

I-1. PROJECT RESEARCHES

Project 1

Project Research on Advances in Isotope-Specific Studies Using Multi-Element Mössbauer Spectroscopy

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OBJECTIVES OF RESEARCH PROJECT:

Irreplaceable feature 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 are the investigation in the frontier of the materials science and the development of advanced experimental methods by using multi-element Mössbauer spectroscopy. Promotion of variety of Mössbauer isotope provides useful and valuable methods in modern materials science even for complicated systems.

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

^{197}Au in R5P1-1; ^{61}Ni in R5P1-2; ^{57}Fe in R5P1-3, R5P1-4, R5P1-5, R5P1-6, R5P1-7, R5P1-8, R5P1-9; and other developments in R5P1-10, R5P1-11

MAIN SUBJECTS AND RESULTS OF THIS REPORT:

Main subjects and results are as follows:

(R5P1-1, H. Ohashi) Temperature Dependence of ^{197}Au Mössbauer Spectra for Au(III) Ions Adsorbed on MnO_2

H. Ohashi *et al.* investigated Au(III) catalyst supported by MnO_2 synthesized from using HAuCl_4 . The temperature-dependent ^{197}Au Mössbauer spectroscopy was performed to confirm the existence of Au(III) component.

(R5P1-2, T. Kitazawa) ^{61}Ni Mössbauer spectroscopy of Fe-Ni Hofmann-type complex

K. Kitase *et al.* investigated spin-crossover phenomenon in Fe-Ni Hofmann-type complex, $\text{Fe}(\text{Allyl Isonicotinate})_2[\text{Ni}(\text{CN})_4]$. The ^{61}Ni Mössbauer spectra of the compound shows similar singlet spectrum to $\text{Fe}_{86}\text{V}_{14}$ alloy. The recoilless fraction was smaller due to organic ligands and flexible framework.

(R5P1-3, K. Shinoda) Mössbauer Spectra and Intensity Tensors for Fe^{3+} and Fe^{2+} of Bridgmanite

K. Shinoda *et al.* measured single crystals of bridgmanite by using the microscopic Mössbauer spectroscopy. The intensity tensors of quadrupole doublets for both Fe^{3+} and Fe^{2+} sites were successfully evaluated.

(R5P1-4, I. Mashino) Electrical conductivity and the valence state of iron in silicate glasses up to Mbar pressures

I. Mashino *et al.* evaluated the valence state of iron bearing enstatite glass to investigate high pressure studies for understanding the behavior of iron silicate melts at the bottom of the mantle.

(R5P1-5, M. Tabuchi) Fe valence control for Fe and Ni substituted Li_2MnO_3 positive electrode material during charge and discharge reactions using ^{57}Fe Mössbauer spectroscopy

M. Tabuchi *et al.* investigated Fe and Ni substituted Li_2MnO_3 electrode for Li-ion battery with Fe:Ni:Mn ratios of 15:15:70. Fe valence components were evaluated by Mössbauer spectroscopy to improve its charge and discharge characteristics.

(R5P1-6, K. Yonezu) Experimental Preliminary Approach on the Precipitation Mechanism of Banded Iron Formation (BIF): Precipitation Behavior of Iron in the Absence and Presence of Silicic Acid

K. Yonezu *et al.* investigated the role of silicic acid in precipitation process to investigate precipitated sedimentary rock at Precambrian age. The results suggested magnetite was formed even at high silicic acid concentrations.

(R5P1-7, Y. Kamihara) Research on Magnetism and Electronic Phase in a H-doped Iron-based Superconductor II

Y. Kamihara *et al.* are investigating H-doped SmFeAsO and F-doped SmFeAsO , iron-based superconductor with high transition temperature of around 55K. The temperature-dependent Mössbauer spectroscopy was performed to clarify its electronic and magnetic properties.

(R5P1-8, K. Okada) Magnetic Measurements of Irons in Soda-lime Glass by Mössbauer Spectroscopy (2)

K. Okada *et al.* performed Mössbauer Spectroscopy of soda-lime glass to evaluate Fe^{2+} and Fe^{3+} components.

(R5P1-9, Y. Kobayashi) ^{57}Fe Mössbauer Study of Fe-Si Magnetic Materials

Y. Kobayashi *et al.* studied magnetic properties of Fe-Si alloy to reveal Fe-Si disordered phase and Fe_3Si phase.

(R5P1-10, R. Masuda) Mössbauer study of nanoparticles synthesized in Y-type Zeolite

R. Masuda *et al.* measured temperature-dependent Mössbauer spectra of nanoparticles in HY-type zeolite to evaluate the Debye temperature for the information of size of the particle.

(R5P1-11, S. Kitao) ^{166}Er Mössbauer Study of ErB_4

S. Kitao *et al.* investigated ^{166}Er Mössbauer spectra of ErB_4 to evaluate magnetic properties. The results showed the relaxation phenomena were observed above the antiferromagnetic transition temperature.

Temperature Dependence of ^{197}Au Mössbauer Spectra for Au(III) Ions Adsorbed on MnO_2

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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/ MnO_2 from HAuCl_4 compounds was known to be difficult. This was because Au(III) ions were partially reduced to Au(0) on the surface of MnO_2 .

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, there remained doubts whether this component was really trivalent gold. In this study, we aimed to solve the above problem by measuring the ^{197}Au Mössbauer spectra for Au(III) ions adsorbed on MnO_2 with varying temperature.

EXPERIMENTS: Manganese dioxide was added to the HAuCl_4 aqueous solution to adjust the pH 9, and the mixture was stirred. 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 10wt%.

