

I-1. PROJECT RESEARCHES

Project 9

Project Research on Advances of Mössbauer Spectroscopy in Isotope-Specific Studies

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OBJECTIVES OF RESEARCH PROJECT

One of the most irreplaceable features of the Mössbauer spectroscopy is to extract several information such as electronic states and magnetic properties for a specific isotope. The main objectives of this project research on advanced isotope-specific investigation on the frontier of materials science by the methods of Mössbauer spectroscopy. Developments of Mössbauer spectroscopy provides more useful and valuable methods in modern materials science.

In this project research, each group performed their research by specific isotopes:

^{61}Ni in R6P9-1; ^{197}Au in R6P9-2, R6P9-3; ^{57}Fe in R6P9-4 to R6P9-12; and other isotopes in R6P9-13, R5P1-14.

MAIN SUBJECTS AND RESULTS OF THIS REPORT

Main subjects and results are as follows:

(R6P9-1, T. Kitazawa) ^{61}Ni Mössbauer spectroscopy of the $\text{PbMn}_2\text{Ni}_6\text{Te}_3\text{O}_{18}$ -type oxides

Y. Doi et al. investigated magnetic behavior of low-dimensional Ni chain system in Mg-doped $\text{PbMn}_2(\text{Ni}_{0.95}\text{Mg}_{0.05})_6\text{Te}_3\text{O}_{18}$. The ^{61}Ni Mössbauer spectra of the compound showed unexpectedly little broadening due to internal magnetic field. The result may imply the magnetic interactions are weakened by the incorporation of diamagnetic Mg^{2+} ions.

(R6P9-2, H. Ohashi) Differences in ^{197}Au Mössbauer Spectra between Adsorbed Gold Samples Prepared with Different Acidity

H. Ohashi et al. investigated mechanism of partial reduction of Au(III) catalysts in different preparation conditions. The ^{197}Au Mössbauer spectra were measured in Au(III) catalysts adsorbed on MnO_2 prepared from acidic solution and alkaline solution. It was found the amount of gold(0) varied greatly depending on preparation conditions.

(R6P9-3, Y. Kobayashi) Recoilless Fraction on ^{197}Au Mössbauer Spectroscopy of Au Particles Supported on TiO_2 and SiO_2

Y. Kobayashi et al. evaluated Debye temperatures of Au particles on TiO_2 and SiO_2 . It was found that of Au/ TiO_2 is lower than that of metallic Au, while Au/ SiO_2 is similar to metallic. It is considered to be due to fine particle size.

(R6P9-4, M. Tabuchi) Utilization of Fe ion in Fe and Ni substituted Li_2MnO_3 positive electrode material for lithium-ion battery

M. Tabuchi et al. evaluated the change of Fe oxidation value before and after charging of the electrode materials.

(R6P9-5, S. Ishiwata) Search for novel spin-charge ordered phases in anomalously high-valence iron oxides

Z. Ma et al. investigated the behavior of magnetic transition of $\text{Ba}_{1-x}\text{La}_x\text{FeO}_3$ ($x = 0.1, 0.2, 0.25$ and 0.33) and evaluated spin-charge ordered phase in charge disproportionation of Fe^{4+} to $\text{Fe}^{3+} + \text{Fe}^{5+}$.

(R6P9-6, K. Shinoda) An Intensity Tensor of Quadrupole Doublet due to Fe Ions Occupying M-sites of Hornblende

K. Shinoda et al. evaluated intensity tensor of hornblende single crystal successfully.

(R6P9-7, S. Takai) Temperature Dependence of Mössbauer Spectra of $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ Solid Solution in the Al-rich Region

S. Takai et al. evaluated composition dependence of QS value, which is due to deviation from spherical symmetry.

(R6P9-8, T. Ohto) Mossbauer Measurement of Spin-Crossover Complex

T. Ohto confirmed the spin crossover behavior in reduced graphene oxide template at high temperature of 410 K.

(R6P9-10, Y. Kamihara) Research on Magnetism and Electronic Phase in a H-doped Iron-based Superconductor

Y. Kamihara et al. studied temperature dependence of H-doped $\text{SmFeAsO}_{1-x}\text{F}_x$ to evaluate Debye temperature.

(R6P9-11, K. Yonezu) Experimental Preliminary Approach on the Precipitation Mechanism of Banded Iron Formation (BIF): Precipitation Behavior of Iron-bearing Siliceous Deposit Formed at Higher Temperature

K. Yonezu et al. prepared the scale samples from geothermal power plant and evaluated iron-bearing compounds.

(R6P9-13, R. Masuda) ^{166}Er Mössbauer spectroscopy of ErB_{66}

R. Masuda et al. evaluated the hyperfine field of Er in magnetic ordering of ErB_{66} at 20K.

(R6P9-14, S. Kitao) Search of ^{166}Er Mössbauer Single-Line Materials

S. Kitao et al. evaluated ^{166}Er Mössbauer spectra of ErF_3 at about 20K, which is a candidate for single-line Er material. It is unfortunately found that a broadened component was observed in ^{166}Er Mössbauer spectrum.

The experiments have not been performed in this term in R6P9-9 and R6P9-12.

^{61}Ni Mössbauer spectroscopy of the $\text{PbMn}_2\text{Ni}_6\text{Te}_3\text{O}_{18}$ -type oxides

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INTRODUCTION: The compounds featuring low-dimensional arrangements of magnetic ions are known to exhibit distinctive magnetic behaviors at low temperatures. Among them, one-dimensional chain systems have attracted a great deal of interest since the proposal of Haldane's conjecture, which has led to the discovery of various quantum phenomena, such as the spin-gap behavior observed in Ni^{2+} ($S = 1$) chains. Recently, we investigated the compound $\text{PbMn}_2\text{Ni}_6\text{Te}_3\text{O}_{18}$, which contains zigzag Ni^{2+} chains, and found that it exhibits low-dimensional magnetic behavior and an antiferromagnetic transition at 86.0 K arising from the collinear ordering of both Ni^{2+} and Mn^{2+} magnetic moments^[1]. Furthermore, this compound has very recently been identified as a potential candidate for a novel ferrotoroidic material^[2]. The fundamental magnetic properties of this compound are primarily governed by the Ni^{2+} chain structure. To gain further insights into the local environment and magnetic characteristics of Ni^{2+} ion, we conducted the ^{61}Ni Mössbauer spectroscopy measurements.

