

I-1. PROJECT RESEARCHES

Project 2

PR2 Project Research on Advances in Isotope-Specific Studies Using Multi-Element Mössbauer Spectroscopy

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OBJECTIVES AND PERFORMED RESEARCH SUBJECTS:

The main objectives of this project research are the investigation of the fundamental properties of new materials and the development of the advanced experimental methods for multi-element Mössbauer spectroscopy. One of the most unique features of the Mössbauer spectroscopy is to extract element-specific or isotope-specific information. Since the Mössbauer resonance line is extremely narrow, hyperfine interactions are well resolved and give us the information on the surrounding electronic states and magnetism. Therefore, promotion of the variety of Mössbauer isotope provides more useful and valuable methods for modern precise materials science of complex systems, such as biological substances, multi-layer films, and complicated-structured matter.

In this project research, each group performed their research by specifying a certain isotope:

- ^{57}Fe in P2-1, P2-2, P2-3 and P2-4
- ^{119}Sn and ^{151}Eu in P2-5
- ^{197}Au in P2-6
- ^{119}Sn and ^{197}Au in P2-7
- Development for other isotopes in P2-8

Due to the influence of COVID-19, a part of planned researches had not been performed. Main subjects from these researches are as follows:

P2-1 Peak intensity of quadrupole doublet of cordierite by single crystal Mössbauer microspectroscopy (K. Shinoda *et al.*)

P2-2 Low-temperature behavior of Mössbauer spectra for $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ solid solution (S. Takai *et al.*)

P2-3 Characterization of steel microstructure using Mössbauer spectroscopy (G. Miyamoto *et al.*)

P2-4 Mössbauer study of diluted iron nanoparticles (R. Masuda *et al.*)

P2-5 Research on magnetism in novel Kondo lattice II (Y. Kamihara *et al.*)

P2-7 ^{119}Sn Mössbauer study of adsorbed Sn on metallic oxide (Y. Kobayashi *et al.*)

P2-8 Development of Single-Line Compounds for ^{166}Er Mössbauer Spectroscopy (S. Kitao *et al.*)

MAIN RESULTS AND CONTENTS OF THIS REPORT:

K. Shinoda *et al.* (P2-1) have developed the Mössbauer

microspectrometer to characterize the electric field gradient tensor from the anisotropic intensity ratios of quadrupole doublets. Thin sections of cordierite ($(\text{Mg,Fe})_2\text{Si}_5\text{Al}_4\text{O}_{18}$) with a hexagonal crystal structure and that with a orthorhombic structure are compared by using the ^{57}Fe -Mössbauer microspectrometer. The results showed the electric field gradient were similar in both cordierites. The results suggest that the second neighboring atoms give little effect to the electric field gradient.

S. Takai *et al.* (P2-2) studied low-temperature behavior of $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ solid solutions. Although the anomalous behavior was found in heat capacity at around 4K, the Mössbauer spectra did not show any drastic change. Therefore, the anomalous behavior in heat capacity is supposed not to be due to the change in the magnetic structure.

G. Miyamoto *et al.* (P2-3) investigated the transformation-induced-plasticity (TRIP) steels, which have high strength and high ductility using metastable retained austenite. The ^{57}Fe -Mössbauer study was performed to understand the microstructures of carbide precipitation and carbon enrichment behavior. The Mössbauer spectra of the specimen with 180-min heat treatment showed a decomposition of fcc phase and the existence of cementite or eta-carbide.

R. Masuda *et al.* (P2-4) studied the iron nanoparticle sample prepared by the laser ablation method. The Mössbauer spectra of diluted iron nanoparticles sealed in the ionic solvent were successfully measured. The spectra confirmed its Fe^{3+} property with a size distribution of the nanoparticles.

Y. Kamihara *et al.* (P2-5) investigated a novel compound of EuSn_2As_2 . The ^{119}Sn - and ^{151}Eu -Mössbauer study have been performed to reveal its magnetic property. Both of Sn and Eu spectra showed the magnetic splitting at 4.2K and the distributions of the internal magnetic fields were obtained from the refined analyses.

Y. Kobayashi *et al.* (P2-7) studied the adsorbed Sn on metallic oxides by ^{119}Sn -Mössbauer spectroscopy. The spectrum of the adsorbed Sn on $\delta\text{-MnO}_2$ was similar to that of SnO_2 . That implies the electronic structure of the adsorbed Sn is close to SnO_2 .

S. Kitao *et al.* (P2-8) performed some improvements for the source preparation in several less-common Mössbauer spectroscopy. As for ^{166}Er -Mössbauer spectroscopy, a single-line source, $\text{Ho}_{0.4}\text{Y}_{0.6}\text{H}_2$ and a single-line absorber, ErH_2 was successfully synthesized. This source and the absorber are useful for various researches for Er Mössbauer spectroscopy even in low temperatures.

PR2-1 Peak intensity of quadrupole doublet of cordierite by single crystal Mössbauer microspectroscopy

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INTRODUCTION: Cordierite ($(\text{Mg,Fe})_2\text{Si}_5\text{Al}_4\text{O}_{18}$) is a rock-forming mineral which belongs to cyclosilicate. The crystal structure of cordierite is characterized by honeycomb rings. The honeycomb rings of cordierite consist of four SiO_4 and two AlO_4 tetrahedra. Governed by the Al-avoidance rule, two Al ions occupy opposite sites in the honeycomb rings, resultantly, Si and Al ions are ordered in tetrahedral site. Ordered cordierite belongs to the orthorhombic crystal system. In cordierite which crystallized at high temperature, Si and Al ions are arranged in disorder state. As the result, the disordered cordierite belongs to hexagonal crystal system. In the crystal structure of cordierite, Fe ion occupies a octahedral site which is surrounded by three tetrahedral sites including Si and Al. Five Si and four Al occupy the added nine tetrahedral site in the unit cell of cordierite. Since nine Si and Al are arranged in the ordered state in the orthorhombic cordierite, Si and Al around the octahedral site are also ordered. On the other hand, Si and Al around the octahedral site disordered in the hexagonal cordierite. Mössbauer spectra of cordierite show quadrupole doublet.

