

I-1. PROJECT RESEARCHES

Project 11

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OBJECTIVES AND PERFORMED RESEARCH SUBJECTS:

The main objectives of this project research are the investigation of the fundamental properties of new materials and the development of the advanced experimental methods by using multi-element Mössbauer spectroscopy. One of the most irreplaceable features of the Mössbauer spectroscopy is to extract element-specific or isotope-specific information. As the Mössbauer resonance line is extremely narrow, hyperfine interactions are well resolved and give us the information on the surrounding electronic states and magnetism. 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 P11-1, P11-2, P11-3, and P11-4,

^{197}Au in P11-5, P11-6, and P11-7.

Development for other isotopes in P11-8.

The subjects of research are as follows:

P11-1 EFG tensor of Fe^{2+} in M2 site of clinopyroxene by single crystal Mössbauer microspectroscopy (K. Shinoda *et al.*)

P11-2 Mössbauer study on the model complexes of heme enzymes (H. Fujii *et al.*)

P11-3 Mössbauer analysis of the nanoclusters prepared by liquid phase pulsed laser ablation on pyrite (Y. Yakiyama *et al.*)

P11-4 Effect of H64L mutation on resonance hybrid of Fe-bound oxygen in myoglobin (Y. Yamamoto *et al.*)

P11-5 Study on the electronic states of gold clusters, $[\text{Au}_{25}(\text{SR})_{18}]^n$ ($n = +1, 0, -1$) by means of ^{197}Au Mössbauer spectroscopy (N. Kojima *et al.*)

P11-6 The state analysis of gold sulfide using ^{197}Au Mössbauer spectroscopy (H. Ohashi *et al.*)

P11-7 ^{197}Au Mössbauer study of supported Au nanoparticles catalysis (Y. Kobayashi *et al.*)

P11-8 Development of Mössbauer spectroscopy for ^{161}Dy and ^{169}Tm (S. Kitao *et al.*)

MAIN RESULTS AND CONTENTS OF THIS REPORT:

K. Shinoda *et al.* (P11-1) have developed Mössbauer microspectrometer using Si-PIN semiconductor detector

and applied to studies of crystallographically-oriented single crystals of thin sections of augite. The electric field gradient (EFG) tensor of Fe^{2+} in M2 site of clinopyroxene was evaluated from the intensity ratio of two quadrupole doublets due to Fe^{2+} in M1 and M2 sites by assuming calculated Fe^{2+} in M1 site.

H. Fujii *et al.* (P11-2) studied the effect of the electron-donating ability on the stability of the intermediate spin state for iron(III) porphyrin hexafluoroantimonate complexes. The results indicated that the spin state of iron(III) center changes from intermediate spin state to the high spin state with decreasing the electron-donor ability of the porphyrin ligand.

Y. Yakiyama *et al.* (P11-3) have developed a new method for Fe-S nanoclusters by pulsed-laser ablation in liquid (PLAL) and evaluated the obtained compounds by Mössbauer and Raman spectroscopy. Even the shortage of samples, hematite nanoparticles was suggested to exist. By further investigation, the results clarified the solvent in laser ablation significantly affected the product composition.

Y. Yamamoto *et al.* (P11-4) studied oxy form of the H64L(His64 by Leu) mutant Myoglobin reconstituted with ^{57}Fe -labeled heme cofactor. By comparing the obtained Mössbauer parameters with those of native proteins, the effect of the removal of His64 through mutation on the resonance hybrid of Fe-bound O_2 in the protein was observed.

N. Kojima *et al.* (P11-5) have studied thiolate-protected gold clusters with different oxidation states. The obtained three components were well attributed as outer layer, core surface, and core Au sites. The change of the isomer shifts by oxidation states is consistent.

H. Ohashi *et al.* (P11-6) evaluated gold sulfides synthesized by sulfide deposition precipitation (SDP) method. The ^{197}Au Mössbauer spectra revealed the chemical state of gold in obtained Au_2S_x was estimated to be monovalent (Au(I)).

Y. Kobayashi *et al.* (P11-7) studied the Au nanoparticle catalysis supported on hydroxyapatite (HAp) using ^{197}Au Mössbauer spectroscopy. The results showed the electronic state of the Au nanoparticles does not have much difference from Au bulk.