EXPERIMENTS: Polycrystalline samples of $\text{PbMn}_2\text{Ni}_6\text{Te}_3\text{O}_{18}$ and its Cd- and Mg-doped derivatives were synthesized via a conventional solid-state reaction method. The starting materials used were PbO , CdO , MnO , NiO , MgO , and TeO_2 . Stoichiometric mixtures of these oxides were thoroughly ground, pressed into pellets, and calcined in a muffle furnace at 973–1073 K for 12–36 hours. Phase purity and structural characterization were confirmed by powder X-ray diffraction combined with Rietveld refinement, revealing that all samples crystallize in the hexagonal structure with space group $P6_3/m$, identical to that of undoped $\text{PbMn}_2\text{Ni}_6\text{Te}_3\text{O}_{18}$. For ^{61}Ni Mössbauer spectroscopy measurements, approximately 0.5 g of powdered sample was loaded into a 10 mm diameter sample holder.

RESULTS: Figure 1 presents the ^{61}Ni Mössbauer spectrum of Mg-doped $\text{PbMn}_2(\text{Ni}_{0.95}\text{Mg}_{0.05})_6\text{Te}_3\text{O}_{18}$ at 20 K. The spectrum appears to exhibit a single peak; however, it shows slight broadening compared to that of the standard $\text{Ni}_{86}\text{V}_{14}$ alloy, suggesting the possible presence of magnetic hyperfine splitting. The Néel temperature of the compound is approximately 80 K, indicating that the Ni^{2+} ions are situated in an internal magnetic field generated by long-range antiferromagnetic ordering. Curve fitting yields an internal field of approximately 4.6 T, which is unexpectedly small given the relatively high transition temperature. This result may imply that the magnetic interactions are weakened by the incorporation of diamagnetic Mg^{2+} ions, which likely disrupt the exchange pathways.

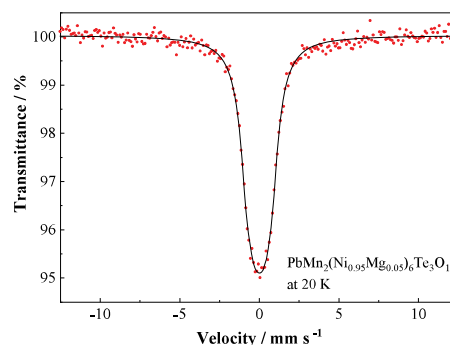


Fig. 1. The ^{61}Ni Mössbauer spectrum of Mg-doped $\text{PbMn}_2\text{Ni}_6\text{Te}_3\text{O}_{18}$.

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Differences in ^{197}Au Mössbauer Spectra between Adsorbed Gold Samples Prepared with Different Acidity

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INTRODUCTION: Gold catalysts have been very famous as heterogeneous catalysts. When preparing gold catalysts from Au(III) compounds, it was known that the preparation conditions differ depending on the support metal oxides. Preparation of Au/MnO₂ from HAuCl₄ compounds was known to be difficult. This was because Au(III) ions were partially reduced to Au(0) on the surface of MnO₂.

We have investigated the mechanism of this automatic reduction to Au(0)[1]. As a conclusion, the Au(III) component with relatively high IS and QS values was important. However, the reason why Au(III) ions were effectively reduced to Au(0) was unknown. In this study, we focused on the slow ligand substitution of Au(III) ions and aimed to observe the change in ^{197}Au Mössbauer spectrum when Au(III) aqueous solution was prepared from the alkaline side and the acidic side.

EXPERIMENTS: Manganese dioxide was added to the HAuCl₄ aqueous solution to adjust the pH 6 from acid media or alkaline media, and the mixture was stirred. The solution of ionic strength was adjusted to 0.10 M with NaCl. The suspension solution was filtered using 0.45 μm membrane filter, and the filtrate was dried at 30°C for 12 hours. The amount of gold was approximately 5wt%.

^{197}Au Mössbauer spectra were measured at Kyoto University Research Institute of Nuclear Science. 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 measurement temperature was 20 K, and the measurement was performed by the transmission method.

RESULTS: Figure 1 shows ^{197}Au Mössbauer spectra at 20 K for the sample of Au(III) adsorbed on MnO₂. It was found that the amount of gold(0) varied greatly depending on whether the aqueous solution was acidic or alkaline (Table 1).

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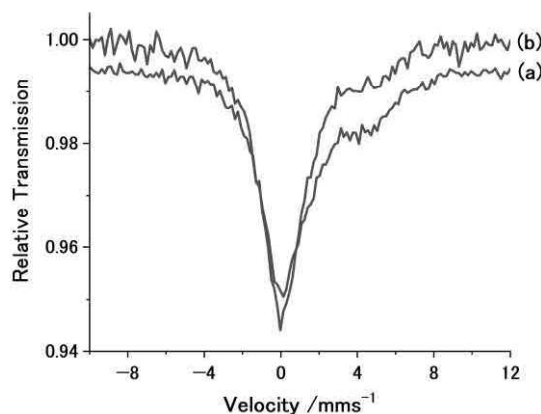


Fig. 1. ^{197}Au Mössbauer spectra at 20 K for the sample of Au(III) adsorbed on MnO₂. (a) prepared from acid solution, (b) from alkaline.

Table 1 Mössbauer parameters for Au(III) adsorbed on MnO₂ samples. (a) Au loaded 5wt%, stirred with pH 6 adjusted from acid solution, (b) Au loaded 5wt%, stirred with pH 6 adjusted from alkaline solution.