Intensities of component peaks in a quadrupole doublet of a thin section as a single crystal are asymmetric and vary depending on the angle between the direction of incident γ -rays and the crystallographic orientation of the thin section. Intensity of quadrupole doublet (I^h / I^{total}) means a ratio between area of the peak of the higher energy (I^h) and total area of the doublet ($I^{\text{total}} = I^h + I^l$) (sum of I^h and area of the lower energy (I^l)). The intensity of component peaks of a ^{57}Fe Mössbauer doublet is related to an electronic field gradient (EFG) tensor of the site containing Fe^{2+} (Zimmermann, 1975 and 1983). Electric gradient is in inverse proportion to the cube of distance between the Mössbauer nuclei and the neighboring atoms. How far is electric gradient at Mössbauer nuclei influenced by the neighboring atoms?

In hexagonal and orthorhombic cordierite, the first neighboring atoms are commonly oxygens. However, the second neighboring atoms in the orthorhombic cordierite are expected to be different from those of hexagonal cordierite. To compare quadrupole doublet of cordierite, Mössbauer spectra of hexagonal and orthorhombic cordierite were measured. In this study, single crystals of natural cordierite were used for this study. In the crystal, black and white crystals coexist. The black crystal shows

hexagonal X-ray diffraction pattern, and the white crystal shows orthorhombic X-ray diffraction pattern. Crystallographically oriented thin sections perpendicular to c^* was prepared by measuring X-ray diffraction patterns by using X-ray precession camera. Mössbauer spectra of thin section of single crystal of cordierite were measured under γ -ray parallel to the c^* -axis.

EXPERIMENTS and RESULTS: 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 $^{57}\text{Co}/\text{Rh}$ of 4mm ϕ in diameter was used as γ -ray source. An ^{57}Fe -enriched iron foil was used as velocity calibrant. The two symmetric spectra were folded and velocity range was $\pm 5\text{mm/s}$. Thickness corrections of raw spectra were not done.

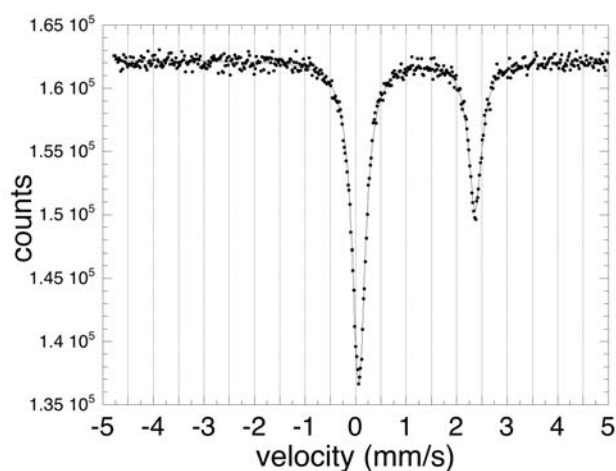


Fig.1 Mössbauer spectrum of hexagonal cordierite measured under γ -ray parallel to the c^* -axis.

Fig.1. Mössbauer spectrum of hexagonal cordierite measured under γ -ray parallel to the c^* -axis. Isomer shift, Q-splitting, line width and intensity of quadrupole doublet were 1.21, 2.30, 0.32 mm/s and 0.31, respectively. Orthorhombic cordierite shows quite resemble spectrum to the hexagonal cordierite. The Mössbauer parameters were also the same values. The results suggest that the second neighboring atoms give little effect to electric gradient at Mössbauer nuclei.

REFERENCES

- [1] Zimmermann, R. (1983) Advances in Mössbauer spectroscopy (Thosar, B.V. Ed.). pp.273-315, Elsevier Scientific Publishing Co. Amsterdam.
- [2] Zimmermann, R. (1975) Nucl. Instr. and Meth. **128**, 537-543

PR2-2 Low-Temperature Behavior of Mössbauer Spectra for Fe₂O₃-Al₂O₃ Solid Solution

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INTRODUCTION: It is well known that solid solution range of Fe₂O₃-Al₂O₃ system is much restricted due to the lattice parameter mismatch, while α -Fe₂O₃ and α -Al₂O₃ possess the isostructure of corundum-type [1]. In recent years, we have reported the formation of corundum-type structured solid solution for Fe₂O₃-Al₂O₃ system by means of mechanochemical method through the whole compositional range. Since the most of composition has been newly prepared by this method, we have investigated these solid solutions by means of EXAFS, Mössbauer spectroscopy, magnetic susceptibility, or heat capacity measurement as well as neutron diffraction.

In the previous study (30121), we have carried out Mössbauer spectroscopy on (Fe₂O₃)_{1-x}(Al₂O₃)_x solid solutions at room temperature and it is revealed that the spectra varies from sextet peaks at $x = 0$ into almost doublet at $x = 0.50$. This indicates that substitution of non-magnetic aluminum ions allows the change in magnetic properties from weak ferromagnetism to paramagnetic state by the dilution of spin interactions. In the last year (31P8-3), we have measured the low temperature Mössbauer spectra down to 10 K, where variation from doublet into sextet spectra is observed with decreasing temperature for $x = 0.5$ of (Fe₂O₃)_{1-x}(Al₂O₃)_x system.