S. Kitao *et al.* (P11-8) have developed Mössbauer sources for several less-common Mössbauer spectroscopy. As for source materials of ^{161}Dy and ^{169}Tm Mössbauer spectroscopy, $\text{Dy}_{0.5}\text{Gd}_{0.3}\text{F}_3$ and Er-Al alloy were successfully synthesized, respectively. These materials were confirmed as well-performed Mössbauer sources.

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INTRODUCTION: ⁵⁷Fe Mössbauer spectroscopy has been widely used for the analysis of Fe in Fe-bearing minerals. Powdered mineral is generally used as a Mössbauer sample, in spite of the usefulness of the conventional method, it is not useful for the Mössbauer analysis of any narrow area in a crystal or mineral grain. To overcome the disadvantage of spatial resolution by powder method, several Mössbauer microspectrometers have been proposed. Mössbauer microspectroscopy will be widely used for measuring spectra of a grain in a thin section in future. 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 ($I^{total} = I^h + I^l$) (sum of I^h and area of the lower energy (I^l)). The intensity of component peaks of a ⁵⁷Fe Mössbauer doublet is related to an electronic field gradient (EFG) tensor of the site containing Fe²⁺ and Fe³⁺ (Zimmermann, 1975 and 1983). Thus, EFG determination is important in Mössbauer measurements of thin section as a single crystal. Zimmermann (1975, 1983) introduced experimental determination of EFG tensor from the Mössbauer spectrum of a single crystal, and proposed a formulation of the EFG tensor from the intensities of the component peaks of asymmetric Mössbauer doublet of a monoclinic crystal as an example. In pyroxene, Fe²⁺ in M1, Fe²⁺ in M2 and Fe³⁺ in M1 sites are possible. As three doublets overlap in Mössbauer spectrum of pyroxene, it is important to reveal EFG of three doublets to analyze Mössbauer spectrum of pyroxene thin section. Tennant *et al.* (2000) revealed the EFG tensor of Fe²⁺ at the octahedral M1 site of clinopyroxene. However, EFG tensors due to Fe²⁺ in M2 site of clinopyroxene remain unknown. In this study, Zimmermann's method was applied for single crystal ⁵⁷Fe Mössbauer spectra of an augite crystal on oriented thin sections to determine the EFG tensor of Fe²⁺ at the M2 site of C2/c clinopyroxene.

EXPERIMENTS and RESULTS: A single crystal of augite was used for this study. Three crystallographically oriented thin sections which are perpendicular to a^* and b^* , and parallel to (-2 0 2) plane were prepared by measuring X-ray diffraction using precession camera. Nine Mössbauer spectra of oriented thin sections were measured. In this study, Cartesian coordinate ($X Y Z$) is set as $X//c^*$, $Y//a$, $Z//b^*$ in order to set b -axis as Z and set a , b , c -axes as right-handed system, where a , b , c are real and a^* , b^* , c^* are reciprocal lattice vectors of augite. 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 ± 5 mm/s. Thickness corrections of raw spectra were not done. Overlapped doublets were observed in nine raw spectra. Two quadrupole doublets due to Fe²⁺ in M1 and M2 sites are assumed in raw spectra for peak decomposition by MossWinn program. Intensity tensor of Fe²⁺ in M1 site was calculated from Tennant *et al.* (2000). Intensity tensor of Fe²⁺ in M2 site was obtained by peak fitting under a constraint of intensity tensor of Tennant *et al.* (2000). The residual doublet that is obtained by subtracting doublet due to M1 from raw data was assigned as M2 doublet. The intensity tensor due to Fe²⁺ in M2 site was

$$\begin{pmatrix} 0.65 \pm 0.19 & 0.06 \pm 0.22 & 0 \\ 0.06 \pm 0.22 & 0.38 \pm 0.18 & 0 \\ 0 & 0 & 0.47 \pm 0.66 \end{pmatrix}.$$

Diagonalized traceless intensity tensor was

$$\begin{pmatrix} 0.24 & 0 & 0 \\ 0 & -0.19 & 0 \\ 0 & 0 & 0.05 \end{pmatrix}.$$

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INTRODUCTION: Iron porphyrin complexes are active sites of many heme proteins in nature. The oxidation state and the spin state of the iron porphyrin complexes are key for controlling the function of the heme proteins. Recently, intermediate spin states have been found in ferrous and ferric porphyrin complexes. These intermediate spin states are unique and have not been clarified well. Previous studies revealed that the intermediate spin state is realized when very weak axial ligand such as hexafluoroantimonate anion is coordinated to ferric iron center. In this project, we studied the effect of the electron-donating ability on the stability of the intermediate spin state by using Mössbauer spectroscopy for iron(III) porphyrin hexafluoroantimonate complexes.