	Component A		Component B		Component A	Component B
	Γ /mms ⁻¹	IS /mms ⁻¹	IS /mms ⁻¹	QS /mms ⁻¹	Area (%)	Area (%)
Sample (a)	2.49	0.01	3.24	2.90	68.3	31.7
Sample (b)	2.40	0.01	3.17	3.27	82.3	17.7

Recoilless Fraction on ^{197}Au Mössbauer Spectroscopy of Au Particles Supported on TiO_2 and SiO_2

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INTRODUCTION: The recoilless fraction is a parameter that reflects lattice vibrations and provides important knowledge in physics, chemistry, etc. In ^{197}Au Mössbauer spectroscopy, the energy of γ -rays is higher than ^{57}Fe , so differences and changes in the recoilless fraction appear significantly. We have succeeded in estimating the Debye temperature not from the absolute amount of spectral absorption area but from its temperature dependence curve and estimated that of $\text{Au}(\text{OH})_3$ and Au_2S [1]. We applied this technique to Mössbauer measurements of Au-supported catalysts. The characteristics of Au-supported catalysts change depending on the supporters. To investigate the influences of the supporters on the Au particles, we measured the ^{197}Au Mössbauer spectrum and the recoilless fraction.

EXPERIMENTS: Prepared samples were Au particles on a TiO_2 supporter (Au/TiO_2) and Au particles on a SiO_2 supporter (Au/SiO_2). The Au contents were 2~10wt% in Au/TiO_2 and 2wt% in Au/SiO_2 . The TiO_2 or SiO_2 powder was put in the HAuCl_4 aqueous solution, and $\text{Au}(\text{OH})_3$ was precipitated on the powder surface by adjusting the pH while stirring. The obtained powder was dried and calcined at 300°C for 4 hours to prepare the sample [2].

Using KUR, the ^{197}Pt γ -ray sources for ^{197}Au Mössbauer measurements were prepared by neutron irradiation to 98%-enriched ^{196}Pt metal foil. The γ -ray source and samples were cooled to the same temperatures using a helium refrigerator.

RESULTS: In the ^{197}Au Mössbauer spectra of the Au/TiO_2 and Au/SiO_2 samples, all components showed a single peak like metallic Au. It was found that Au was chemically in the metallic Au state in all samples. No interface or surface components were observed, even in the Au 2wt% Au/TiO_2 sample, which is considered the smallest Au particles.

The Debye temperatures of the Au/TiO_2 samples and Au/SiO_2 sample obtained from the temperature change of the spectral absorption area. It was close to that of bulk metallic Au in the Au 10wt% Au/TiO_2 sample. However, it was lower than metallic Au in the Au 2wt% sample. This is thought to be due to a decrease in the recoilless fraction due to fine particle size. On the other hand, the Au 2wt% Au/SiO_2 sample had a Debye temperature close to that of metallic Au, suggesting that the particles were not as small as those in Au/TiO_2 . In X-ray diffraction, the peaks of metallic Au were not observed in the 2wt% Au/TiO_2 sample due to the fine particle size, whereas it was observed in the Au/SiO_2 sample. The results of the recoilless fractions are consistent with the X-ray diffraction. The lattice vibrations affect the adsorption and movement of adsorbed molecules on the Au particle surface. Therefore, it is thought to affect catalytic activity.

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Utilization of Fe ion in Fe and Ni substituted Li_2MnO_3 positive electrode material for lithium-ion battery

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INTRODUCTION: Large scale lithium-ion battery (LIB) is needed for EV and ESS applications. To stabilize a cost of the LIB, low-cost positive electrode material is necessary. Especially, utilization of Fe ion redox is attractive. Fe and Ni substituted Li_2MnO_3 is a suitable positive electrode material for above object [1, 2]. In this report, $\text{Li}_{1+x}(\text{Fe}_{0.2}\text{Ni}_{0.1}\text{Mn}_{0.7})_{1-x}\text{O}_2$ ($0 < x < 1/3$) was selected to check the change in valence state of Fe ion using ^{57}Fe Mössbauer spectroscopy during the electrochemical activation process.

EXPERIMENTS: The sample was prepared by coprecipitation-calcination method [2]. After calcination in air, the sample was calcined by reductive atmosphere (4% H_2 -96% N_2 gas) at 425 °C for 3h. The electrochemical activation process was constructed as follows; The charged capacity increased from 80 mAh/g (1st) by 40 mAh/g step until 200 mAh/g (4th) after discharged to 2.0 V for Li/sample cell. At 5th cycle, the cell charged to 4.8 V and then discharged to 2.0 V to finish activation process. The active material was sealed in Al-laminate sheet for ^{57}Fe Mössbauer measurement. The isomer shift (IS) value was calculated using α -Fe as standard material.

RESULTS: The as-prepared (asp.) and first charged (1c) sample's XRD pattern can be fitted by a single-phase of monoclinic Li_2MnO_3 structure, whereas fifth charged (5c) and then discharged (5d) samples had monoclinic NaNiO_2 one. Both structures belong to layered rock-salt one.

^{57}Fe Mössbauer spectra (Fig. 1) for the as-prepared sample fitted by two symmetric doublets. The main A component (90%, IS=+0.34 mm/s) was assigned as high-spin trivalent Fe [3], whereas minor B one (10%, IS=-0.22 mm/s) was attributed as tetravalent state ($4+\delta$ state, $0 < \delta < 0.5$) [3]. After first charging (1c), minor B (20%) and C (7%) components appeared. Both components had highly negative IS values (-0.32 and -0.46 mm/s for B and C ones, respectively). The B and C components were assigned as $4.5+$ and $5+$ states [4]. The fact indicates that attractive $\text{Fe}^{3+/5+}$ redox coexisted with normal $\text{Fe}^{3+/4+}$ one on initial charging. At the end of charging

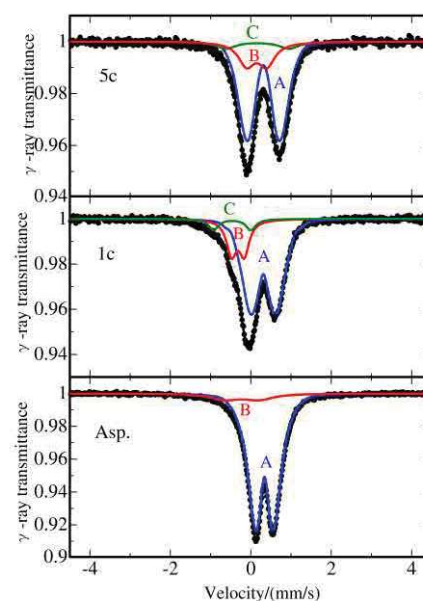


Fig. 1 ^{57}Fe Mössbauer spectra for before and after charged samples.