On the other hand, heat capacity measurement showed the anomalous behavior at 4 – 5 K as shown in Fig. 1. Since no additional information in this region has been obtained, we have carried out Mössbauer spectroscopy in the liquid helium temperature.

EXPERIMENTS: Stoichiometric mixture of γ -Fe₂O₃ and γ -Al₂O₃ reagents were put into a silicon nitride milling pod with 10 milling balls. In the present study, the compositions were selected as $x = 0.50$ for (Fe₂O₃)_{1-x}(Al₂O₃)_x system. Mechanical alloying has been carried out using a planetary ball milling machine operated at 800 rpm for 240 min. The crystalline phase of the obtained sample was confirmed by X-ray diffraction.

For the measurement of Mössbauer spectroscopy, ⁵⁷Co in Rh was employed as the γ -ray source. Doppler velocity scale has been calibrated by using Fe foil. The Mössbauer spectra have been measured at various temperatures using a liquid He cryostat.

RESULTS: The Mössbauer spectra measured at various temperatures are represented in Fig. 2. It is consistent with the previous measurement that the profile showing doublet at 300 K changes into sextet below 40 K.

As for the data collected at 4.2 K, drastic change in profile is not observed from 10 K. Then the heat capacity anomaly observed at low temperature is supposed not to be accompanied by significant change in magnetic structure. Further investigation should be made to explain the anomalous heat capacity behavior.

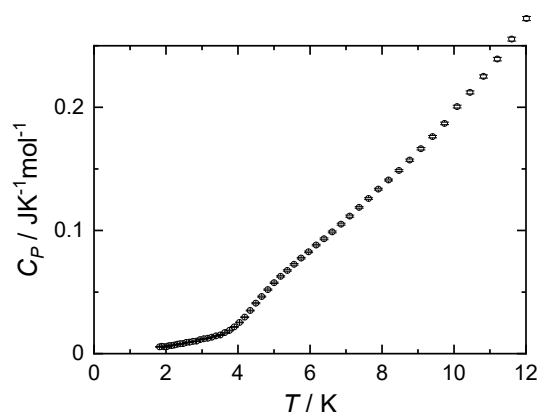


Fig. 1 Heat capacities of (Fe₂O₃)_{0.5}(Al₂O₃)_{0.5}.

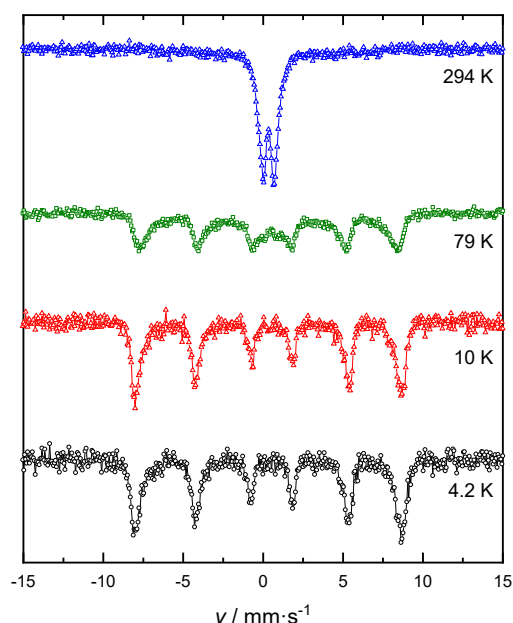


Fig. 2 Temperature dependence of Mössbauer spectra for (Fe₂O₃)_{0.5}(Al₂O₃)_{0.5}.

REFERENCES:

- [1] A. Muan et al., *J. Am. Ceram. Soc.*, 39 (1956) 207-214.
- [2] S. Takai et al., *Solid State Ionics*, 313 (2017) 1-6.

PR2-3 Characterization of steel microstructure using Mössbauer spectroscopy

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INTRODUCTION: TRIP steels with high strength and high ductility using metastable retained austenite have been developed and commercialized in order to improve both fuel efficiency and crash safety of automobiles. Understanding the stability of austenite is a key factor for improving the properties of TRIP steels.

In TRIP steels, the austenite is stabilized by enriching the carbon in the austenite through phase transformation during heat treatment. On the other hand, if the heat treatment conditions are inappropriate, carbides may form and inhibit the carbon enrichment [1, 2]. Therefore, a quantitative understanding of carbide precipitation and carbon enrichment behavior in austenite is important for microstructure control of TRIP steels.

Since the Mössbauer spectrum is sensitive to the energy levels of Fe atoms, it has the potential to identify and quantify the amount of austenite and carbide types in steel. Therefore, the purpose of this study is to investigate the amount of austenite and carbide precipitation behavior in TRIP steel using Mössbauer measurements.

EXPERIMENTS: Fe-2Mn-1.5Si-0.4C TRIP steel heat treated at various temperature and conditions were used. Thin foils of about 20 μ m in thickness were prepared from the heat-treated specimen and Mössbauer measurement is performed on the thin foil at room temperature to identify and quantify the amount of austenite and carbides. In order to elucidate the faint signal from the small amount of austenite or carbide, Mössbauer measurements were carried out for 12-13 days, that is four to five times longer than normal measurement.

RESULTS: Fig. 1 shows Mössbauer spectra taken from the TRIP steels heat-treated at 400°C for 30 min and 180 min. Both spectra consist of six bcc peaks and one fcc peak. Intensity of bcc peak after 180 min is much weaker than that for 30 min, indicating decomposition of fcc phase after 180 min treatment. Volume fraction of fcc phase for 30 min and 180 min estimated from Mössbauer are 19.3% and 4.1%, respectively, and they are in good agreement with those fractions estimated from XRD measurements, 22.2 % and 5.2 %.

