manganese dioxide by ^{197}Au Mössbauer spectroscopy (T. Yokoyama *et al.*).
- P13-5 Mössbauer Spectroscopy of Novel Ferroelectric Materials (S. Nakamura, *et al.*).
- P13-6 Mössbauer spectra of oriented thin sections and small grain of magnetite single crystal (T. Kamiryo, *et al.*).
- P13-7 Electronic States of Negative/Zero Thermal Expansion Materials (I. Yamada *et al.*).
- P13-9 Mössbauer Study of Fe-Based Superconductors, $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ (S. Kitao, *et al.*).

MAIN RESULTS AND CONTENTS OF THIS REPORT: The following reports were contributed by research groups in this project research.

T. Okano *et al.* (P13-2) have measured ^{57}Fe Mössbauer spectra of Cr-doped CeFePO, for which they demonstrated a novel ferromagnetic QCP. From the obtained spectra, they showed that transition metal Cr substitution for Fe in CeFePO gradually generates a FM ordering of Ce sublattice and suppresses the ferromagnetic ordering by further doping, whereas Fe sublattice does not show magnetic ordering.

T. Yokoyama *et al.* (P13-3) performed ^{197}Au Mössbauer spectroscopic study of manganese dioxides, and the information obtained from the analysis of the measured spectra indicated a formation of Au(III) surface complex on manganese dioxide.

To investigate the origin of the multiferroics and identify phase relation in the ferroelectric catalysis, S. Nakamura *et al.* (P13-5) studied spinel type FeCr_2O_4 and Sn/BaTiO_3 as multiferroics and ferroelectric catalysis, respectively. From the ^{57}Fe Mössbauer spectrum of FeCr_2O_4 at 4.2 K in applied magnetic field of 2T and the ^{119}Sn Mössbauer spectrum of Sn/BaTiO_3 specimen at room temperature, the electronic states relevant to multiferroics were discussed.

T. Kamiryo, *et al.* (P13-6) measured Mössbauer spectra of oriented thin sections of natural magnetite to observe the dependence of absorption peak intensities on the crystallographic orientation, and the proposed model were discussed to explain the result.

To develop zero thermal expansion (ZTE) materials, I. Yamada *et al.* (P13-7) studied the chemical substitution effect of cubic perovskite oxide $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$ on thermal expansion property by X-ray diffraction, thermal analysis, and Mössbauer spectroscopy, and the obtained results indicate that the unusual thermal expansion properties of $\text{LaCu}_3\text{Fe}_{4-x}\text{Mn}_x\text{O}_{12}$ are associated with valence transitions of Fe ions.

To understand the nature of the Fe-oxypnictide superconductors, S. Kitao *et al.* (P13-9) studied the magnetic properties of the optimally-doped superconductor $\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2$, and under-doped superconductor $\text{Ba}_{0.8}\text{K}_{0.2}\text{Fe}_2\text{As}_2$ using Mössbauer spectroscopy. From the obtained spectra, the co-existence of magnetism and superconductivity was not observed in the optimally-doped $\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2$. On the other hand, Mössbauer spectra of under-doped $\text{Ba}_{0.8}\text{K}_{0.2}\text{Fe}_2\text{As}_2$ showed magnetic order below around 100 K, implying that the superconductivity and magnetic order co-exist.

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INTRODUCTION: A continuous phase transition, which is stimulated by an external pressure, magnetic field, and/or chemical doping at zero temperature, is called a quantum phase transition (QPT). The critical point of QPT is called a quantum critical point (QCP), where second-order phase transitions have been suppressed to zero from finite temperatures. QCPs have attracted much attention since some materials exhibit superconductivity in chemical compositions proximity to a QCP. [1–5] An iron oxypnictide CeFePO is a related compound of an iron-based superconductor LaFePO [6] CeFePO is also one of heavy-fermion materials with Ce 4f-electron's sublattice inducing Kondo screening. [7,8] In the case of Ruderman-Kittel-Kasuya-Yosida (RKKY) exchange interaction exceeding Kondo screening, long range magnetic order appears. While many Ce-based Kondo lattices show antiferromagnetic (AFM) ground states, only few systems are known with ferromagnetic (FM) order competing Kondo screening. In CeFePO, magnetic ordering is almost quenched and/or suppressed. [8] For Cr-doped CeFePO, we demonstrate a novel ferromagnetic QCP. [1] These ferromagnetic 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.