^{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 20-60 K, and the measurement was performed by the transmission method.

RESULTS: Figure 1 shows ^{197}Au Mössbauer spectra at 20 - 60 K for the sample of Au(III) adsorbed on MnO_2 . The spectra were divided into three peaks and analyzed temperature changes in the areas of peaks with relatively high IS and QS values using the same method as previously reported[2]. The results showed that it behaved similarly to other Au(III) compounds. It was estimated that the peak was Au(III).

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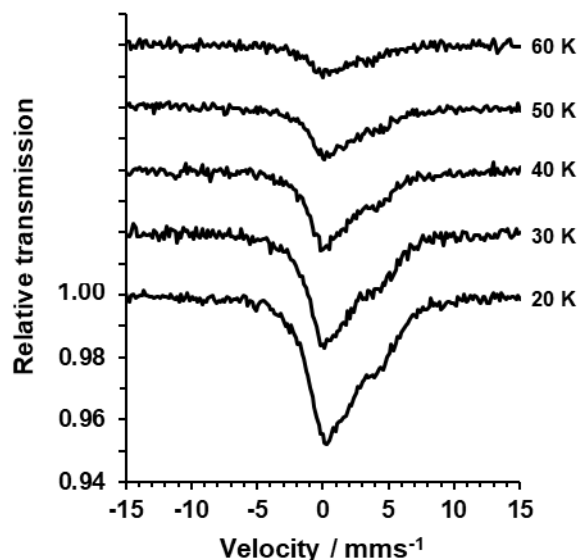


Fig. 1. ^{197}Au Mössbauer spectra at 20-60 K for the sample of Au(III) adsorbed on MnO_2 .

^{61}Ni Mössbauer spectroscopy of Fe-Ni Hofmann-type complex

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INTRODUCTION: Spin-crossover (SCO) phenomenon is a reversible spin transition between high-spin and low-spin state. Hofmann-type complex is the one of coordination polymer which consist of center metal ion, bridging ligand $[\text{M}(\text{CN})_4]$, pyridine-type ligand. In Hofmann-type SCO complex, SCO phenomenon usually occurs in Fe center. ^{57}Fe Mössbauer spectroscopy is useful tool to investigate Hofmann-type SCO complex since the isomer shift (IS), quadrupole splitting (QS), and spectrum shape of ^{57}Fe Mössbauer spectroscopy are sensitive to the coordination environments or spin state of Fe sites, so ^{57}Fe Mössbauer spectroscopy is widely used by many researchers to investigate SCO phenomenon of Fe center in Hofmann-type complex. Hofmann-type complex contains other Mössbauer active nuclei such as Ni, Au. Nevertheless, other type of Mössbauer spectroscopy such as ^{61}Ni Mössbauer spectroscopy is much less researched than ^{57}Fe Mössbauer spectroscopy. Now we synthesized Fe-Ni Hofmann-type complex $\text{Fe}(\text{Allyl Isonicotinate})_2[\text{Ni}(\text{CN})_4]$ and researched the properties of this complex by ^{61}Ni Mössbauer spectroscopy.

EXPERIMENTS: The complex was synthesized using Mohr's salt $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, citric acid, $\text{K}_2[\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O}$, and pyridine-type ligand ethyl nicotinate. First, Mohr's salt and ligand were dissolved into water. Then aqueous solution of $\text{K}_2[\text{Ni}(\text{CN})_4]$ was dropped into this solution. The powder sample was obtained as two types of colors, large amount of yellow powder and small amount of orange powder. We can separate yellow powder from orange powder. We confirmed that both types of powder are same formula and isostructural by elemental analysis and powder X-ray diffraction measurement. We charged 1.969 g of powder of this complex into a 10 mm diameter holder for ^{61}Ni Mössbauer spectroscopy. The thickness of Ni atom in this sample is c.a. 0.282 g cm^{-2} .

RESULTS: Fig. 1 shows ^{61}Ni Mössbauer spectroscopy of $\text{Ni}_{86}\text{V}_{14}$ alloy and $\text{Fe}(\text{Allyl Isonicotinate})_2[\text{Ni}(\text{CN})_4]$. Both spectra has singlet peak. The parameter of former spectrum is IS = 0 (definition), FWHM = 0.96 mm s^{-1} , and relative peak area is 0.0411 whereas that of latter spectrum is IS = -0.002 mm s^{-1} , FWHM = 1.07 mm s^{-1} , and relative peak area is 0.0326. The thickness of the $\text{Fe}(\text{Allyl isonicotinate})_2[\text{Ni}(\text{CN})_4]$ sample (c.a. 0.282 g cm^{-2} for Ni atom) is thicker than the $\text{Ni}_{86}\text{V}_{14}$ alloy sample (0.0907 g cm^{-2} , c.a. 0.0794 g cm^{-2} for Ni atom). Nevertheless, the absorption intensity of the spectrum of $\text{Fe}(\text{Allyl isonicotinate})_2[\text{Ni}(\text{CN})_4]$ is smaller than $\text{Ni}_{86}\text{V}_{14}$ alloy. This result could be explained as Hofmann-type coordination polymers contains organic long ligands and flexible framework. As result, the recoil fraction in $\text{Fe}(\text{Allyl isonicotinate})_2[\text{Ni}(\text{CN})_4]$ is smaller than that of $\text{Ni}_{86}\text{V}_{14}$ alloy.