Fig. 2 compares magnified Mössbauer spectra with fitted ones, where only bcc and fcc phases are considered in the fitting. Fitted curve reproduces measurement quite well in the 30 min specimen, that indicates the specimen contains only bcc and fcc phases. On the other hand, fitting and measurement deviates significantly in 180 min specimen as indicated by red arrows and this discrepancy

is considered to be the presence of other phase, namely iron carbide. Preliminary fitting assuming one of the cementite and eta-carbides cannot explain this discrepancy but fitting assuming both cementite and eta-carbide gives better agreement. Therefore, simultaneous precipitation of cementite or eta-carbide may occur 180 min heat treatment.

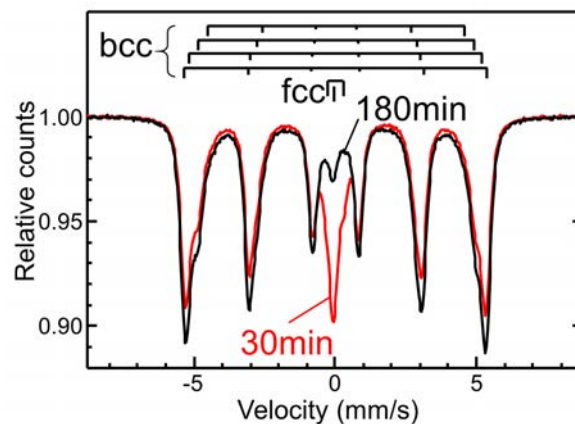


Fig. 1 Mössbauer spectra taken from the TRIP steel transformed at 400°C for 30 min and 180 min respectively.

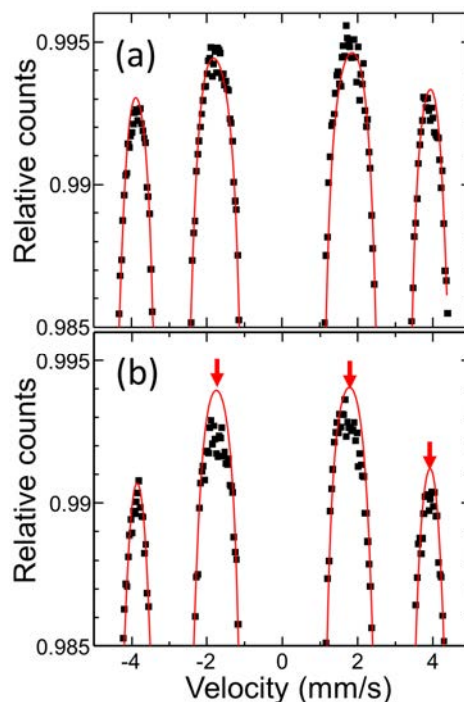


Fig. 2 Magnified Mössbauer spectra taken from the TRIP steel transformed at 400°C for (a) 30 min and (b) 180 min. Red curves are fitted one assuming only bcc and fcc phases.

REFERENCES:

- [1] Y. Xia *et al.*, *Acta Mater.*, **91**(2015), 10-18.
- [2] H. Wu *et al.*, *Acta Mater.*, **149**(2018), 68-77.

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INTRODUCTION: Recently, a laser ablation method has been developed. A bulk metal in a solution is locally evaporated by laser ablation to produce nanoparticles through a cooling process of the agglomeration of the evaporated metal in the solution. The nanoparticles produced by this method are easy to handle in air because of the protection by the solution, but they do not have a coating different to the nanoparticles synthesized by the conventional chemical reduction method. It has been pointed out that they may show high reactivity with appropriate isolation, due to the loss of the “protection” by the coating materials.

This catalytic property is attributed to electronic states such as valence. However, the nanoparticles prepared by the laser ablation method are protected by the solvent and the solvent also disturbs various measurement methods to evaluate the electronic states. Therefore, the aim of this work is to elucidate the electronic structure of the Fe nanoparticles prepared by this method by Mössbauer spectroscopy using gamma-rays with high penetrating power.

EXPERIMENTS: The iron nanoparticle sample was prepared by the laser ablation method using an ⁵⁷Fe-enriched iron foil. The nanoparticles are sealed in ionic liquid. It was cooled down to around 4 K in a refrigerator cryostat to solidify the liquid and to enhance the recoilless fraction of the sample. The Mössbauer spectra was measured using ⁵⁷Co/Rh radioactive gamma-ray source in KURNS. The velocity scale was calibrated by another ⁵⁷Fe enriched iron foil.

RESULTS: The Mössbauer spectra measured in 17 days are shown in Fig. 1. Although the concentration of the nanoparticles was considerably less than 100 ppm, the analyzable Mössbauer spectra was successfully obtained. The spectrum showed at least two sites and thus we evaluated it by a two-site model: the non-magnetic doublet and magnetic sextet. The evaluated parameters are summarized in Table I. It is known that the nanoparticle sample sometimes show this type of two-site spectrum due to the magnetic relaxation; when the size of the nanoparticles is not unified and has some distribution, the relatively big nanoparticles show the magnetic sextet, although the relatively small nanoparticles show the non-magnetic doublet, due to the superparamagnetism. In that case, the isomer shifts of the two sites should be identical. The results of our spectrum agree with this condition and thus it is reasonable for us to analyze our spectrum on the basis of two-site model reflecting the

size distribution and magnetic relaxation. In fact, the line width of magnetic site is considerably wider than that of the non-magnetic site; this difference is due to the distribution of magnetic hyperfine field, which reflects the size distribution [1,2].