(5c) state, the IS values of the B (21%) and C (8%) components were raised to +0.15 and +0.16 mm/s, respectively. These components are assigned as $3.5+$ state [3], indicating that oxidized Fe ion was reduced incompletely at the end of charging. At the end of discharging (5d) state, all of Fe component was trivalent state. The result showed that the $\text{Fe}^{3.5+}$ ion utilized on fifth discharging. In summary, at $\text{Li}_{1+x}(\text{Fe}_{0.2}\text{Ni}_{0.1}\text{Mn}_{0.7})_{1-x}\text{O}_2$ composition, constituent Fe ion act as redox center on both charging and discharging. The obtained result contributes to accelerate the development of low-cost positive electrode material.

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Search for novel spin-charge ordered phases in anomalously high-valence iron oxides

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INTRODUCTION: Charge disproportionation of Fe^{4+} , described by $2\text{Fe}^{4+} \rightarrow \text{Fe}^{3+} + \text{Fe}^{5+}$, was widely observed in perovskite-type iron oxides with anomalous high valence state, and is closely linked to the emergence of novel magnetic phases. For instance, charge disproportionation of iron was observed in $\text{Sr}_{2/3}\text{La}_{1/3}\text{FeO}_3$, originated from the spin-charge ordering (SCO) phase, where the three-fold charge ordering was coupled with the six-fold spin ordering. [1] In our previous work, we revealed a plausible SCO phase in $\text{Ba}_{1-x}\text{La}_x\text{FeO}_3$ when $x = 0.2$. In order to further understand the magnetic ordering, the valence of iron was studied with the Mössbauer spectra for $\text{Ba}_{1-x}\text{La}_x\text{FeO}_3$ with $x = 0.1, 0.2, 0.25$ and 0.33 , measured below the phase transition temperature.

EXPERIMENTS: Polycrystalline samples of $\text{Ba}_{1-x}\text{La}_x\text{FeO}_3$ were synthesized by annealing $\text{Ba}_{1-x}\text{La}_x\text{FeO}_{3-\delta}$ with oxidizing agent (NaClO_3) at 500°C and 8 GPa for 1 h in a cubic-anvil-type high-pressure apparatus. The ^{57}Fe Mössbauer spectra were measured with a ^{57}Co source in Rh. The velocity was calibrated with $\alpha\text{-Fe}$.

RESULTS: Figure 1(a) shows the Mössbauer spectra for $\text{Ba}_{1-x}\text{La}_x\text{FeO}_3$ with $x = 0.1, 0.2, 0.25$ and 0.33 , measured below the phase transition temperature. The spectrum for $x = 0$ was reproduced from previous report.[2] The spectra for $x = 0.1, 0.2, 0.25$ and 0.33 can be well fitted by the superposition of two sextets corresponding to two Fe ions with different valence states, indicating charge disproportionation. As shown in Figures 1(b-c), the sextet with an isomer shift (IS) of approximately 0.5 mm/s and a hyperfine field (HF) around 45 T is attributed to Fe^{3+} . The other sextet, with an IS of around 0.1 mm/s and an HF of approximately 25 T , is attributed to Fe^{5+} . For $x = 0.25$ and 0.33 , the charge disproportionation is consistent with the emergence of SCO I phase.[3] For $x = 0.2$, the ratio for Fe^{3+} and Fe^{5+} are 53% and 47% , respectively, which is close to the expected ratio of $3:2$, suggesting a novel SCO II phase. The broadening of the sextets for the Fe^{3+} and Fe^{5+} is observed for lower La content x . The broadening of the peaks in $x = 0.25$ is attributed to the coexistence of HM and SCO I phases, as it is at the boundary of the phase diagram. For $x = 0.2$, the significant broader peaks indicate spin fluctuations.

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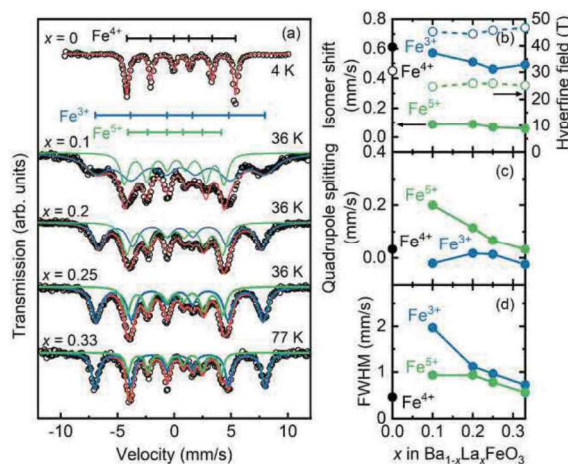


Fig. 1. (a) The Mössbauer spectra for $\text{Ba}_{1-x}\text{La}_x\text{FeO}_3$ ($x = 0.2, 0.2, 0.25$ and 0.33) under phase transition temperature. (b) Isomer shift, and hyperfine field, (c) quadrupole splitting, (d) Full width at half maximum (FWHM) obtained by the fitting of the Mössbauer spectra.

An Intensity Tensor of Quadrupole Doublet due to Fe Ions Occupying *M*-sites of Hornblende

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INTRODUCTION: Hornblende is a typical amphibole mineral that widely occurs in igneous and metamorphic rocks. General chemical composition of hornblende is $\text{NaCa}_2(\text{Mg}, \text{Fe}^{2+}, \text{Al})_5(\text{Si}, \text{Al})_8\text{O}_{22}(\text{OH})_2$. Hornblende is a major multi-site solid solution mineral that includes M1, M2, M3 and M4 sites. Mg and Fe^{2+} ions occupy the smaller M1, M2, and M3 sites and Na and Ca ions occupy the larger M4 site. Pyroxene is also multi-site solid solution minerals the include M1 and M2 sites. The intensity tensor for Fe ions at M-sites is important property for analyzing Mössbauer spectra of single crystal of multi-site solid solution minerals. Although chemical dependences of intensity tensors in Ca-rich pyroxene [1] and Ca-poor orthopyroxene [2] are revealed, intensity tensor due to Fe ions in M-sites of amphibole is not revealed. The intensity tensor is a symmetric tensor of which components are I_{XX} , I_{YY} , I_{ZZ} , I_{XY} , I_{YZ} and I_{XZ} . I_{YZ} and I_{XZ} of monoclinic crystal can be fix as 0 by its symmetry. The peak intensity (I) defined as $I_h/(I_h+I_l)$, where I_l and I_h are the lower and higher peak's intensity, respectively [3].