EXPERIMENTS: Mössbauer spectroscopy was conducted in conventional transmission geometry by using ⁵⁷Co-in-Rh(50 mCi) as γ -ray source. The Doppler velocity scale was calibrated using an Fe metal foil at room temperature. 5,10,15,20-tetraphenyl porphyrin (**F0**) and 5,10,15,20-Tetrakis(pentafluorophenyl)porphyrin (**F20**) was purchased from Sigma Aldrich. 2,3,7,8,12,13,17,18-Octafluoro-5,10,15,20-tetrakis(pentafluorophenyl)porphyrin (**F28**) was prepared by literature methods. ⁵⁷Fe was purchased from commercial as a powder and changed to iron(II) acetate. Iron(III) porphyrin chloride complexes were prepared by the published method. Iron(III) porphyrin hexafluoroantimonate complexes were prepared by the reaction of the chloride complexes with silver hexafluoroantimonate in dichloromethane or fluorobenzene in a glove box.

RESULTS: We measured Mössbauer spectra of iron(III) hexafluoroantimonate complexes of **F0**, **F20**, and **F28**. The δ and ΔE_Q values for these complexes are estimated to be 0.4 mm/s and ~ 4.0 mm/s, respectively. These values indicate the intermediate spin states of these complexes. Importantly, as the electron-withdrawing effect of the porphyrin ligand is stronger, the ΔE_Q value becomes smaller. This indicates that the electron-donor ability of the porphyrin ligand is a key factor to be the intermediate spin state. This result was further confirmed by the aqua complexes. When the hexafluoroantimonate complexes are contacted with air, water in air bind to the iron center to form the aqua complex. Fig 1 shows Mössbauer spectra of the aqua complexes of **F0**, **F20**, and **F28**. As the electron-withdrawing effect of the porphyrin ligand is stronger, the ΔE_Q value becomes smaller (see green lines of Fig 1). All of these results indicated that the spin state of iron(III) center changes

from the intermediate spin state to the high spin state with decreasing the electron-donor ability of the porphyrin ligand.

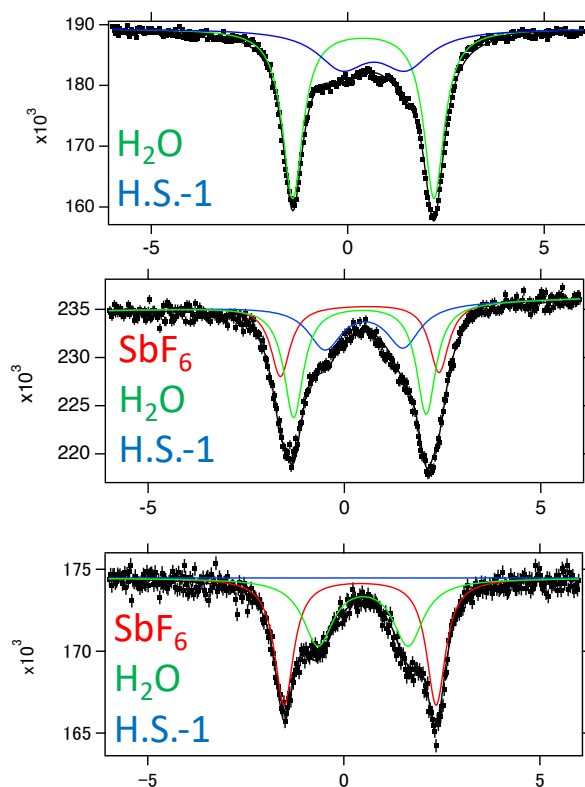


Fig 1. Mössbauer spectra (6 K) of complexes after aeration of iron(III) porphyrin hexafluoroantimonate complexes of **F0** (top), **F20** (middle), and **F28** (bottom). Red line: hexafluoroantimonate complex, green line: aqua complex, blue line: further decomposed complex.