Mössbauer parameters in Table. I shows the electronic states of the nanoparticles is rather Fe³⁺ state than the metallic state. The large internal magnetic field over 50 T is similar to oxides, such as hematite and magnetite. In addition, in literature [2], superparamagnetization effect is seen in the Mössbauer spectra of hematite nanoparticles with the size of typically 10 nm. This size agrees with the size distribution of this nanoparticles evaluated by the electronic microscope; the average and standard deviation of the size was 7.1 nm and 3.5 nm, respectively. This agreement also supports the Fe³⁺ state of the nanoparticles in our sample.

In summary, the Mössbauer spectrum of the very diluted iron nanoparticles synthesized by laser ablation method was successfully measured in situation condition. The spectrum reflects the size distribution of the nanoparticles and shows that the iron was in Fe³⁺ state.

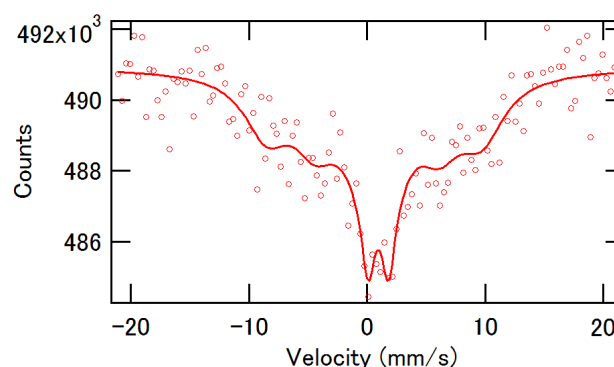


Fig. 1. Mössbauer spectrum of the diluted Fe nanoparticles at 4 K.

Table I. Evaluated parameters of the Mössbauer spectrum.

Site	Non-magnetic	Magnetic
Area ratio	1 (fixed)	5±1
Center shift (mm/s)	0.9±0.1	0.7±0.3
Quadrupole shift (mm/s)	1.7±0.2	0.3±0.4
Internal magnetic field	-	56±2
Line width (mm.s)	1.4±0.4	5±1

REFERENCES:

- [1] S. Morup: J. Magn. Magn. Mater. 37 (1983) 39-50.
- [2] P. Gütlich, et al., Mössbauer spectroscopy and transition metal chemistry: fundamentals and applications (Springer, Berlin, 2011).

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INTRODUCTION: The compounds with a 1:2:2 compositional ratio (so-called "122 compounds") are attractive for thermoelectric materials. Several researchers have defined these materials as "so-called" Zintl phase, although definitions of the Zintl phase are controversial or variety group of concepts by many researchers. EuSn_2As_2 is a "so-called" Zintl phase. [1] In 2018, we succeed to make a high quality polycrystalline samples of EuSn_2As_2 using a new synthesis technique. [2] In 2020, thermoelectric properties of EuSn_2As_2 are demonstrated. [3] Theoretical magnetic phase of Eu sub lattice are calculated as ferromagnetic along to (a, b) axis and antiferromagnetic along to c axis. These magnetic phase are due to s - f interaction between Eu 4f electrons via itinerant electrons. A Neel temperature of the Eu sublattice, which has been measured for single crystalline sample, is about 24 K.

In the polycrystalline sample, the Eu sublattice exhibits ferromagnetic phase with spontaneous magnetic moments $\sim 5 \mu_B$ at 2 K under finite magnetic fields. The spontaneous magnetic moments are smaller than those of theoretical Eu^{2+} ions with spontaneous magnetic moments $\sim 7 \mu_B$. A possible mechanism, which should be origin for the difference between experimental and theoretical magnetic moments of Eu^{2+} , is controversial. In this report, we demonstrate element-specific distributed internal magnetic fields for the polycrystalline EuSn_2As_2 .

EXPERIMENTS: According to our previous report, polycrystalline samples of EuSn_2As_2 were prepared from Eu ingots and Sn-As pellets via a liquid phase reaction in carbon crucibles within evacuated silica tubes. [2] X-ray diffraction measurements at room temperature (RT) were performed in order to characterize the crystallographic phases of powdered sample of as-grown EuSn_2As_2 and the crystallographic orientation of small single crystalline EuSn_2As_2 , which are picked up from the powdered ingot. In this research, we had measured ^{151}Eu and ^{119}Sn Mössbauer spectra for polycrystalline EuSn_2As_2 using conventional optical setting. Both of ^{151}Eu and ^{119}Sn Mössbauer spectra demonstrates magnetic splitting at 4.2 K. The experimental spectra had been reported in 2020. [4] The spectra were fitted to Lorentzian line shapes using the MossWinn [5] Program.

RESULTS: Assuming distributed internal magnetic field ($B_{\text{int}} = \mu_0 H$), refined internal magnetic field distribution (W) are obtained for both spectra. Figure 1 and Figure 2 show the W of internal B_{int} for ^{151}Eu and ^{119}Sn Mössbauer spectra (MS) at temperature = 4.2 K respectively. [6]

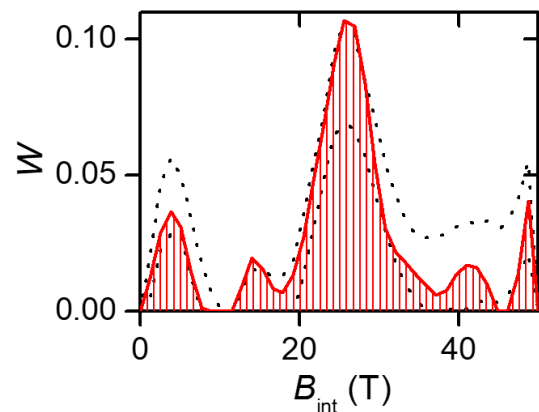


Fig. 1. Distribution (W) of internal magnetic field ($B_{\text{int}} = \mu_0 H$) based on the ^{151}Eu Mössbauer spectroscopy (MS) of polycrystalline EuSn_2As_2 . [6]