EXPERIMENTS: A single crystal of hornblende from Ikenohukuro, Sakai, Suwa, Nagano prefecture, Japan was used for this study. Three crystallographically oriented thin sections perpendicular to *a*, *b* and *c* were prepared by measuring X-ray diffraction methods. Nine Mössbauer spectra of oriented thin sections and one powder spectrum were measured. Cartesian coordinate (*X Y Z*) is set as *X*//*c**, *Y*//*a*, *Z*//*b**. Mössbauer measurements were carried out in transmission mode on a constant acceleration spectrometer with an Si-PIN semiconductor detector (XR-100CR, AMPTEK Inc.) and multi-channel analyzer of 1024 channels. A 3.7GBq ⁵⁷Co/Rh of 4mmφ in diameter was used as γ-ray source. An ⁵⁷Fe-enriched iron foil was used as velocity calibrant. The two symmetric spectra were folded, and velocity range was ± 4mm/s. Mosswin program was used for peak separation.

RESULTS: Peak separation of powder sample was performed by three quadrupole doublets of equal intensity peak ($I = 0.5$) assuming Fe ions at three M-sites. As the result, three kinds of successful peak separation were obtained. Peak separations of single crystal were done in the three ways by fixing IS_n , QS_n and LW_n ($n=1, 2, 3$) of powder sample, and unfixing peak intensity (I). For three different peak separations, three intensity tensors ($I_{(c'')\%&}(p, q = X, Y, Z)$) were obtained by fixing I_{YZ} and I_{XZ} as 0. To examine the validity of three intensity tensors, intensity tensors ($I_{(c'')\%&}^{*''''0}$) by unfixing I_{YZ} and I_{XZ} as 0 were also calculated. Comparing $I_{(c'')\%&}^{(0)}$ and $I_{(c'')\%&}^{*''''0}$ the best matched intensity tensor was selected as the intensity tensor of this hornblende. Fig.1 shows Mössbauer spectrum of hornblende single crystal under γ-ray //a-axis and the best peak separation among three different parameters (IS_n , QS_n and LW_n).

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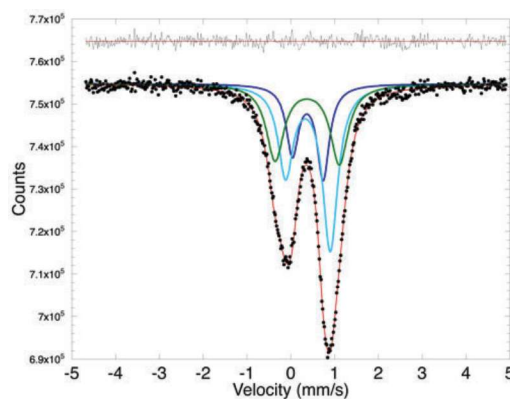


Fig. 1. Mössbauer spectra of hornblende single crystal under γ-ray //a-axis and a peak separation with three QS doublets.

Temperature Dependence of Mössbauer Spectra of $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ Solid Solution in the Al-rich Region

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INTRODUCTION: While $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Al}_2\text{O}_3$ exhibit the corundum-type structure, the solid solution range is much restricted around the endmembers of the composition. We have reported the successful preparation of $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ solid solutions across the entire compositional range using mechanical alloying techniques starting from $\gamma\text{-Fe}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$. The compositional dependence of the solid solution exhibits Vegard's law, and the radial distribution function obtained by EXAFS shows the gradual decrease at Fe-Fe distance, whereas it remains almost constant at Fe-O. We measured the Mössbauer spectra of $(\text{Fe}_2\text{O}_3)_{1-x}(\text{Al}_2\text{O}_3)_x$ solid solutions at room temperature in the previous study. The spectra change from sextet to doublet with increasing aluminum concentration, which should be ascribed to the spin interaction decrease due to the substitution of non-magnetic aluminum ions for iron. While the doublet profile is observed for the solid solution of $x = 0.5$ at room temperature, it changes to a sextet with decreasing temperature. The spin fluctuation is thought to be restricted by reducing the temperature, and long-range spin interaction becomes evident. In the present study, we deduced the magnetic parameters from fitting the spectra with the doublet and sextet profiles.

EXPERIMENTS: Mössbauer spectroscopy was performed on $(\text{Fe}_2\text{O}_3)_{0.5}(\text{Al}_2\text{O}_3)_{0.5}$ through the conventional transmission mode using a ^{57}Co in Rh γ -ray source (1.85 GBq). Liquid helium and liquid nitrogen were employed as coolants below and above 77 K, respectively. The Doppler velocity scale was calibrated using an iron foil reference, and the spectral profiles

were analyzed in Velocity Buffer File (VBF) mode. The profile fitting was carried out by RECOIL program to yield some magnetic parameters.

RESULTS: Fig. 1 shows measured and fitted profiles of the Mössbauer spectra for on $(\text{Fe}_2\text{O}_3)_{0.5}(\text{Al}_2\text{O}_3)_{0.5}$. Single doublet peaks are employed for the spectra of 300K, while sextet peaks are for 10 K. These combinations are used at intermediate temperatures. Fig. 2 represents the quadrupole splitting obtained from the sextet and doublet components. The negative values of QS for sextet components indicate a weak-ferromagnetic state rather than antiferromagnetic for the measured temperature range. As for the doublet component, the QS values increase with decreasing temperature, which should be ascribed to the deviation from spherical symmetry due to the suppression of spin fluctuation.