EXPERIMENTS: Polycrystalline CeFe_{1-x}Cr_xPO ($x = 0.000\text{--}0.692$) were prepared by a solid state reaction. Samples were characterized by X-ray diffraction (XRD), magnetization measurements, and ⁵⁷Fe Mössbauer spectroscopy (MS) at various temperatures. Magnetization measurements were performed on a superconducting quantum interference device (SQUID).

RESULTS:

Almost all XRD diffraction peaks are assigned to calculated Bragg positions of the CeFePO phase with space group $P4/nmm$ (No. 129), although there are several weak peaks which can be attributed to Cr₂P, Ce₂O₃, and CeO₂. These impurities provide no significant influence on magnetic measurements of CeFe_{1-x}Cr_xPO because it has been confirmed that they do not show ferromagnetic phase down to 2 K. Samples contained less than 1 at.% of Cr₂P and 2 at.% of Ce₂O₃ for $x = 0.500$. However, for $x > 0.500$, a ratio of Ce₂O₃ phase increases rapidly and CeO₂ phase emerges. Figure 1 shows ⁵⁷Fe MS of $x = 0.10$

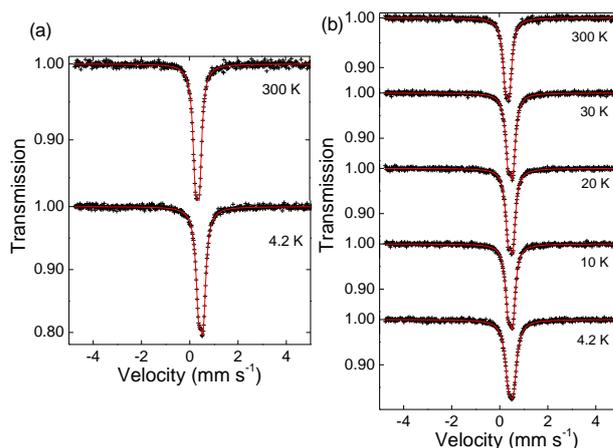


Fig. 1 Observed ⁵⁷Fe MS of $x = 0.100$ (a), 0.200 (b) for CeFe_{1-x}Cr_xPO at several temperatures. Each solid line is a theoretical spectrum that includes a finite quadrupole splitting. All MS can be fitted with no magnetic splitting indicating paramagnetic phase of Fe sublattice.

and 0.20 for CeFe_{1-x}Cr_xPO from 4.2 K to 300 K. Our results show that transition metal Cr substitution for Fe in CeFePO gradually generates a FM ordering of Ce sublattice and suppresses the FM ordering by further doping, whereas Fe sublattice does not show magnetic ordering. The ground state of Ce 4f orbital in CeFePO is dependent on interlayer distances.[9] Arrott plot of the M - H curves determines a ferromagnetic transition temperature (T_c) for Cr-doped CeFePO. [1]

REFERENCES:

- [1] T. Okano, S. Kitao, M. Seto, T. Atou, M. Itoh, M. Matoba, and Y. Kamihara, *J. Appl. Phys.*, 117 (2015) 17E123/1-4.
- [2] C. Krellner, K. S. Kini, E. M. Brüning, K. Koch, H. Rosner, M. Nicklas, M. Baenitz, and C. Geibel, *Phys. Rev. B*, 76 (2007) 104418.
- [3] E. M. Brüning, C. Krellner, M. Baenitz, A. Jesche, F. Steglich, and C. Geibel, *Phys. Rev. Lett.*, 101 (2008) 117206/1-4.
- [4] S. Doniach, *Physica B+C*, 91 (1977) 231-234.
- [5] K. Yoshida, A. Okiji, *Prog. Theor. Phys.*, 34 (1965) 505-522.
- [6] Y. Kamihara, H. Hiramatsu, M. Hirano, R. Kawamura, H. Yanagi, T. Kamiya, and H. Hosono, *J. Am. Chem. Soc.*, 128 (2006) 10012-10013.
- [7] T. Nakamura, T. Yamamoto, M. Matoba, Y. Einaga, and Y. Kamihara, *J. Phys. Soc. Jpn.*, 81 (2012) 064714/1-4.
- [8] S. Kitagawa, H. Ikeda, Y. Nakai, T. Hattori, K. Ishida, Y. Kamihara, M. Hirano, and H. Hosono, *Phys. Rev. Lett.*, 107 (2011) 277002/1-5.
- [9] S. Kitagawa, K. Ishida, T. Nakamura, M. Matoba, and Y. Kamihara, *J. Phys. Soc. Jpn.*, 82 (2013) 033704/1-4.