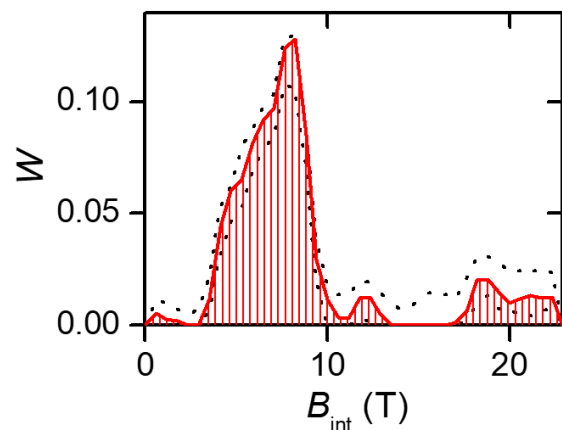


Fig. 2. Distribution (W) of internal magnetic field ($B_{\text{int}} = \mu_0 H$) based on the ^{119}Sn Mössbauer spectroscopy (MS) of polycrystalline EuSn_2As_2 . [6]

REFERENCES:

- [1] M. Q. Arguilla, *et al.*, Inorg. Chem. Front. 4, 378 (2017).
- [2] R. Sakagami, *et al.*, Mater. Sci. Tech. Jpn. 55, 72 (2018) in Japanese.
- [3] R. Sakagami, *et al.*, J. J. Appl. Phys. 60, 035511 (2021).
- [4] Y. Kamihara, *et al.*, KURNS Progress Report 2019, PR8-6 (2020).
URL: <https://www.rri.kyoto-u.ac.jp/PUB/report/PR/ProgRep2019/PR8.pdf>
- [5] Z. Klencsar: MossWinn Program, Budapest, 2001 [<http://www.mosswinn.com/>].
- [6] R. Sakagami, *et al.*, "Magnetic splitting of a Mössbauer spectra of ^{151}Eu and ^{119}Sn of rhombohedral crystal Kondo lattice system EuSn_2As_2 ", The Physical Society of Japan, 2020 Autumn Meeting online (10 Sept. 2020) in Japanese.

Recoil-free fraction in ^{197}Au Mössbauer Spectroscopy for precursor of supported gold cluster catalysts

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INTRODUCTION:

Though sulfide deposition-precipitation (SDP) method was a kind of new DP method, it was a very unique method and different from DP on several points such as preparation pH. However, until now, the structure of gold sulfide as a precursor synthesized by the SDP method was unknown.

On the other hand, Mössbauer effect (recoilless nuclear resonance) is the phenomenon of resonant absorption of γ -radiation, emitted at the radioactive decay of a nucleus in a radioactive material, which act as absorber. This method is widely used in material research that contains iron (^{57}Fe) and tin (^{119}Sn), which are easy to obtain radioactive isotopes that are radiation sources. However, ^{197}Au Mössbauer spectroscopy has not been widely used because radiation source, ^{197}Pt has short half-life.

The purpose of this study was to analyze the state of gold valence and Au-S bond on gold sulfide synthesized by a similar method of SDP using ^{197}Au Mössbauer spectroscopy.

EXPERIMENTS:

The gold sulfide (Au_2S_x) and activated carbon supported gold sulfide were synthesized by the similar SDP method already reported[1]. Samples obtained were characterized by X-ray Absorption Fine Structure (XAFS) and ^{197}Au Mössbauer spectroscopy. Au L_3 edge XAFS spectra were measured at Kyushu University Beamline (SAGA-LS/BL06). ^{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 14 - 20 K, and the measurement was performed by the transmission method.

RESULTS:

The ^{197}Au Mössbauer spectra for the Au_2S_x and activated carbon supported gold sulfide were showed in Fig.1. It showed that the Mössbauer spectrum of Au_2S_x consisted of doublets in shape. Based on the value of IS-QS derived from the synthesized Au_2S_x and $\text{Na}_3[\text{Au}(\text{S}_2\text{O}_3)_2]$, the chemical state of gold in Au_2S_x was estimated to be monovalent ($\text{Au}(\text{I})$). Shown in Fig.1 (a), the spectrum of activated carbon supported gold sulfide did not appear when accumulating over 2,500,000 γ -ray-counts. Since XANES spectrum of the sample were similar to that of Au_2S_x , chemical state of gold in the sample was estimated to be Au_2S_x . These results suggested that recoil-free fraction of the sample was quite small, which were exceptionally rare phenomenon. We are going to discuss the details on the fraction.

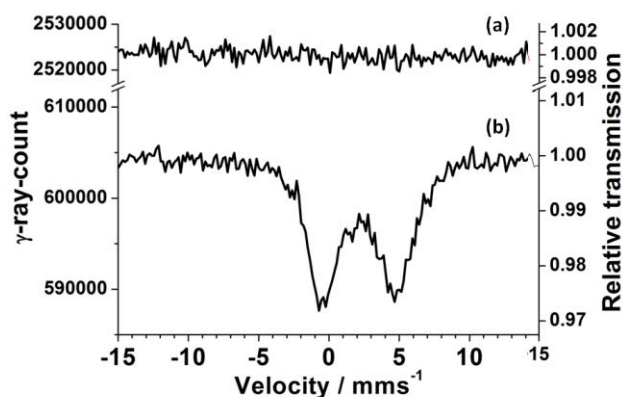


Fig.1. ^{197}Au Mössbauer spectra for activated carbon supported Au_2S_x (a) and Au_2S_x (b) prepared by similar SDP method.