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INTRODUCTION: Pyrite (FeS_2), which composed of Fe-S bonds, is one of the most abundant minerals on the earth and has been recently focused on as a component of photovoltaic semiconductors. In addition, the related compounds, Fe-S clusters represented by Fe_2S_2 and Fe_4S_4 , are the most essential structures found in enzymes, which play important roles in metabolism. For example, the Fe-S clusters are the main contributor in hydrogenase or nitrogenase for transferring electrons to the active site. However, studies on their detailed mechanisms are not smoothly progressed, since the conventional synthesis of the model complexes including Fe-S clusters require long steps and special cares. Therefore, the development of new methods for the preparation of Fe-S clusters, especially here, pulsed-laser ablation in liquid (PLAL) using pyrite as a target is meaningful for both materials and biological chemistry. In this project, we tried the PLAL using pyrite and examined the products using Mössbauer and raman spectroscopy, clarifying that the solvent significantly affected the product composition.

EXPERIMENTS: The sample was prepared by the PLAL technique in water with surfactants (polyvinylpyrrolidone (PVP), sodium dodecyl sulfate (SDS) and hexadecyltrimethylammonium bromide (CTAB)) or in organic solvents (EtOH, toluene, and acetone) [1]. ^{57}Fe Mössbauer measurement was performed at KURNS.

RESULTS: As shown in Fig. 1, the presence of hematite was suggested in Mössbauer spectrum for nanoparticles surrounded by PVP (Fig. 1). Other samples prepared by using different surfactants were also afforded hematite as the main product. This was supported by raman measurement for all the samples (Fig. 2). However, because of the shortage of the samples ($< 100 \mu\text{g}$), further investigation using Mössbauer spectroscopy was impossible. Instead, we continued the sample examination by raman measurement and selected area electron diffraction (SAED) measurement. revealed that the solvent used in laser ablation significantly affected the product composition. Especially the coordinative solvent such as acetone

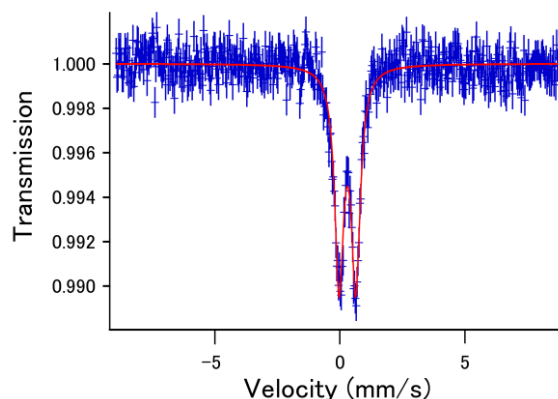


Fig. 1. Mössbauer spectrum for the nanoparticles surrounded by PVP obtained by PLAL method in water.

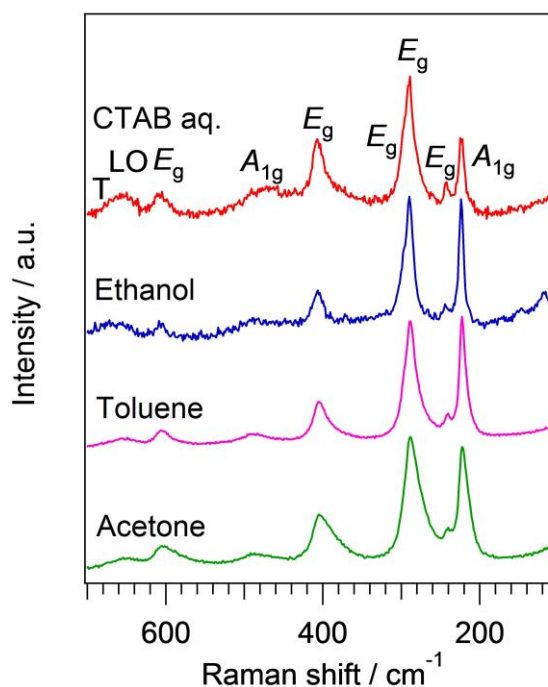


Fig. 2. Raman spectra of the hematite nanoparticles obtained by PLAL of pyrite.

gave the product containing sulfur in addition to hematite.