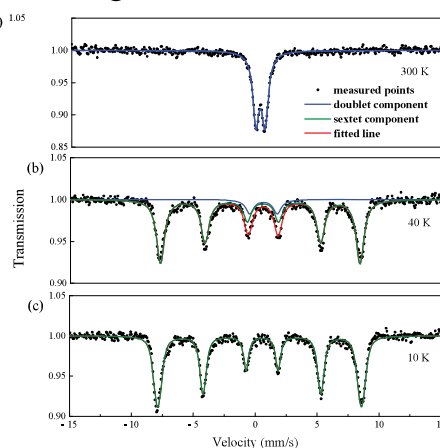


Fig. 1 Measured and fitted Mössbauer spectra for $(\text{Fe}_2\text{O}_3)_{0.5}(\text{Al}_2\text{O}_3)_{0.5}$. (a) 10 K, (b) 40 K, and (c) 300 K.

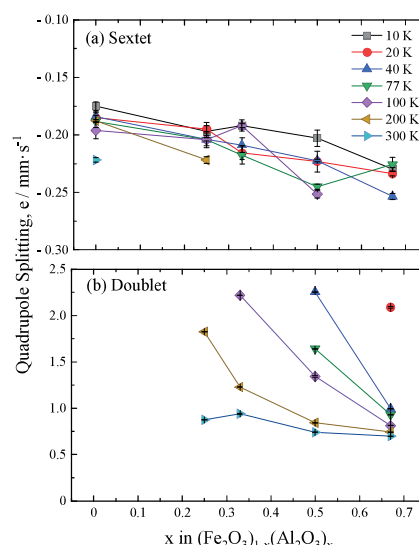


Fig. 2 Compositional dependence of the quadrupole splitting of $(\text{Fe}_2\text{O}_3)_{1-x}(\text{Al}_2\text{O}_3)_x$ under variable temperatures obtained from (a) sextet and (b) doublet component.

Mössbauer Measurement of Spin-Crossover Complex

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INTRODUCTION: Despite a clear demonstration of bistability in spin-crossover (SCO) materials, the absence of long-range magnetic order and poor electrical conductivity limit their prospect in spintronic and nanoelectronic applications. Intending to create hybrid devices made of spin-crossover (SCO)-2D architecture, here, we report an easily processable Fe-based SCO nanostructures grown on 2D reduced graphene oxide (rGO). The heterostructure shows enhanced cooperativity due to formation of interfacial charge transfer induced inter-molecular interaction. The spin transition temperature is controlled by tuning the coverage area of SCO nanostructured networks over the 2D surfaces, thus manipulating hysteresis (aka memory) of the heterostructure. The enhanced magnetic coupling of the heterostructure leads to the spontaneous magnetization states with a large coercive field of ~ 3000 Oe. Additionally, the low conductivity of the pristine SCO nanostructures is addressed by encapsulating them on suitable 2D rGO template, enabling detection of magnetic bistable spin states during high-spin/low-spin conductance change. This adds spin functionality in conductance switching for realizing hybrid 2D spintronic devices. Ab-initio calculations, on the experimentally proposed nanostructures, corroborate the enhanced magnetic interaction in the proposed architecture facilitated by interfacial charge transfer and provide insights on the microscopic mechanism.

EXPERIMENTS: Conventional ^{57}Fe Mössbauer spectroscopy was performed using ^{57}Co source in Rh matrix with nominal activity of 1.85 GBq. The velocity scale was calibrated with $\alpha\text{-Fe}$. For the low temperature measurements, a mixture of the compound with silicone grease was used as the Mössbauer absorber. We pelletized mixture of the compound with BN and polyethylene powder for the room temperature $\sim$ high temperature measurements.

RESULTS:

The ^{57}Fe Mössbauer spectroscopy was performed for the low concentration and high concentration samples starting from room temperature (297K) to different temperatures until 410K high temperature to reveal the electronic states of Fe centres in the nanocomposites and to confirm the Fe II SCO behaviour in a rigorous and accurate way. The low spin and high spin states of Fe(II) can be clearly distinguished through their different hyperfine parameters in a quadrupolar interaction.

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Research on Magnetism and Electronic Phase in a H-doped Iron-based Superconductor III

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INTRODUCTION: The research in 2024 is to clarify the bulk element specific magnetic properties of polycrystalline superconducting $\text{SmFeAsO}_{1-x}\text{H}_x$ (H-doped Sm1111) prepared by high temperature and high pressure synthesis and $\text{SmFeAsO}_{1-x}\text{F}_x$ (F-doped Sm1111) prepared by conventional method.[1-5] ^{57}Fe Mössbauer spectra are demonstrated for the H-doped Sm1111 at several low temperatures. Present spectra are very similar to that of superconducting F-doped Sm1111. [5, 6]

EXPERIMENTS: The phase purity, lattice constants, and crystal structure of the sintered powders were examined by powder x-ray diffraction (XRD) Rigaku Rint2500 using Cu K alpha radiation from a rotating anode. The magnetic moment (M) of polycrystalline H-doped Sm1111 was measured using a SQUID magnetometer (Quantum Design MPMS) at several temperatures (T) and magnetic fields (H). ^{57}Fe Mössbauer spectroscopy was observed at T = 4.2, 10, 20, 50, 77, 300 K for the H-doped Sm1111. The ^{57}Fe Mössbauer spectroscopy was performed using 14.4 keV γ -rays from a ^{57}Co source.

RESULTS: Figure 1 exhibits ^{57}Fe Mössbauer spectra at T = 4.2, 10, 20, 50, 77, 300 K for H-doped Sm1111. The Mössbauer spectra of H-doped Sm1111 were analyzed using the code Moss Winn [7], and the apparent isomer shift was determined. In this study, the spectrum was refined by considering the electronic state around the Fe nucleus as a mixture of singlet and doublet. Subsequently, the obtained isomer shift (δ) values, which were obtained at each T, were used along with the theoretical formula to refine the δ -T plot data. In 2025, we will derive and refine the Debye temperature for the H-doped Sm1111. Magnetic phases of the H-doped Sm1111 are paramagnetic at T = 4.2-300 K.