A study of formation of Au(III) surface complex on manganese dioxide by ^{197}Au Mössbauer spectroscopy

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INTRODUCTION: It is known that gold nanoparticles supported on metal oxide have been used as various oxidation-reduction catalysts. Gold catalyst made by deposition-precipitation (DP) method has been often used for catalytic study. However, it has been still poorly understood how Au(III) ions are precipitated on the surface of metal oxide. We have studied for Au(III) ions adsorption on the surface of metal oxide. In our study, we concluded that adsorbed Au(III) ions were not physically adsorption but chemical adsorption with surface complex (M—O—Au, M:metal). We did not prove straightforwardly the formation of Au(III) surface complex on metal oxide, which the aim of this study is to prove by means of ^{197}Au Mössbauer spectroscopy.

EXPERIMENTS: Au(III) ion adsorbed on manganese oxide was prepared by batch method. Manganese dioxide (Chuo Denki Kogyo Co., Ltd.) was added into an aqueous solution of HAuCl_4 under stirring and maintaining pH 6. The suspended solution was filtered with 0.45 μm membrane filter.

The chemical state of gold in the solid samples obtained was determined by ^{197}Au Mössbauer spectroscopy (home-made equipment). The ^{197}Pt isotope ($T_{1/2} = 18.3$ h), γ -ray source feeding the 77.3 keV Mössbauer transition of ^{197}Au , was prepared by neutron irradiation of isotopically enriched ^{196}Pt metal at the Kyoto University Reactor. The absorbers were particle specimens. The source and specimens were cooled with a helium refrigerator. The temperature of the specimens was in the range 8 – 15 K. The zero velocity point of the spectra was the peak point of pure bulk gold. The spectra for all the solid samples were fitted to a single Lorentzian function.

RESULTS: Figure 1 shows ^{197}Au Mössbauer spectra of standard materials and Au(III) adsorbed on manganese dioxides. Figure 2 shows relative absorption area estimated from spectra in Fig.1 based on area of gold plate. The area is a measure of the recoilless fraction which is a function of the degree of fluctuation of Au nuclei (structural hardness). In Fig. 2, area of KAuBr_4 is considerably smaller than that of $\text{Au}_{\text{ad}}/\text{MnO}_2$. The result suggests that Au nuclei in KAuBr_4 can fluctuate more easily than that in $\text{Au}_{\text{ad}}/\text{MnO}_2$, deducing that the latter Au(III) ion

may be fixed tightly on the surface of MnO_2 due to the formation of Au-O-Mn bond (surface complex).

In conclusion, information arising from the analysis of ^{197}Au Mössbauer spectroscopy indicated Au(III) ion adsorbed chemically to form surface complexes before spontaneous reduction of the Au(III) to Au(0).