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PR11-4 Effect of H64L Mutation on Resonance Hybrid of Fe-bound Oxygen in Myoglobin

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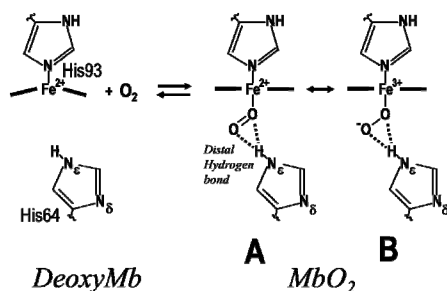
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INTRODUCTION: Myoglobin (Mb), an oxygen storage hemoprotein, is one of the most thoroughly studied proteins and has been used as a paradigm for the structure-function relationships of metalloproteins. Dioxygen (O₂) and also carbon monoxide (CO) are reversibly bound to a ferrous heme Fe atom in Mb. As a respiratory protein, Mb must favor the binding of O₂ compared to the toxic ligand CO ubiquitously produced from a variety of sources in biological systems. Distal His (His64) contributes significantly by increasing the O₂ affinity of the protein by stabilizing Fe-bound O₂ through a hydrogen bonding interaction between the His64 N_εH proton and the bound O₂ (Scheme 1).¹ We found that both the O₂ affinity and CO/O₂ discrimination of the protein are regulated by the intrinsic heme Fe reactivity through the heme electronic structure.² We revealed that the control of the CO/O₂ discrimination is achieved through the effect of a change in the electron density of the heme Fe atom (ρ_{Fe}) on the O₂ affinity, which can be reasonably interpreted in terms of the effect of a change in the ρ_{Fe} value on the resonance process between the Fe²⁺-O₂ and Fe³⁺-O₂⁻-like species³ (Scheme 1). On the other hand, in contrast to O₂ binding, the CO affinity of the protein was shown to be almost independent of the ρ_{Fe} value.² In this study, we characterized the effect of the removal of the distal His64, through the replacement of His64 by Leu (H64L mutation), on the control of the intrinsic heme Fe reactivity through the resonance hybrid of Fe-bound O₂.



Scheme 1. Oxygenation of deoxy Mb. The binding of O₂ to the heme Fe is stabilized by the hydrogen bonding between the Fe-bound O₂ and His64.¹ Structure (B) of the oxy form is only a proposed one.³

EXPERIMENTS: Iron-⁵⁷Fe (95 atom %, Merck) was used to prepare ⁵⁷Fe-enriched heme cofactor. The expres-

sion and purification of the H64L mutant Mb were carried out according to the methods described by Springer *et al.*⁴, and then apoprotein was prepared from the H64L Mb mutant using the procedure of Teale⁵. Apoprotein of the H64L mutant protein was reconstituted with ⁵⁷Fe-labelled heme cofactor, and oxy form of the reconstituted protein in 50 mM potassium phosphate buffer, pH 7.40, were cooled in liquid nitrogen bath. The Mössbauer measurement was performed at 6 K.

RESULTS: The Mössbauer spectrum of oxy form of the H64L mutant Mb reconstituted with ⁵⁷Fe-labeled heme cofactor indicated the values of 2.09 ± 0.017 mm/s and 0.322 ± 0.008 mm/s for quadrupole splitting (QS) and isomer shift (IS) of the protein, respectively. These values are compared with the corresponding ones of the native protein, i.e., 2.28 ± 0.008 mm/s and 0.258 ± 0.004 mm/s for the QS and IS, respectively. The differences in the QS and IS between the two proteins possibly reflect the effect of the removal of His64 through the mutation on the resonance hybrid of Fe-bound O₂ in the protein. Unfortunately, the spectrum of CO form of the protein contaminated in the sample appears in Figure 1, and hence another measurement is essential to confirm the QS and IS obtained for the H64L mutant protein.

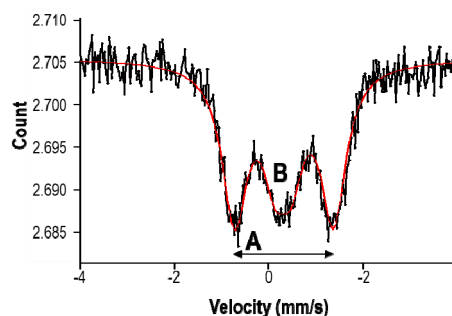


Figure 1. Mössbauer spectrum of oxy form of the H64L mutant Mb reconstituted with ⁵⁷Fe-labeled heme cofactor at 6 K. The spectrum is composed of two components **A** and **B** due to oxy form and contaminated CO one of the protein.