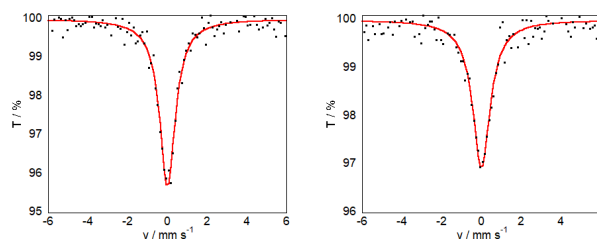


Fig. 1. ^{61}Ni Mössbauer spectroscopy of $\text{Ni}_{86}\text{V}_{14}$ alloy (left) and $\text{Fe}(\text{Allyl isonicotinate})_2[\text{Ni}(\text{CN})_4]$ (Right).

Mössbauer Spectra and Intensity Tensors for Fe³⁺ and Fe²⁺ of Bridgmanite

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INTRODUCTION: Bridgmanite is a high-pressure mineral that is supposed to be the major mineral in the Earth's lower mantle. Bridgmanite belongs to orthorhombic system. Crystal structure of bridgmanite is based on the perovskite structure. Although bridgmanite is a nominally anhydrous mineral, bridgmanite incorporates hydrogen as OH⁻ in the crystal structure and is supposed to act as 'water reservoir' of Earth's mantle. Purevjav et al. (2023) synthesized high-quality single crystal of bridgmanite with a composition of (Mg_{0.88} Fe²⁺_{0.05} Fe³⁺_{0.05} Al_{0.03}) (Si_{0.88} Al_{0.11} H_{0.01}) O₃, evaluated the crystallographic position of hydrogen by single crystal neutron diffraction and infrared spectroscopy. In Purevjav et al. (2023), the ratio of ferrous to ferric irons was determined by Mössbauer spectra of the single crystal of the synthesized bridgmanite. In the analyses of Mössbauer spectra, two quadrupole doublets due to Fe²⁺ and Fe³⁺ and either doublet of the same intensity of lower and higher Doppler velocities were assumed. However, the lower (*I_l*) and higher peak's intensity (*I_h*) of quadrupole doublets due to Fe ions in a single crystal generally show different intensities. The peak intensity (*I*) defined as *I_h*/(*I_h*+*I_l*) depends on the angle between crystallographic axes and direction of γ -ray. To analyze Mössbauer spectra of single crystal bridgmanite, intensity tensors for Fe³⁺ and Fe²⁺ of bridgmanite are necessary as indicated by [2]. In this study, crystallographically oriented crystals of bridgmanite were prepared by X-ray diffraction, and Mössbauer spectra of single crystal of bridgmanite were measured to examine intensity tensors.

EXPERIMENTS and RESULTS: Two single crystals of bridgmanite, which were synthesized by [1], were used to measure Mössbauer spectra. 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 4mm ϕ 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 ± 7 mm/s. Nine Mössbauer spectra of crystallographically oriented single crystals of bridgmanite were measured. The incident γ -ray directions were chosen to uniformly distribute against crystal axes. By normalizing all spectra and averaging the normalized spectra, an averaged Mössbauer spectrum of bridgmanite was obtained. Isomer shift and quadrupole splitting for Fe³⁺ and Fe²⁺ were obtained from the averaged spectrum by fixing peak intensity as 0.5 during peak analyses using Mosswinn program. Figure 1 shows Mössbauer spectrum of bridgmanite measured under γ -ray parallel to the *c*-axis, where black dots are raw data, broken line is due to Fe³⁺ and dotted line is due to Fe²⁺. Peak separations were done by fixing isomer shift and quadrupole splitting as obtained from the averaged spectrum. According to Zimmermann (1975) [3], three tensors' components (*I_{xx}*, *I_{yy}*, *I_{zz}*) for Fe³⁺ and Fe²⁺ of bridgmanite were obtained from nine spectra as (0.461, 0.468, 0.571) for Fe³⁺ and (0.587, 0.449, 0.464) for Fe²⁺, respectively.

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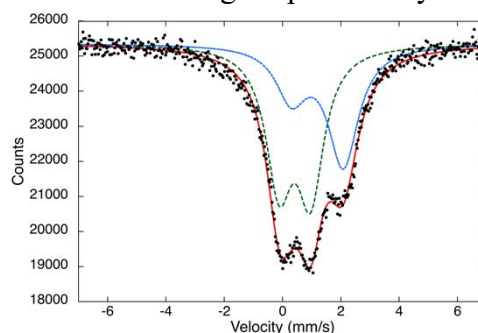


Fig.1. Mössbauer spectrum of bridgmanite measured under γ -ray parallel to the *c*-axis.

Electrical conductivity and the valence state of iron in silicate glasses up to Mbar pressures

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INTRODUCTION: Silicate melt is expected to exist at the bottom of the mantle, but its stability is still under debate. Previous studies [1,2] showed that the iron partition coefficient between the melt and solid changes at around ~ 80 GPa, which would produce a denser melt with negative buoyancy. They suggested that the observed discontinuity of the iron partition coefficient could be explained by spin transition of iron in the melts or the change in crystal chemistry of the co-existing mineral. The spin transition of iron affects not only the partitioning behavior but also the physical properties such as density, electrical and thermal conductivities. To understand the valence/spin states of iron in silicate melts, we are conducting high-pressure electrical conductivity measurements of iron-bearing enstatite glass which has a representative composition of the mantle, because silicate glasses have been considered as good analogues of silicate melts.