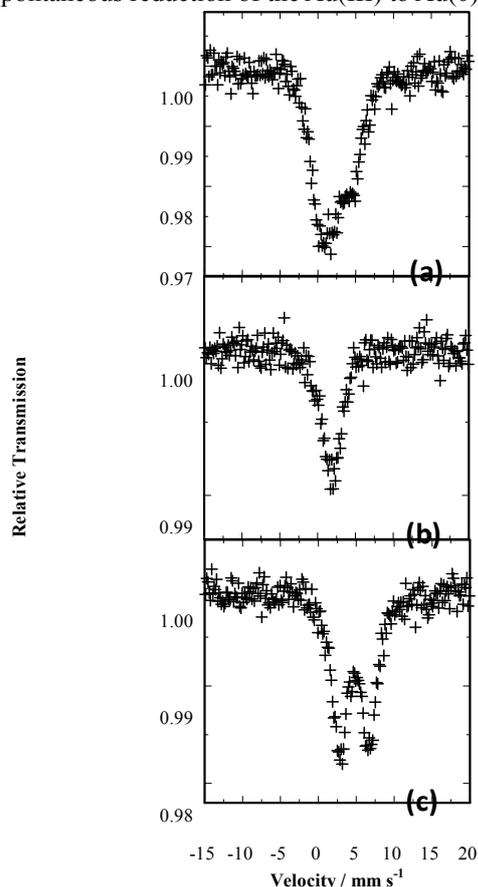


Fig. 1. ^{197}Au Mössbauer spectra for $\text{Au}_{\text{ad}}/\text{MnO}_2$ (a), KAuBr_4 (b) and AuMe_2acac (c).

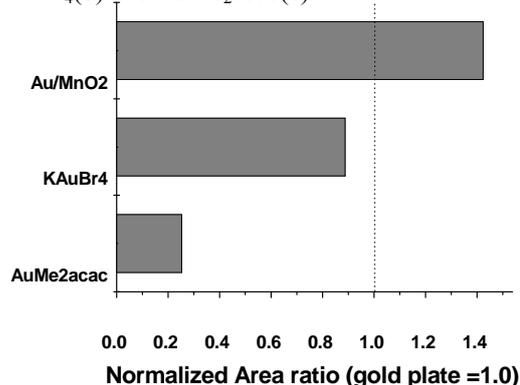


Fig. 2. Normalized area ratio of ^{197}Au Mössbauer spectra for AuMe_2acac , KAuBr_4 and $\text{Au}_{\text{ad}}/\text{MnO}_2$.

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INTRODUCTION: Recently, novel materials related to ferroelectrics have attracted much interest. One example is multiferroics that has at the same time ferromagnetic (or antiferromagnetic) order and ferroelectric order. The other example is ferroelectric catalysis that is composed of metal nanoparticles supported on ferroelectric particles. In order to investigate the origin of the multiferroics, or identify phase relation in the ferroelectric catalysis, Mössbauer spectroscopy is a useful probe [1-6]. In this research, we deal with a spinel type FeCr_2O_4 and Sn/BaTiO_3 as multiferroics and ferroelectric catalysis, respectively. FeCr_2O_4 reveals a ferrimagnetic order below around 70 K (tetragonal phase), followed by a spiral magnetic order below 35 K (orthorhombic phase). In the spiral magnetic state, a multiferroic state is expected. On the other hand, Sn/BaTiO_3 is expected as a new catalyst for the exhaust emission. The phase relation of the supported Sn compound was not clear, because its amount is too little to be identified by usual X ray diffraction.

EXPERIMENTS: For FeCr_2O_4 , a single crystal specimen of (100) platelet was used as an absorber. In order to obtain a single domain state in the low temperature phases, a slight compression along [001] axis was added by attaching epoxy resin on its both edges. ^{57}Fe Mössbauer spectroscopy was conducted in conventional transmission geometry by using ^{57}Co -in-Rh (50 mCi) as γ ray source. The spectrum was measured at 4.2 K with application of a magnetic field of 2 T. The direction of the γ ray and the magnetic field were parallel to the [100] axis. While for Sn/BaTiO_3 , a powder specimen was used as an absorber. ^{119}Sn Mössbauer spectroscopy was conducted by using ^{119}Sn -in- CaSnO_3 (20 mCi) as γ ray source. The spectrum was measured at room temperature.