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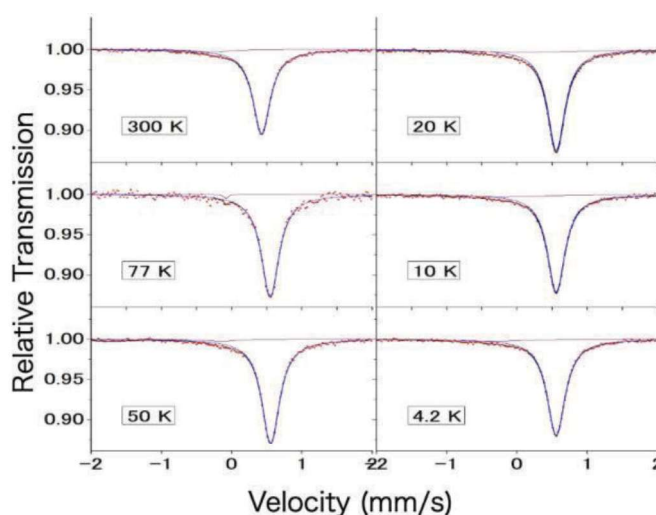


Fig. 1. ^{57}Fe Mössbauer spectra at T = 4.2, 10, 20, 50, 77, 300 K for H-doped Sm1111.

Experimental Preliminary Approach on the Precipitation Mechanism of Banded Iron Formation (BIF: Precipitation Behavior of Iron-bearing Siliceous Deposit Formed at Higher Temperature

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INTRODUCTION: Banded Iron Formation (BIF) is chemically precipitated sedimentary rock at Precambrian age. Current iron resource widely used in our industries largely depends on BIF. Commonly the hydrothermal water, anoxic water was mixed with oxic seawater (e.g., Otake and Otomo, 2021). However, the formation mechanism of BIF was not yet clarified. In order to approach the formation mechanism, we have done ambient temperature batch experiments, elevated temperature batch experiments and the experiments using natural system (geothermal fluid mixed with seawater and silica scale characterization formed at around 100 degree C). Therefore, this study aims to understand the formation mechanism of iron-bearing siliceous deposits at higher temperature in Olkaria geothermal power plant in Kenya.

EXPERIMENTS: Several scale samples were collected from multiple locations of the Olkaria geothermal power plant, including separators, atmospheric silencers, brine lines, scrubbers, vent stations, and cooling towers. The samples were analyzed by XRD, XRF, petrograph and NMR (²⁹Si and ²⁷Al).

RESULTS: As shown in Fig. 1, ²⁷Al NMR results suggested that most of Al is present as 4-coordinated structure with minor 6 coordinated structure. Combined with the data from SEM-EDX, aluminum was seen to be uniformly distributed in the silica phase, especially in the samples from the separators, suggesting that the 4-coordinate aluminum ion (AlO₄ unit) was present at the silicon site (SiO₄ unit) in the silica phase by isomorphous substitution. The chemical composition of those samples are mainly composed of SiO₂, followed by Al₂O₃ and Fe₂O₃ (up to 2.3wt%). Mineralogically, those samples are amorphous phase. Additionally, ²⁹Si NMR spectra indicated that the structure considered for Si was Q⁴. The detailed peak deconvolution was conducted and revealed that there are several mineral phases in one sample as suggested by XRD pattern with the presence of opal. The role of Al in the precipitation of siliceous deposit was well discussed, however iron-bearing siliceous deposit in neutral to alkaline pH conditions with high temperature has not yet discussed. For further discussion on the formation mechanism of iron-bearing siliceous deposit would be an important key to understand the formation mechanism of BIF.

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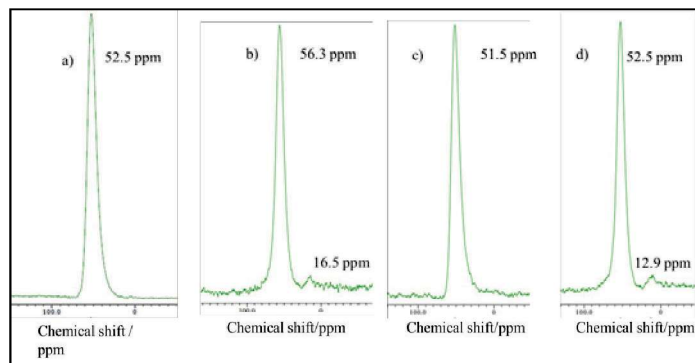


Fig. 1. ²⁷Al MAS NMR spectrum for the representative samples

^{166}Er Mössbauer spectroscopy of ErB_{66}

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INTRODUCTION: Boron-rich rare earth borides recently attract researchers as magnetically-diluted insulators. In fact, we can control the ratio of the constituent magnetic atom, i. e. rare earth atoms; REB_4 , REB_6 , REB_{12} , and REB_{66} (RE=rare earth) are typically stable. Erbium atom is a rare earth element with $L=6$ and $S=3/2$ ($J = 15/2$) and ErB_{66} is a semiconductor boride with diluted magnetic atoms. Its crystal structure is cubic $\text{Fm}\bar{3}\text{c}$, same as other rare earth REB_{66} . The clear magnetic ordering is seen below 0.5 K as the maximum in the ac susceptibility measurement and above the temperature, a spin glass state is discussed [1]. Recently, ^{166}Er Mössbauer spectroscopy using ^{166}Ho ($T_{1/2}=26.8\text{h}$) source is available in KURNS [2,3]. Therefore, we performed ^{166}Er Mössbauer spectroscopy to observe the electronic state of ErB_{66} in microscopic viewpoint.

EXPERIMENTS: The Mössbauer spectroscopy was performed at Tracer Laboratory at KURNS using cryostat by a refrigerator by cooling both source and sample. The source was $(^{166}\text{Ho},\text{Y})\text{H}_2$ powder synthesized by the neutron irradiation to the dihydride with natural Ho, that is, Ho consisted of only ^{165}Ho . The irradiation condition was 2.5 hours under 1MW KUR operation. The sample was non-enriched ErB_{66} powder, that is, including 33.5 % of ^{166}Er , shaped to the pellet of 10 mm ϕ . The γ -rays from the source penetrated the sample and were detected by a CeBr_3 scintillator. The detail of the Mössbauer measurement system is shown in ref. [3].