EXPERIMENTS: Iron-bearing enstatite glass (hereafter Fe-glass) was synthesized from reagent MgO, Fe₂O₃ and SiO₂ powders. The mixtures of oxides were placed in a platinum foil capsule and melted in air using an electric furnace at 1650 °C. The sample was subsequently quenched by immersing the base of the crucible in water. The conventional ⁵⁷Fe-Mössbauer spectroscopy was performed using a ⁵⁷Co source in Rh matrix with nominal activity of 1.85 GBq at Institute for Integrated Radiation and Nuclear Science, Kyoto University. The velocity scale is referenced to α -Fe.

RESULTS: Fig. 1 shows the Mössbauer spectrum of Fe-glass. The obtained spectrum was fitted using a two-doublet model, one with higher center shift (CS) (doublet#1) and one with lower CS (doublet#2). According to our previous measurements of iron-bearing glass, we fixed the quadrupole splitting (QS) value of doublet#2 to 1.2 (mm/s) (Table 1). Compared with hyperfine parameters in silicate glasses previously reported at ambient condition [3,4], doublets#1 and #2 can be assigned to Fe²⁺ and Fe³⁺ in octahedral site. We are now proceeding with the high-pressure experiments and then will discuss the effects of the valence/spin states of iron on the conductivity.

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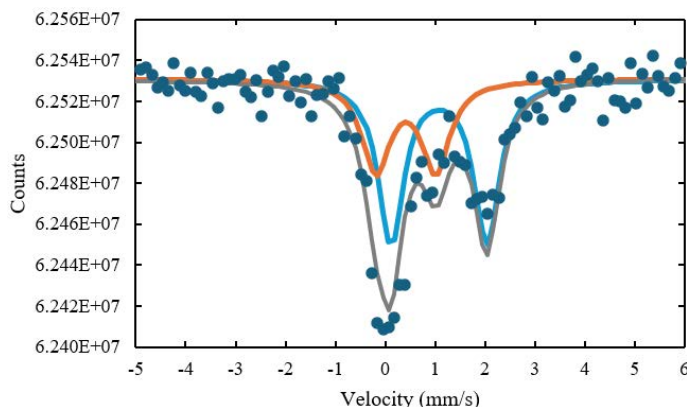


Fig.1. Mössbauer spectrum of Fe-glass. Blue and orange curves represent doublets#1 and #2 respectively

Table 1.

Fitting results of the ambient conventional Mössbauer spectrum of Fe-glass

	IS (mm/s)	QS (mm/s)	FWHM (mm/s)	Aria (%)
Doublet 1 (Fe ²⁺)	1.08±0.03	1.93±0.07	0.62±0.11	62±8
Doublet 2 (Fe ³⁺)	0.41±0.07	1.2(fix)	0.67±0.23	38±8

Fe valence control for Fe and Ni substituted Li_2MnO_3 positive electrode material during charge and discharge reactions using ^{57}Fe Mössbauer spectroscopy

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INTRODUCTION: Lithium-ion battery (LIB) is utilized as large power source for electrical vehicle (EV) and Energy storage system (ESS). Further development for such applications, minimizing Co and Ni contents in positive electrode is necessary, because both elements are recognized as rare metals. Present Fe and Ni substituted Li_2MnO_3 has features of Co-free and minimizing Ni content (<20% per total transition metal content) [1]. However, precise Fe valence state analysis is important for further improve charge and discharge characteristics. Therefore, ^{57}Fe Mössbauer spectroscopy was selected.

EXPERIMENTS: Target materials were prepared by coprecipitation-calcination method [2]. The Fe:Ni:Mn ratio was set to 15:15:70, $(\text{Li}_{1+x}(\text{Fe}_{0.15}\text{Ni}_{0.15}\text{Mn}_{0.70})_{1-x}\text{O}_2, 0 < x < 1/3)$. First and second (final) calcination atmospheres are air and nitrogen, respectively. Calcination temperatures of 1st and 2nd ones were 650 and 900 °C for 5 h, respectively. Products were characterized by XRD, charge and discharge data and ^{57}Fe Mössbauer spectroscopy.

RESULTS: XRD data for as-prepared sample showed formation of single-phase with monoclinic Li_2MnO_3 type structure. Its ^{57}Fe Mössbauer spectrum can be fitted by a symmetric doublet (isomer shift (IS) = +0.33 mm/s). Only high-spin Fe^{3+} ion was contained. Fig. 1 (left) showed ^{57}Fe Mössbauer spectrum for first charged electrode. In addition to trivalent iron (A) component (71%), B and C ones were observed, both had highly negative IS values (29%, see left figure). The IS value for B component was close to pentavalent one (-0.4 mm/s), whereas that for C one corresponded to intermediate (4.5+) between tetravalent (-0.1 mm/s) and pentavalent irons. Fig. 1 (left) showed ^{57}Fe Mössbauer spectrum for fifth charged electrode. The fraction of high valence state B component (IS=-0.39 mm/s, 5+ state) was changed to small (5.6%), indicating that Fe reduction was occurred on deep charging. However, no high valence component was detected for the sample with lower 2nd calcination temperature (850 °C). The fact means that present calcination condition is a suitable for utilizing Fe as 3+/5+ redox center.