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PR11-5 Study on the Electronic States of Gold Clusters, $[\text{Au}_{25}(\text{SR})_{18}]^n$ ($n = +1, 0, -1$) by Means of ^{197}Au Mössbauer Spectroscopy

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INTRODUCTION: Thiolate (SR)-protected gold clusters have attracted much attention as a prototypical system for fundamental studies on quantum size effect and as a building block of nanoscale devices [1]. Among many thiolate-protected Au clusters, the $\text{Au}_{25}(\text{SR})_{18}$ cluster has been studied most extensively as a prototype system of stable $\text{Au}_n(\text{SR})_m$ clusters. From the single crystal X-ray analysis [2], $\text{Au}_{25}(\text{SR})_{18}$ is composed of an icosahedral Au_{13} core whose surface atoms are completely protected by six staples, $-\text{S}(\text{R})-[\text{Au}-\text{S}(\text{R})-]_2$ (Fig. 1). As shown in Fig. 1, the Au atoms in $\text{Au}_{25}(\text{SR})_{18}$ are classified into three in terms of chemical environment: twelve Au atoms on the outermost layer, which are bound by two thiolates (**Au1**); twelve Au atoms at the core surface, each of which are bound by a single thiolate (**Au2**); and a single central Au atom at the core (**Au3**). In the present work, we investigated the electronic states of $[\text{Au}_{25}(\text{PET})_{18}]^n$ (PET = 2-phenylethanethiol, $n = +1, 0, -1$) by means of ^{197}Au Mössbauer spectroscopy.

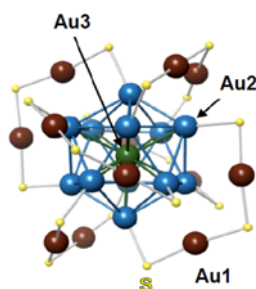


Fig. 1. Molecular structure of $\text{Au}_{25}(\text{PET})_{18}$ [2]. Large and small balls represent Au and S atoms, respectively.

EXPERIMENTS: ^{197}Au Mössbauer measurements were carried out at Institute for Integrated Radiation and Nuclear Science, Kyoto University. The γ -ray source (77.3 keV), ^{197}Pt , was generated by neutron irradiation to a 98%-enriched ^{196}Pt metal foil. The γ -ray source and samples were cooled down to 16 K. The isomer shift (IS) of Au foil was referenced to 0 mm/s. The spectra were calibrated and referenced by using the six lines of a body-centered cubic iron foil (α -Fe).

RESULTS: The ^{197}Au Mössbauer spectra of $[\text{Au}_{25}(\text{PET})_{18}]^n$ ($n = +1, 0, -1$) were analyzed, which is based on that of $[\text{Au}_{25}(\text{SG})_{18}]^{-1}$ (SG = glutathione) [3]. The three sites of Au atoms (Au1, Au2, Au3) in $[\text{Au}_{25}(\text{SR})_{18}]^n$ exhibit different isomer shift (IS) and quadrupole splitting (QS) due to the difference in electronic structures of each site; In Au atoms, the main contribution to IS and QS are the density of s-electrons at the nucleus and the symmetry of

charge distribution around the nucleus, respectively. The ^{197}Au Mössbauer spectra of $[\text{Au}_{25}(\text{PET})_{18}]^n$ ($n = +1, 0, -1$) were fitted by the superposition of two sets of doublet Lorentzians and a singlet Lorentzian, which is listed in Table 1. The doublet with the largest IS and QS (Au1) is assigned to the twelve Au atoms on the outermost layer coordinated by two thiolates. These parameters, IS and QS , are typical of Au(I) coordinated by two sulfur atoms [4]. The second doublet (Au2) is assigned to the twelve Au atoms at the surface of icosahedron, which are bound by single thiolate. The singlet (Au3) is assigned to the central Au atom of icosahedron. As shown in Table 1, the IS and QS values of Au1, Au2 and Au3 for $[\text{Au}_{25}(\text{PET})_{18}]^{-1}$ are consistent with those for $[\text{Au}_{25}(\text{SG})_{18}]^{-1}$. According to a spherical superatom model [5], the superatomic 6s-electron configuration in the icosahedron (Au_{13}) for $[\text{Au}_{25}(\text{SR})_{18}]^{-1}$ is described as $(1S)^2(1P)^6$ corresponding to a noble gas-like configuration, which is responsible for the most stable cluster among $[\text{Au}_{25}(\text{SR})_{18}]^n$ ($n = +1, 0, -1$). When $[\text{Au}_{25}(\text{PET})_{18}]^n$ is oxidized from $n = -1$ to $+1$, the IS values of Au2 and Au3 sites remarkably change from 0.36 mm/s to 1.36 mm/s, and from 1.29 mm/s to 0.40 mm/s, respectively, while the IS of Au1 remains almost unchanged, which implies that not only the core surface site (Au2) but also the central core site (Au3) for the icosahedron in $[\text{Au}_{25}(\text{SR})_{18}]^n$ is oxidized on going from $n = -1$ to $+1$. In connection with this, the following should be noted. The remarkable decrease of IS at the central core site (Au3) for $n = +1$ is attributed to the decrease of 6s-electron density due to the oxidation.