REFERENCE:

[1] H. Ohashi *et al.*, "Method for dispersing and immobilizing gold fine particles and material obtained thereby", Patent No. 5010522.

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Due to the influence of COVID-19, only some of the submitted projects could be conducted.

INTRODUCTION

There are various compounds and ions in the hydrosphere. Besides, many compounds exist in a state of being attached or adsorbed on the surface of a substance. Sn is one of the ions with many valences, and it forms a variety of compounds in nature. Mössbauer measurements for adsorbed Sn on various metal oxides were performed to investigate the details of the chemical state in nature. It is also important to investigate various adsorptions for the development of new catalysts.

^{119}Sn is the second most measured Mössbauer nucleus after ^{57}Fe . The Mössbauer nuclear transition of ^{119}Sn is a transition between nuclear spins $1/2$ and $3/2$, and the information from the obtained Mössbauer parameters is almost the same as ^{57}Fe . Due to the similar parameters of the hyperfine structure, the same equipment as the ^{57}Fe Mössbauer measurement can be used for the ^{119}Sn . On the other hand, the change in isomer shift due to the difference in valence is large, so it is a powerful tool for Sn valence evaluation. On ^{119}Sn Mössbauer spectra, the half-width of the peak is wider than Fe, so resolution is inferior.

EXPERIMENTS

^{119}Sn Mössbauer spectroscopy was measured with a conventional Mössbauer device. The radiation source was $^{119\text{m}}\text{Sn}$ with a half-life of 293.1 days, and the radiation source matrix is CaSnO_3 . A 75 μm thick Pd foil was used as a filter to remove 26 keV fluorescent X-rays from the γ -ray source. A Xe proportional counter was used for the detector. The velocity scale was calibrated by replacing the γ -ray source and measuring the ^{57}Fe Mössbauer spectrum of α -Fe with the same spectrometer. The zero-velocity position is the peak position of BaSnO_3 . This is a commonly used reference position for Sn Mössbauer measurements.

RESULTS

Figure 1 shows the ^{119}Sn Mössbauer spectrum of the compounds SnO and SnO_2 , and the lowermost is the Mössbauer spectrum of adsorbed Sn on $\delta\text{-MnO}_2$. There are impurity components in the SnO spectrum

that are thought to be due to the deterioration of the sample. The position of the center of gravity of the spectra differs greatly between SnO and SnO_2 . This shift (isomer shift) is a parameter that reflects the difference in the valence of Sn. The Sn adsorbed on $\delta\text{-MnO}_2$ has a peak at the same position as SnO_2 , indicating that the Sn atoms are Sn^{4+} . The spectrum of adsorbed Sn does not show wide splitting, such as the spectrum of SnO. This splitting (quadrupole splitting) reflects the symmetry around the Sn atom, and the smaller splitting means the higher symmetry. Since the splitting of the adsorbed-Sn sample is small, it is considered that the Sn atoms are not isolated and adsorbed on the surface but are adsorbed in an environment close to that of a compound such as SnO_2 . Details of the spectra and comparison with other conditions will be made in the future.

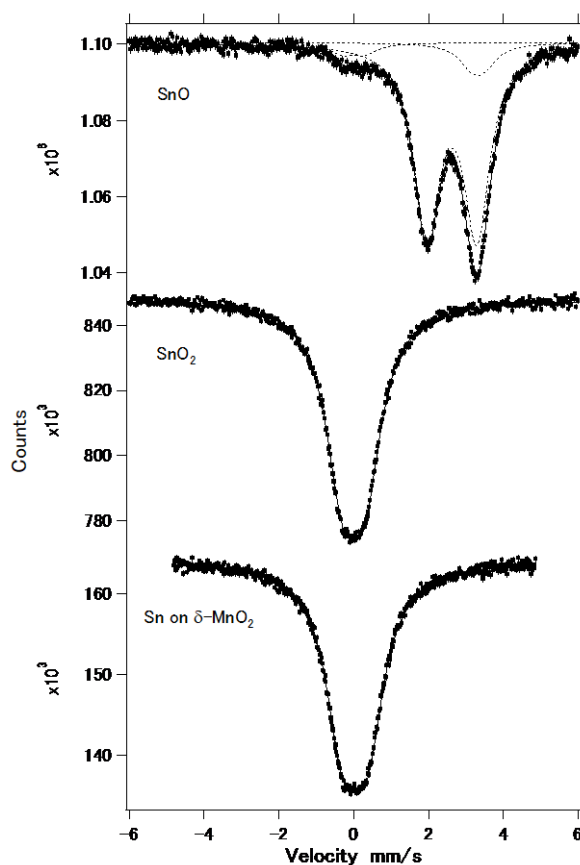


Fig. 1 ^{119}Sn Mössbauer spectra of SnO, SnO_2 and adsorbed Sn on $\delta\text{-MnO}_2$.