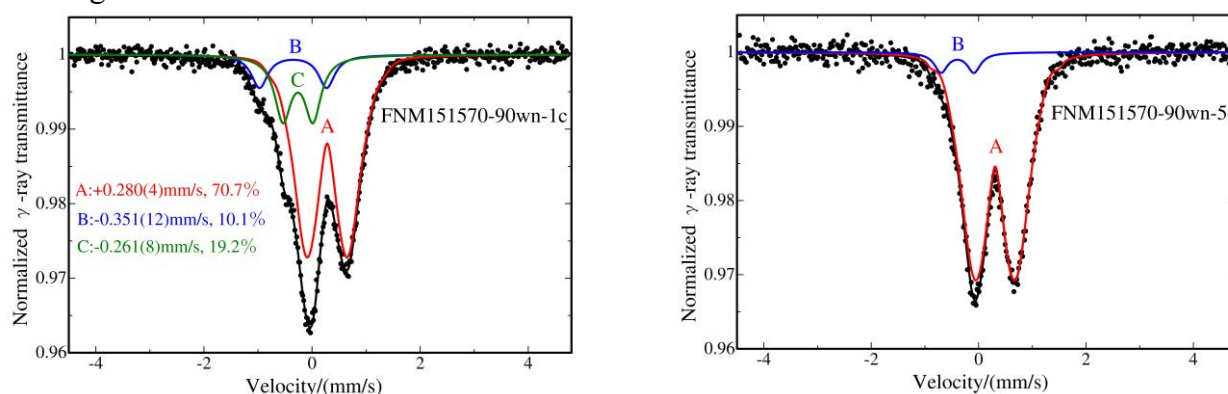


Fig. 1 ^{57}Fe Mössbauer spectra for first (left) and fifth charged (right) electrodes. First and fifth charged states correspond to 80mAh/g delithiation and 4.8 V charging, respectively.

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Experimental Preliminary Approach on the Precipitation Mechanism of Banded Iron Formation (BIF): Precipitation Behavior of Iron in the Absence and Presence of Silicic Acid

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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. The formation of BIF was closely related with seafloor hydrothermal activity. In addition, the hydrothermal water, anoxic water was mixed with oxic seawater (e.g., Otake and Otomo, 2021). However, there are many mysteries remained on the formation mechanism of BIF. One of the biggest issues are the alternation of iron bearing mineral and silicate minerals. Therefore, this study aims to understand the formation mechanism, especially redox condition during the formation of BIF. Here, we would like to report the precipitation behavior of iron in the absence and presence of silicic acid. For further understanding of the formation mechanism, comprehensive analyses on the precipitates are necessary.

EXPERIMENTS: The sample solutions were prepared by the iron chloride and silicic acid stock solutions. Initial concentration of Fe and silicic acid is adjusted by the dilution with ultra pure water to be 50 – 1500 ppm and 0 – 10 ppm, respectively. In case of the absence of silicic acid, the sample solution was adjusted to pH 8 after the dilution and this timing was regarded as T=0. Precipitation reaction was allowed for 15 minutes with stirring and the monitoring of redox potential and dissolved oxygen concentration. After 15 minutes, the suspension was filtered by 0.45 μ m membrane filter. Filtrate was immediately kept in acidic condition and used for the determination of Fe by ICP-AES and the residue on the filter was kept for solid characterization. This time, we focused on the results from filtrate.

RESULTS: As shown in Fig. 1(a), precipitation % of Fe was almost 100 % when initial concentration was low. Under such condition, precipitated iron species was amorphous phase. In contrast, when initial concentration of Fe was high and precipitation % is less than 30 %, the iron species precipitated was mostly magnetite based on XRD analysis, suggesting that magnetite is more likely to form under conditions where there is a certain limit to the amount of oxygen. Fig. 1(b) showed more effective precipitation of Fe (major solid phase by XRD was magnetite) in the presence of silicic acid. These results may imply that it is possible that magnetite was formed even at high silicic acid concentrations because silicic acid can be adsorbed on iron hydroxide since iron hydroxide is formed at the same timing of magnetite formation. Further evidence will be obtained from Mossbauer analysis at KURNS.

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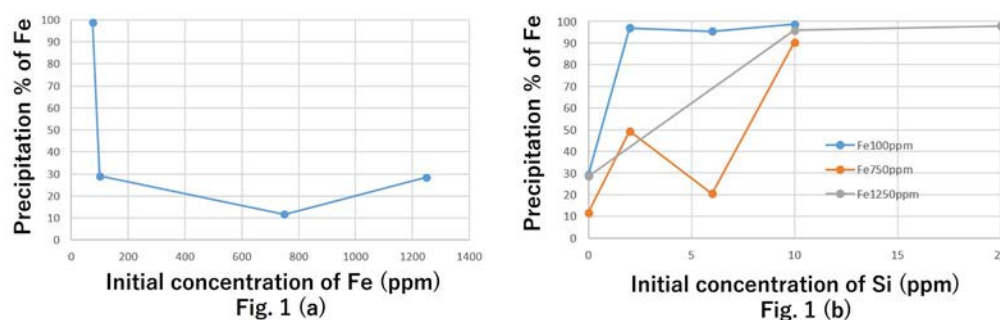


Fig. 1. Precipitation behavior of Fe as a function of the initial concentration of (a) Fe and (b) silicic acid contained with fixed Fe concentration of Fe.

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

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INTRODUCTION: The research in 2023 is the second year of a three-year plan to clarify the bulk electrical and magnetic properties of polycrystalline $\text{SmFeAsO}_{1-x}\text{H}_x$ (H-doped Sm1111) prepared by high temperature and high pressure synthesis as a preliminary step for Mossbauer spectroscopy in 2024.