RESULTS: In Fig. 1, ^{57}Fe Mössbauer spectrum of FeCr_2O_4 at 4.2 K in applied magnetic field of 2 T is shown. The spectrum is composed of two subspectra, which indicates that the magnetic structure is not a simple cone spiral type. Although both magnetic moments lie approximately in the orthorhombic c -plain, one is directed along the a -axis (corresponding to the cubic [100]), whereas the other inclines about 60° from the a -axis. The observed fields (H_{obs}) decrease by 2 and 1 T, respectively, due to the applied magnetic field. This is well consistent

with the estimated direction of the magnetic moments. Note that the quadrupole splitting $e^2qQ/2$ changes from -3.11 ($H_{\text{ex}} = 0$) to -3.23 mm/s ($H_{\text{ex}} = 2$ T), which may be indicative of the multiferroicity of this material.

In Fig. 2, ^{119}Sn Mössbauer spectrum of Sn/BaTiO_3 specimen at room temperature is shown. The spectrum is composed of a quadrupole doublet with isomer shift of -0.015 mm/s and quadrupole splitting of 0.519 mm/s. Thus we can identify that the supported Sn is in the form of SnO_2 . The absorption line width is rather large (0.879 mm/s), which is a result of a distribution in quadrupole splitting due to the particle size of nanometers.

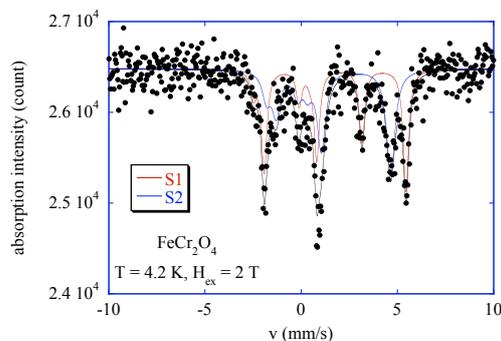


Fig.1 ^{57}Fe Mössbauer spectrum of FeCr_2O_4 at 4.2 K

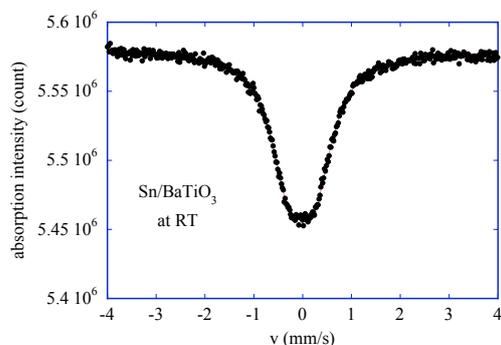


Fig. 2 ^{119}Sn Mössbauer spectrum of Sn/BaTiO_3 specimen at room temperature

REFERENCES:

- [1] S. Nakamura *et al.*, J. Phys. Conf. Ser. **200**, 012140 (2010).
- [2] S. Nakamura *et al.*, J. Phys. Soc. Jpn. **83**, 044701 (2014).
- [3] S. Nakamura *et al.*, J. Phys. Soc. Jpn. **84**, 024719 (2015).
- [4] S. Nakamura *et al.*, J. Phys. Conf. Ser. **592**, 012122 (2015).
- [5] T. Okamoto *et al.*, Hyperfine Interactions **219**, 147-152 (2013).
- [6] J. Kano *et al.*, Jpn. J. Appl. Phys. **53**, 05FB24 (2014).

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INTRODUCTION: We have made Mössbauer micro-spectrometer using a multi-capillary X-ray lens (MCX) and estimated beam size of γ -ray at the focus in order to measure Mössbauer spectra of a single crystal in petrographic thin sections (KURRI Progress Report 2013). As powdered crystals are generally used for conventional Mössbauer spectroscopy, anisotropy of crystal against incident γ -ray can be cancelled by random orientation of powders, and sextet peaks due to internal magnetic field are averaged into intensity ratio of 3:2:1:1:2:3. On the other hand, intensity ratio of sextet of single crystal depends on the crystal orientation. In this study, to observe crystallographic orientational dependence of sextet, Mössbauer spectra of oriented thin sections of natural magnetite were measured.