RESULTS: The Mössbauer spectrum of ErB_{66} at 20 K is shown in Fig. 1. The magnetic hyperfine splitting is clearly shown even at 20 K, by far higher than the temperature of maximum of the ac susceptibility. This result is clear evidence for the existence of a kind of magnetic ordering, which is discussed as spin-glass state. Furthermore, the spectrum was not a typical shape of the simple one element with magnetic splitting. It can be analyzed by a model with the distribution of magnetic hyperfine fields. The normal distribution of magnetic hyperfine fields with the mean of 628 T and the standard deviation of 38.4 T explains the spectra, as shown in Fig. 1. The existence of such distribution agrees with the spin-glass state and implies that the glass state includes the distribution of atomic magnetic moments. If we use the conversion factor 87.1 T/ μ_B derived from the ^{166}Er Mössbauer spectroscopy of antiferromagnetic Er_3Ge_4 [4], these parameters correspond to the mean of 7.21 μ_B and the standard deviation of 0.441 μ_B .

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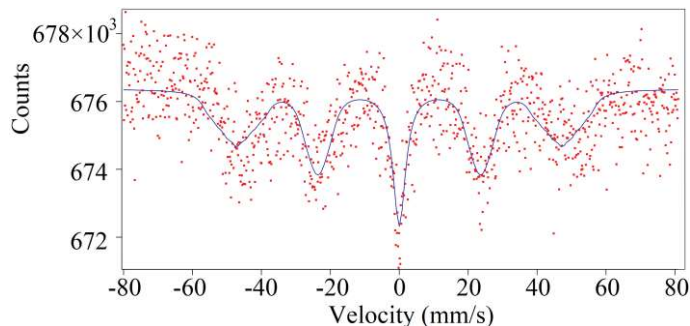


Fig. 1 The Mössbauer spectrum of ErB_{66} at 20 K. The red dots are experimental data and the line is a fitting with a distribution of the magnetic hyperfine interaction.

Search of ^{166}Er Mössbauer Single-Line Materials

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INTRODUCTION:

The Mössbauer spectroscopy is one of the most powerful methods to investigate electronic states and magnetic properties by extracting the information of a specific isotope. Mössbauer spectroscopy in general is performed for quite limited isotopes, such as ^{57}Fe and ^{119}Sn . On the contrary, the neutron irradiation facility at Kyoto University Reactor (KUR) at KURNS can be used to produce various radioactive isotopes for the Mössbauer sources. Moreover, some isotopes can be complementarily produced by high-energy γ -ray irradiation converted from electron beam from the electron linear accelerator (KURNS-LINAC). We have been developing practical methods for Mössbauer spectroscopy for various isotopes. Mössbauer spectroscopy are available at present in following isotopes(source in parentheses): $^{61}\text{Ni}(^{61}\text{Co})$, $^{125}\text{Te}(^{125m}\text{Te})$, $^{129}\text{I}(^{129}\text{Te}, ^{129m}\text{Te})$, $^{161}\text{Dy}(^{161}\text{Tb})$, $^{166}\text{Er}(^{166}\text{Ho})$, $^{169}\text{Tm}(^{169}\text{Er})$, $^{170}\text{Yb}(^{170}\text{Tm})$, $^{197}\text{Au}(^{197}\text{Pt})$, etc.

Among these isotopes, ^{166}Er Mössbauer spectroscopy is one of the most useful methods for studies of electronic or magnetic state for Er compounds. For some former studies, HoAl_2 was used as a Mössbauer source [1]. However, the measurement temperature had not to be cooled below around 40 K, since HoAl_2 has magnetic transition at 25 K. To overcome this disadvantage, another source material, $\text{Ho}_{0.4}\text{Y}_{0.6}\text{H}_2$ had been successfully synthesized with similar method in the references [2,3] and confirmed a single-line ^{166}Er Mössbauer spectra as low as 18K [4]. As for ^{166}Er Mössbauer spectroscopy, not only the source material, but also single-line Er compound is important. The single-line Er compound can also be used as a reference material for synchrotron-radiation-based Mössbauer spectroscopy. Although ErH_2 can be used as a single-line Er compound, it has disadvantages of low recoilless fraction and degradation at ambient atmosphere. Er-Al alloys can also be used as a single-line Er compound, which is stable at ambient atmosphere. However, the recoilless fraction is still low. Therefore, it is important to search for another useful single-line Er compound.

In this report, a study of an Er compound, ErF_3 is described. ErF_3 is expected as a compound with high recoilless fraction. However, the Mössbauer spectra of ErF_3 has not been well known at low temperature.

EXPERIMENTS AND RESULTS:

The source material $\text{Ho}_{0.4}\text{Y}_{0.6}\text{H}_2$ has been synthesized by hydridation of $\text{Ho}_{0.4}\text{Y}_{0.6}$ alloy. The neutron irradiation was performed at pneumatic tube of KUR for 150 minutes at 1MW operation or 30 minutes at 5MW operation. The ^{166}Ho source with a half-life of 26.8 h was obtained and used for the ^{166}Er Mössbauer measurement for 2 or 3 days. The source material can be irradiated repeatedly, when it is kept in a vacuum desiccator after use to avoid degradation. The ErF_3 was purchased from Mitsuwa Chemicals Co., Ltd. The measurement temperature was controlled by keeping both the source and the absorber in a He-gas filled space using a closed cycle He-refrigerator.

The obtained spectra of ErF_3 at about 20K are shown in Fig. 1. The spectrum showed that magnetic splitting was not clearly observed. However, the spectra contained a broadened component. It may result from relaxation phenomenon of magnetic ordering. Therefore, ErF_3 is unfortunately found to be unsuitable for a single-line material. However, it is worth researching on property of ErF_3 to search for another candidate for single-line compounds in related compounds.

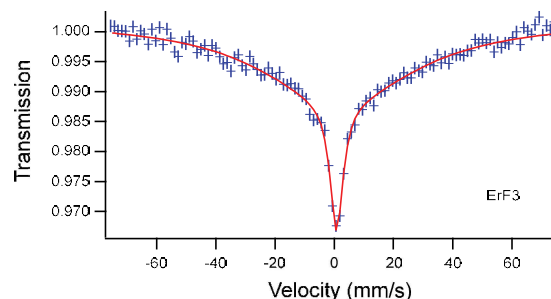


Fig. 1. ^{166}Er -Mössbauer spectrum of ErF_3 using $^{166}\text{Ho}_{0.4}\text{Y}_{0.6}\text{H}_2$ source at about 20 K.

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