Among the Fe-SC, $\text{SmFeAsO}_{1-x}\text{F}_x$ (F-doped Sm1111) and H-doped Sm1111, whose mother compound is an antiferromagnetic (AFM) metal SmFeAsO , exhibit $T_c \sim 55$ K under ambient pressure. This feature is similar to an electronic and magnetic phase diagram for high- T_c cuprate superconductors, whose mother compound exhibit antiferromagnetic phase of copper sublattice. [1-6] A novel ^{57}Fe Mössbauer spectra of H-doped Sm1111 will appear during 2024-2025.

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 performed at a low temperature.

RESULTS: Figure 1 exhibits lattice constants and volume as a function of the H-doped Sm1111 samples. The F contents are determined using Volume Vegard's rule. [7]

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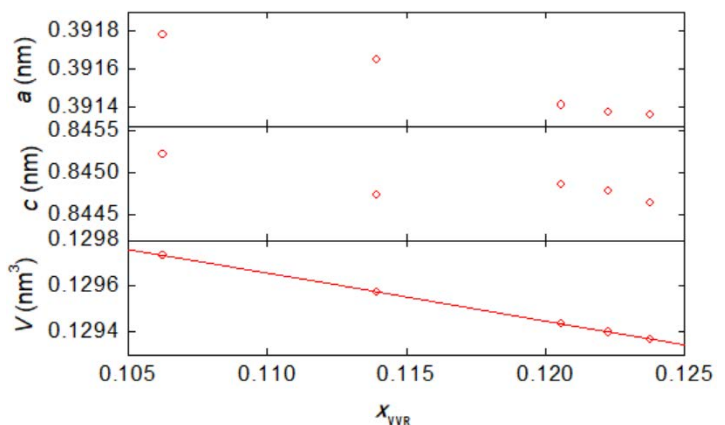


Fig. 1. Lattice constant (a, c) and lattice volume for the H-doped Sm1111.

Magnetic Measurements of Irons in Soda-lime Glass by Mössbauer Spectroscopy (2)

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SPRING-8/JASRI

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INTRODUCTION: Glass is used in many applications in our every-day lives and has exciting new applications related to the energy. Soda-lime glass is made of mainly silica (SiO_2) and additive many other materials, such as magnesium, sodium, calcium, aluminum, iron, sulfur, and so on. Our reference glass composition, in percent by weight (wt%), was 72.25 SiO_2 , 1.75 Al_2O_3 , 4.00 MgO , 8.00 CaO , 14.00 Na_2O as basic components, and 0.015-5 iron in terms of Fe_2O_3 as coloring components. Iron contaminants of less than 0.0005-0.01 wt% from raw materials, and iron injection up to 1.5-5 wt%. The iron oxides in a glass composition are thought to be present in forms of Fe^{3+} and Fe^{2+} . The control parameters for irons are two: (1) the total iron mass weight percent in terms of Fe_2O_3 , and (2) the ratio of Fe^{2+} to total iron ions ($\text{Fe}^{2+}/\Sigma_n\text{Fe}$). The Fe^{3+} component adds a light yellow tint to the glass and absorption in the ultraviolet and visible band, while the Fe^{2+} component adds a blue tint to the glass and absorption in the near-infrared band (1 μm). The transmission from ultraviolet to infrared in glass cannot be explained by simple Fe^{2+} and Fe^{3+} structures. Then, to reveal the exact local structures of irons (Fe^{2+} and Fe^{3+}) is necessary. Many scientists proposed many new theories and local structures [1-2], but they did not resolve it completely.

We have prepared reference glass samples with using the Mössbauer isotope ^{57}Fe (natural abundance is about 2.119 %) and sample glass with natural Fe for measurements. The chemical composition of iron oxide in the ^{57}Fe enrichment glass was from 0.015 to 5 wt%, and the $\text{Fe}^{2+}/\Sigma_n\text{Fe}$ was from 0 to 0.6. We have investigated these samples by nuclear resonant inelastic scattering and XAFS methods at synchrotron radiation to reveal the local atomic structure around and neighboring iron atoms in sub-nanometer region [3]. And then we have investigated No. 100 sample glass with 30 wt% chemical composition of natural iron oxide by Mössbauer experiments to reveal the magnetic property in glass under recycled process.

EXPERIMENTS: The measurements were performed using conventional Mössbauer spectrometer. The specimens for Mössbauer measurements were tuned to 10 mm-phi pellet. We investigated two samples with 30 wt% chemical composition of natural iron oxide.

RESULTS: There were difference between the data of the 1st and the 3rd recycled samples as shown in Fig. 1, and the six line structures in the data of recycle 1st indicated the $\alpha\text{-Fe}_2\text{O}_3$, which was not melted completely.

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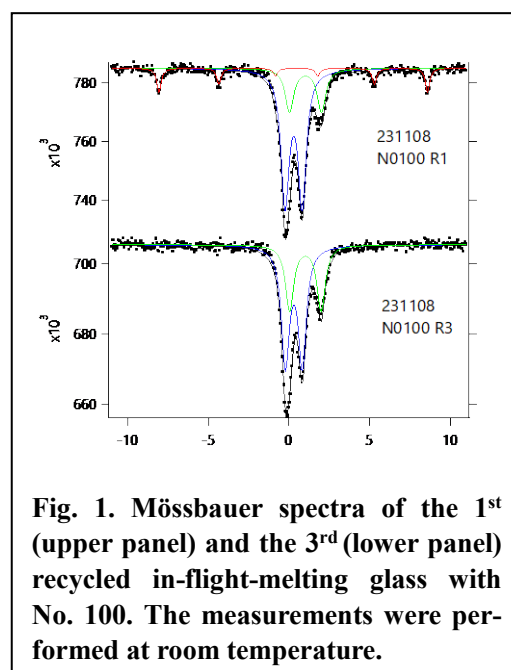


Fig. 1. Mössbauer spectra of the 1st (upper panel) and the 3rd (lower panel) recycled in-flight-melting glass with No. 100. The measurements were performed at room temperature.