EXPERIMENTS and RESULTS: Two natural magnetite single crystals were prepared. Using X-ray precession camera, (100), (110) and (111) oriented thin sections were made for Mössbauer spectra measurements. Vacancy x ($\text{Fe}_{3-x}\text{O}_4$, $0 < x < 0.33$) of Brazil and Russia magnetites was estimated to approximately 0 and 0.2, respectively, from Mössbauer spectra. Peak fittings as two sets of sextet were done for 6 thin sections. Sextet of 49T and 46T magnetic fields are shown in table as Fe^{3+} and $\text{Fe}^{2.5+}$, respectively. Relative intensity in the table is that of the second peak (peak 2) against the third peak (peak 3) among separated 6 peaks. For powdered magnetites, the relative intensity of peak 2 is always 2. But they were deviated from 2 due to crystal anisotropy.

occurrence	index	$\text{Fe}^{2.5+}$	Fe^{3+}
Brazil	(100)	1.96	1.72
	(110)	2.70	2.31
Russia	(111)	2.86	2.56
	(100)	1.98	1.83
	(110)	2.73	2.64
	(111)	2.75	2.63

Table. Relative intensity of peak 2 against peak 3 among sextet of magnetite.

The following two models were discussed to explain this result. In the first model, supposing that magnetic domains with the easiest magnetization axis of crystallographically equivalent $\langle 100 \rangle$ or $\langle 110 \rangle$ or $\langle 111 \rangle$ are present equally in oriented thin sections, the peak 2 ration were always 2 in all cases. This model is not consistent with this result. In the second model, supposing shape magnetic anisotropy, which means possibly high magnetic domains with the magnetized orientation parallel to the thin sections and low magnetic domains normal to the thin sections, this result can be explained only by the $\langle 111 \rangle$ easiest magnetization axis. This is consistent with the general easiest magnetization axis of spinel ferrite.

Mössbauer spectra measurements of small single grains of magnetite with MCX were not done, because the Tracer Laboratory was not opened for Mössbauer spectroscopy.

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INTRODUCTION: Positive thermal expansion (PTE) is an essential property of materials. A limited number of materials shrink with heating, which is described as negative thermal expansion (NTE). NTE property contributes to development of zero thermal expansion (ZTE) materials, in which the thermal expansion coefficient is almost zero. ZTE materials are desired in a wide range of applications such as precise mechanics, optics, and electronics. We investigated the chemical substitution effect of cubic perovskite oxide $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$ on thermal expansion property by X-ray diffraction, thermal analysis, and Mössbauer spectroscopy. Eventually, we obtained almost ZTE in Mn-doped sample, $\text{LaCu}_3\text{Fe}_{4-x}\text{Mn}_x\text{O}_{12}$ [1].

EXPERIMENTS: $\text{LaCu}_3\text{Fe}_{4-x}\text{Mn}_x\text{O}_{12}$ samples were synthesized under high-pressure and high-temperature conditions of 15 GPa and 1473 K, respectively. Synchrotron X-ray powder diffraction (SXRD) data were collected at temperatures between 100 and 450 K at the BL02B2 beamline of SPring-8. ^{57}Fe Mössbauer spectroscopy measurements were conducted at temperatures in transmission geometry using $^{57}\text{Co}/\text{Rh}$ as a radiation source.

RESULTS: Fig. 1 shows temperature dependence of the unit cell volume for $\text{LaCu}_3\text{Fe}_{4-x}\text{Mn}_x\text{O}_{12}$. A systematic trend from abrupt volume expansion/shrinkage ($x = 0-0.5$), NTE ($x = 0.75$), ZTE ($x = 1$), and PTE ($x = 1.5$) was confirmed [1]. This indicates that the thermal expansion properties of this system are adjustable by chemical doping. Fig. 2 shows Mössbauer spectra of the $x = 0.75$ and 1 samples collected at temperatures between 77 and 320 K. Nonmagnetic component are predominant above room temperature whereas magnetically split sextets are predominant at 77 K. The isomer shift values increased by ~ 0.05 mm/s at magnetic transition temperatures, which is attributed to the Fe valence reduction by inter-site charge transfer ($\text{Cu}^{2+} + \text{Fe}^{4+} \rightleftharpoons \text{Cu}^{3+} + \text{Fe}^{3+}$). These results indicate that the unusual thermal expansion properties of $\text{LaCu}_3\text{Fe}_{4-x}\text{Mn}_x\text{O}_{12}$ are associated with valence transitions of Fe ions.