PR2-8 Development of Single-Line Compounds for ^{166}Er Mössbauer Spectroscopy

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INTRODUCTION:

The Mössbauer spectroscopy is a powerful method for various investigations of electronic states, magnetic properties, chemical properties, and so on. One of remarkable features is that this method can extract the information of specific isotope. Although about one hundred of Mössbauer energy levels are known, recent Mössbauer activities are quite limited to ^{57}Fe and ^{119}Sn , whose sources are commercially available. In order to promote studies for other less-common Mössbauer isotopes, we have been developing short-lived Mössbauer sources by neutron irradiation at Kyoto University Reactor (KUR). Moreover, some short-lived isotopes can be complementarily produced by high-energy γ -ray irradiation using the electron linear accelerator (KURNS-LINAC). We have already developed preparation methods of the Mössbauer sources for various isotopes (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 researches, an improvement of ^{166}Er Mössbauer spectroscopy is described in this report.

The 80.6keV level of ^{166}Er is the most useful for Er Mössbauer spectroscopy. Since the natural abundance of ^{165}Ho is 100 %, ^{166}Ho with a half-life of 26.8 hours can be obtained as the Mössbauer source without by-product nuclides even by neutron irradiation of natural Ho. As for the source material, we had used HoAl_2 , by arc-melting method from Ho and Al. Several ^{166}Er experiments have already been performed using HoAl_2 at KUR[1]. However, since HoAl_2 has a Curie temperature of about 25 K[2,3], the source temperature had to be kept above 40 K to avoid line broadening by magnetic splitting. To overcome this disadvantage, rare-earth dihydrides can be used as single-line compounds at the temperatures down to 4 K[4].

EXPERIMENTS AND RESULTS:

In this study, we have synthesized rare-earth dihydrides for ^{166}Er Mössbauer experiments, $\text{Ho}_{0.4}\text{Y}_{0.6}\text{H}_2$ as the source and ErH_2 as the absorber. The synthesis procedure is basically similar to that in ref. 4. We used TiH_2 instead of H_2 gas bombe for the H_2 gas source[5]. Since the TiH_2 decomposes by heating and generates H_2 gas, this method is convenient and safer for the H_2 gas handling. The $\text{Ho}_{0.4}\text{Y}_{0.6}$ was prepared by the arc-melting method from Ho and Y metals. The $\text{Ho}_{0.4}\text{Y}_{0.6}$, doubly-rapped with Ti and Ta foils, was evacuated in quartz tubes in an electric furnace. The pelletized powder of TiH_2 , rapped with Ti foil, is separately evacuated in quartz tubes in another electric furnace. Two tubes are connected by a tube

through a liquid N_2 trap with a valve. The valve was open and the evacuation was stopped when the hydridation proceeded. The furnace for the $\text{Ho}_{0.4}\text{Y}_{0.6}$ was kept at 850 °C before and during the hydridation. The temperature of the furnace for the TiH_2 was changed from about 400 to 800 °C to control the pressure of decomposed H_2 . After the hydridation, the quartz tube of $\text{Ho}_{0.4}\text{Y}_{0.6}\text{H}_2$ was quenched into the water. The ErH_2 is prepared similarly using Er metal. The obtained $\text{Ho}_{0.4}\text{Y}_{0.6}\text{H}_2$ was sealed into coin-shaped polyethylene container using polystyrene resin. Typical irradiation condition for the $\text{Ho}_{0.4}\text{Y}_{0.6}\text{H}_2$ containing 20 mg Ho was 15-min irradiation using the pneumatic tube in 1 MW operation of KUR to obtain 140 MBq of ^{166}Ho . The observed Mössbauer spectrum of ErH_2 using ^{166}Ho source in $\text{Ho}_{0.4}\text{Y}_{0.6}\text{H}_2$ at the temperature of 18 K is shown in Fig. 1. Since the recoilless fraction of Er compounds is low at high temperature, the sample and the source were necessary to be cooled. The gamma-rays with the energy of 80.6 keV have been measured by a CeBr_3 scintillation detector. The obtained spectrum successfully showed a single-line shape, indicating both the $\text{Ho}_{0.4}\text{Y}_{0.6}\text{H}_2$ source and the ErH_2 absorber has a single-line shape. This source and absorber are useful for various application in Er Mössbauer studies even for the low temperatures. Moreover, the preparation method of rare-earth dihydrides is applicable to synthesize a single-line source or absorber for other rare-earth Mössbauer spectroscopies.

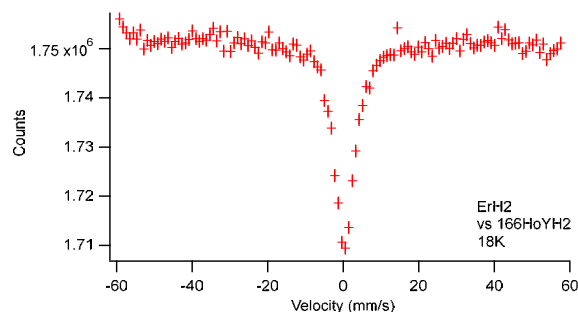


Fig. 1. ^{166}Er -Mössbauer spectrum of ErH_2 at 18 K using ^{166}Ho source in $\text{Ho}_{0.4}\text{Y}_{0.6}\text{H}_2$.

REFERENCES:

- [1] S. Nakamura, H. Yokota, S. Kitao, Y. Kobayashi, M. Saito, R. Masuda, M. Seto, *Hyperfine Interact.* **240**, 75 (2019).
- [2] E. Munck, D. Quitmann, S. Hufner, *Z. Naturforsch.* **21A**, 847 (1966).
- [3] E. Munck, D. Quitmann, S. Hufner, *Phys. Lett.* **24B**, 392 (1967).
- [4] J. Stöhr and J. D. Cashion, *Phys. Rev. B* **12**, 4805 (1975).
- [5] D. B. Prowse, A. Vas and J. D. Cashion, *J. Phys. D: Appl. Phys.* **6**, 646 (1973).