⁵⁷Fe Mössbauer Study of Fe-Si Magnetic Materials

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INTRODUCTION: Fe-Si alloy is a soft magnetic material used in many devices, such as transformers. A method of pressing powdered alloys is used to produce complex shapes, such as transformer cores. The alloy powders are prepared using the gas atomization method, in which the melted alloy is splayed into gas. We performed Mössbauer spectroscopy to investigate the state of the powder created using the gas atomization method.

EXPERIMENTS: The Fe-Si powder samples were prepared using the atomizing process with nitrogen gas. Base alloys were Fe-6.5wt%Si. The powder samples were annealed at 850°C for 3 hours for homogenization. ⁵⁷Fe Mössbauer measurements were performed at room temperature using the conventional Mössbauer spectrometer. About 30 mg of sample and about 100 mg of boron nitride were mixed and put in the sample holder with a diameter of 10 mm for Mössbauer transmission measurement. α -Fe was used for velocity calibration. The Mossbauer spectra were fitted with a MossWinn [1] program.

RESULTS: Two Fe sits in Fe₃Si ordered phase (D0₃ structure): the A site, where four of the eight nearest neighbors in the bcc structure are Si, and the B site, where all the nearest neighbors are Fe. The Fe atomic ratio of each site is 2:1. Figure 1 shows the Mössbauer spectra of Fe₃Si and Fe-6.5wt%Si powder samples. The spectrum of Fe₃Si consists of two magnetic components. The component with the large internal magnetic field is due to the B site, whose nearest neighbors are all Fe, and the component with the small internal magnetic field is due to the A site, whose four nearest neighbors are Si, and their area ratio is approximately 1:2.

The spectrum of the Fe-6.5wt%Si sample can be analyzed with four components whose internal magnetic fields are 34~24T and two components with almost the same parameters as the Fe₃Si sample (bold solid lines in the spectrum). The former four components are derived from the Fe-Si disordered phase of the bcc structure [2]. The previous work shows that the composition is divided according to how many Si atoms are present in the nearest or the second-nearest neighbor of Fe atoms. As the number of adjacent Si increases, the internal magnetic field becomes smaller, and the proportion of each component can be estimated from the binomial distribution of the Si concentration. The area ratios estimated from calculations generally agreed with those determined from the spectra.

Analysis of these spectra revealed that the Fe-6.5wt%Si powder sample consists of a Fe-Si disordered alloy and a small amount (6%) of Fe₃Si ordered phase.

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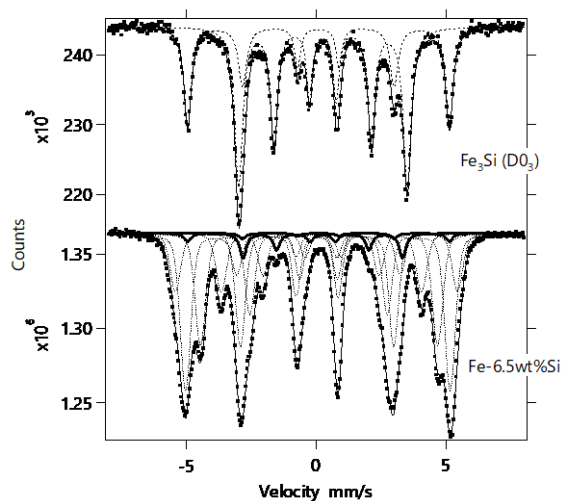


Fig. 1 Mössbauer spectra of Fe₃Si and Fe-6.5wt%Si samples.

Mössbauer study of nanoparticles synthesized in Y-type Zeolite

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INTRODUCTION: Mössbauer studies sometimes requires energy standard, especially for the determination of the isomer shift. In the Mössbauer spectroscopy by ^{57}Fe nuclide, which is the most common case, it is the center of the absorption profile of Fe metal foil. Such energy standards also exist in the Mössbauer spectroscopy by nuclides other than ^{57}Fe . However, those for some nuclides are not perfectly agreed by researchers as Fe foil for ^{57}Fe is [1]. This is because some of the following desirable conditions are not satisfied: i) high recoilless fraction (i. e. strong Mössbauer effect), ii) no hyperfine splitting or clearly split hyperfine structure, and iii) chemical stability in the air. Considering these conditions, nanoparticles might be also candidates for such energy standard because the superparamagnetic property often cancel the magnetic hyperfine structure.

Recently we focused on the nanoparticles synthesized chemically using the zeolite, which is porous in nanometers scale. Large amount of nanoparticles in the size of its cage of the zeolite framework can be synthesized chemically. Furthermore, if the γ -ray energy used in Mössbauer spectroscopy is in the hard X-ray region, zeolite framework is relatively transparent because the framework includes only light elements, such as Al, Si, and O. Here, to study the nanoparticles synthesized by this method, we measured their Mössbauer spectra of the Fe nanoparticles.

EXPERIMENTS: The sample was prepared by the chemical displacement of cations in HY-type zeolite by Fe. The resultant chemical composition was $\text{Si}_{149.9}\text{Al}_{52.3}\text{Na}_{1.6}\text{Fe}_{4.3}$, evaluated by electron probe micro analyzer (EPMA). The Mössbauer spectra were measured under temperatures down to 100 K through a cryostat using liquid N_2 in KURNS. Velocity was calibrated by enriched Fe foil at room temperature.