REFERENCES:

[1] I. Yamada *et al.*, Appl. Phys. Lett., **105** (2014) 231906.

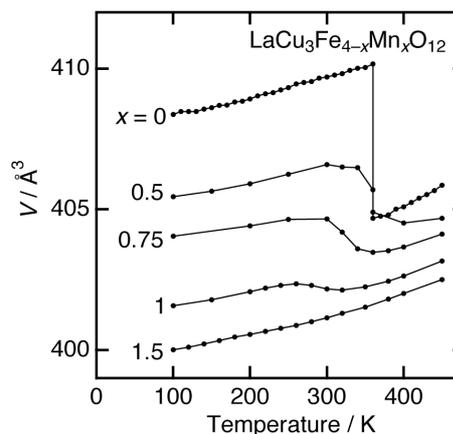


Fig. 1. Temperature dependence of the unit cell volume for $\text{LaCu}_3\text{Fe}_{4-x}\text{Mn}_x\text{O}_{12}$.

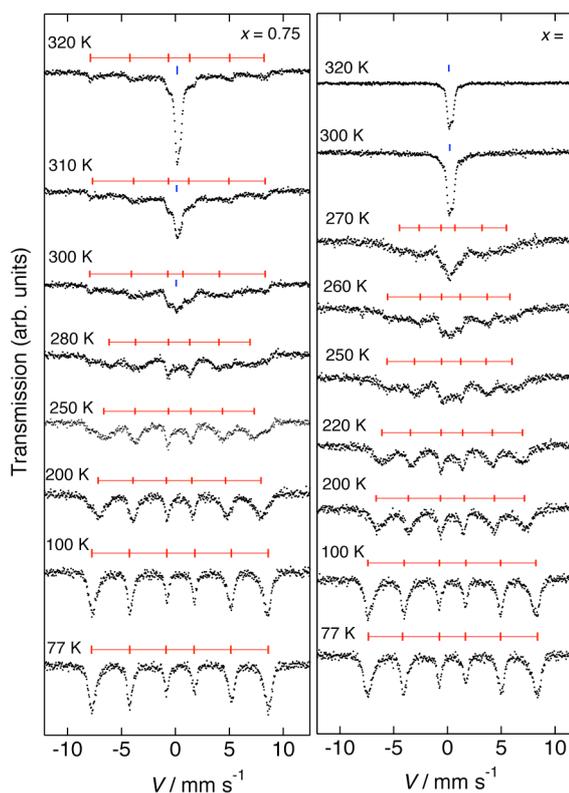


Fig. 2. Mössbauer spectra of $\text{LaCu}_3\text{Fe}_{4-x}\text{Mn}_x\text{O}_{12}$ ($x = 0.75, 1$).

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INTRODUCTION: After the discoveries of the so-called “1111” series of Fe-oxipnictide superconductors, $LaFePO$ [1] and $LaFeAsO_{1-x}F_x$ [2], 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 K-doping (*i.e.* hole-doping) of $BaFe_2As_2$ [3]. This series has become one of the main groups of Fe-based superconductors, since the various superconductors have been found not only by hole-doping but by electron-doping and even by isovalent doping. Such variety of superconductors provides complexity in the understanding of the mechanism of superconductivity, since the character of each Fe-based superconductor shows various different properties.

To promote the understanding of the superconducting mechanism, studies of their Fe magnetism is one of the main approaches, since it is supposed that the Fe acts as a key element and that the magnetism must relate to the superconductivity. To investigate the nature of its magnetism, ^{57}Fe -Mössbauer spectroscopy is an essential method. Until today, a number of Mössbauer studies on these Fe-based superconductors have been carried out and revealed many important facts, for example, that the superconductivity and magnetic order do not co-exist in $LaFeAsO_{1-x}F_x$ [4]. However, in $Ba_{1-x}K_xFe_2As_2$, unlike $LaFeAsO_{1-x}F_x$, it is known that the superconductivity and magnetic order co-exist in some doping region of the under-doped $Ba_{1-x}K_xFe_2As_2$ [5].