RESULTS: The temperature dependence of the Mössbauer spectra of the nanoparticles were shown in Fig. 1. They showed quadrupole splitting of typically 0.8 mm/s, center shift of typically 0.4 mm/s. From these Mössbauer parameters, the chemical composition of the nanoparticles would be close to hematite, $\alpha\text{-Fe}_2\text{O}_3$. Even the hematite nanoparticles with the diameter of approximately 5 nm showed magnetic splitting in 120 K [2], the diameter of the nanoparticles in this study would be less than that. If we assume that the absorption area is proportional to the recoilless fraction, the characteristic temperature under the Debye model for the fraction was $2.8 (\pm 0.6) \times 10^2$ K, which is much less than that of bulk hematite. From these results, we successfully evaluate both the absence of magnetic hyperfine splitting down to 100 K, which also yields the information of the size of the particles and the recoilless fraction of the nanoparticles.

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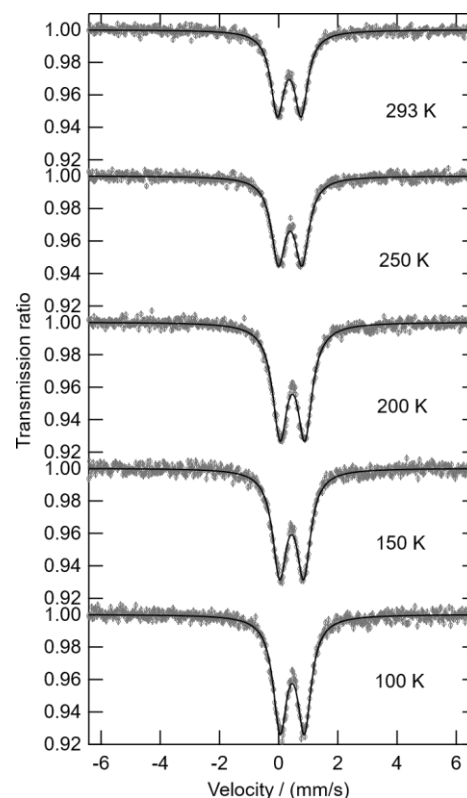


Fig. 1. Temperature dependence of the Mössbauer spectra of iron nanoparticles synthesized using HY-type zeolite.

^{166}Er Mössbauer Study of ErB_4

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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 product various radioactive isotopes (RIs) for the Mössbauer sources. Moreover, some RIs

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. Available Mössbauer isotopes at present are as follows (source nuclides in parentheses): ^{61}Ni (^{61}Co), ^{125}Te ($^{125\text{m}}\text{Te}$), ^{129}I (^{129}Te , $^{129\text{m}}\text{Te}$), ^{161}Dy (^{161}Tb), ^{166}Er (^{166}Ho), ^{169}Tm (^{169}Er), ^{170}Yb (^{170}Tm), ^{197}Au (^{197}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].

In this report, the study of a typical Er compound, ErB_4 is described. ErB_4 is expected as a compound with high re-coilless fraction. Since it has an antiferromagnetic transition temperature, T_N of 15 K, the spectrum is expected as a single-line above T_N . However, the temperature dependence of Mössbauer spectra of ErB_4 has not been known around the transition 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 if it is kept in a vacuum desiccator after using to avoid deterioration. The ErB_4 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 ErB_4 at 22K and 50K are shown in Fig. 1. The spectrum at 22 K was apparently magnetically split. The internal magnetic field was evaluated as about 790 T. In the spectrum at 22 K, a small line with large broadening has been observed. In the spectrum at 50 K, the magnetically-split component was reduced and the line with large broadening has been mainly observed. The results showed the antiferromagnetic phase was observed even above the transition temperature of 15 K. Moreover, a broad component was observed above the transition temperature possibly due to a relaxation phenomenon. These information will be useful for the studies for related several erbium borides.

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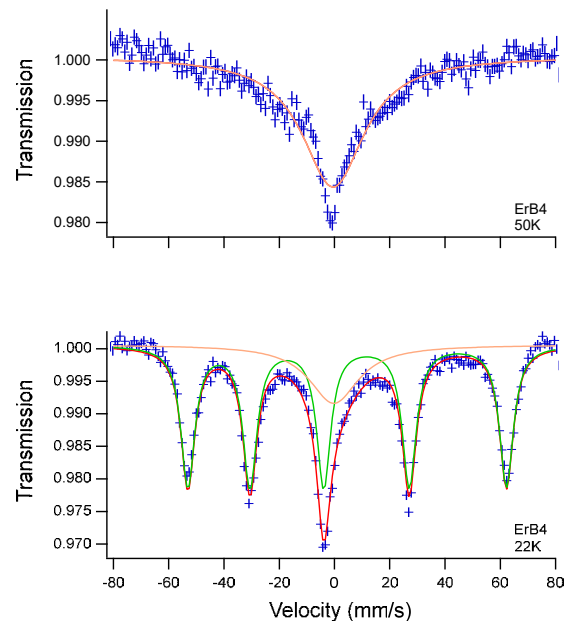


Fig. 1. ^{166}Er -Mössbauer spectrum of ErB_4 using $^{166}\text{Ho}_{0.4}\text{Y}_{0.6}\text{H}_2$ source at 50 and 22 K.