In this study, a detailed temperature dependence of Mössbauer spectra was measured to investigate the magnetic properties of the parent compound, $BaFe_2As_2$, optimally-doped superconductor, $Ba_{0.6}K_{0.4}Fe_2As_2$, and under-doped superconductor, $Ba_{0.8}K_{0.2}Fe_2As_2$.

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[3]. K-doped $Ba_{1-x}K_xFe_2As_2$ was synthesized similarly, except that excess amount of K was added and heated in lower temperature. The obtained polycrystalline powder was characterized by x-ray diffraction and magnetic susceptibility measurements. The superconducting transition was observed in $Ba_{0.6}K_{0.4}Fe_2As_2$ and $Ba_{0.8}K_{0.2}Fe_2As_2$ at around 30 to 40 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.

RESULTS AND DISCUSSION: Typical Mössbauer spectra for $BaFe_2As_2$ are shown in Fig. 1. The magnetic transition was clearly observed by the temperature dependence of the Mössbauer spectra. The observed internal magnetic field reached around 5.4 T at 2.5 K. The magnetic transition was clearly observed at around 150 K. These values well agreed with the former report[5].

On the other hand, $Ba_{0.6}K_{0.4}Fe_2As_2$ showed only a single peak spectrum down to 4 K, implying no magnetic transition occurs in optimally-doped superconductor. Thus, the co-existence of magnetism and superconductivity was not observed in the optimally-doped $Ba_{0.6}K_{0.4}Fe_2As_2$. This fact was similar to the “1111” compound, $LaFeAsO_{1-x}F_x$ [4]. However, Mössbauer spectra in under-doped $Ba_{0.8}K_{0.2}Fe_2As_2$ showed magnetic order below around 100 K, implying that the superconductivity and magnetic order co-exist in the under-doped $Ba_{0.8}K_{0.2}Fe_2As_2$. This co-existence in some of Fe-based superconductors is still one of the main controversial issues. Further Mössbauer study will be performed to investigate this issue.

REFERENCES:

- [1] Y. Kamihara, H. Hiramatsu, M. Hirano, R. Kawamura, H. Yanagi, T. Kamiya and H. Hosono, *J. Am. Chem. Soc.* **128** (2006)10012.
- [2] Y. Kamihara, T. Watanabe, M. Hirano and H. Hosono, *J. Am. Chem. Soc.* **130** (2008) 3296.
- [3] M. Rotter, M. Tegel, and D. Johrendt, *Phys. Rev. Lett.* **101** (2008) 107006.
- [4] S. Kitao, Y. Kobayashi, S. Higashitaniguchi, M. Saito, Y. Kamihara, M. Hirano, T. Mitsui, H. Hosono and M. Seto, *J. Phys. Soc. Jpn.* **77** (2008) 103706.
- [5] M. Rotter, M. Tegel, I. Schellenberg, F. M. Schappacher, R. Pöttgen, J. Deisenhofer, A. Günther, F. Schrettle, A. Loidl and D. Johrendt, *New J. Phys.* **11** (2009) 025014.

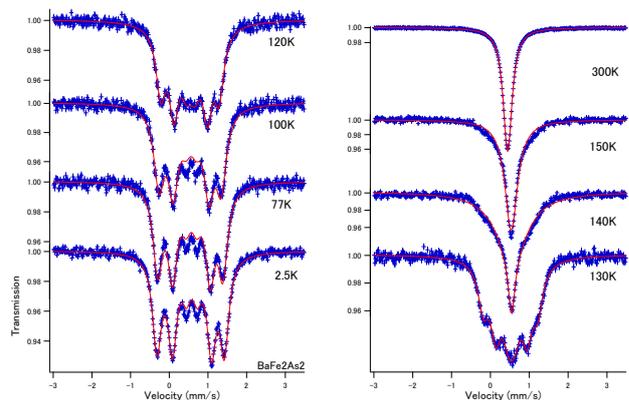


Fig. 1. Typical Mössbauer spectra of $BaFe_2As_2$.