Table 1. ^{197}Au Mössbauer parameters (IS (mm/s), QS (mm/s), area (%)) of $[\text{Au}_{25}(\text{SR})_{18}]^n$ ($n = +1, 0, -1$) at 16 K

| $[\text{Au}_{25}(\text{SR})_{18}]^n$ | | IS (mm/s) | QS (mm/s) | Area (%) |
|--|------|----------------|----------------|-------------|
| $[\text{Au}_{25}(\text{SG})_{18}]^{-1}$ | Au 1 | 2.78 | 6.36 | 46.1 |
| | Au 2 | 0.34 | 4.14 | 44.8 |
| | Au 3 | 0.94 | 0 | 9.1 |
| $[\text{Au}_{25}(\text{PET})_{18}]^{-1}$ | Au 1 | 2.90 | 6.55 | 36.1 |
| | Au 2 | 0.36 | 4.48 | 52.0 |
| | Au 3 | 1.29 | 0 | 11.9 |
| $[\text{Au}_{25}(\text{PET})_{18}]^0$ | Au 1 | 3.21 | 5.95 | 42.0 |
| | Au 2 | 0.55 | 3.94 | 50.4 |
| | Au 3 | 0.24 | 0 | 7.7 |
| $[\text{Au}_{25}(\text{PET})_{18}]^{+1}$ | Au 1 | 2.77 | 6.28 | 43.4 |
| | Au 2 | 1.36 | 4.68 | 48.7 |
| | Au 3 | 0.40 | 0 | 7.9 |

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PR11-6 The State Analysis of Gold Sulfide Using ^{197}Au Mössbauer Spectroscopy

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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. The purpose of this study aimed 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) were synthesized by the similar SDP method already reported^[1]. In addition, trisodium dithiosulfatoaurate(I) ($\text{Na}_3[\text{Au}(\text{S}_2\text{O}_3)_2]$)^[2] as a standard material with Au-S bond was measured.

^{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 of the Au_2S_x and the standard sample were showed in Fig.1. It showed that the Mössbauer spectrum of Au_2S_x consisted of doublets in shape. Compared to the spectrum of $\text{Na}_3[\text{Au}(\text{S}_2\text{O}_3)_2]$, value of the isomer shift was small, and the FWHM value was large.

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 (Au(I)).

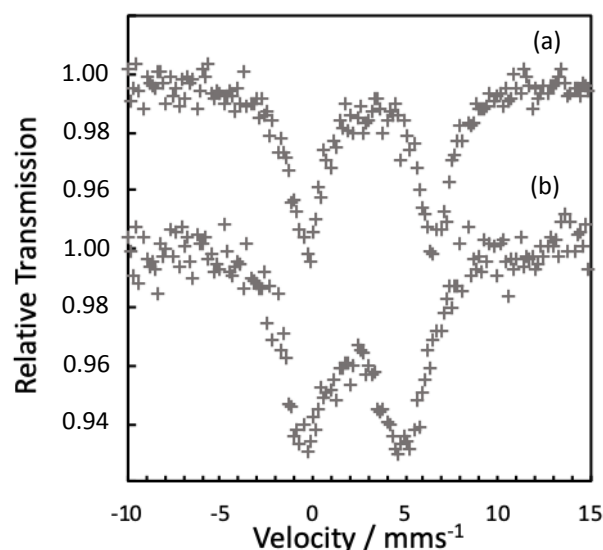


Fig.1. ^{197}Au Mössbauer spectra for $\text{Na}_3[\text{Au}(\text{S}_2\text{O}_3)_2]$ (a) as a reference and Au_2S_x (b) prepared by similar SDP method.

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INTRODUCTION: The normal surface of metallic gold does not adsorb small molecules like hydrogen and oxygen, thus, gold is not generally considered as a good catalyst. Small particles have many edges, corners and metastable surfaces, and they are different from bulk for catalytic activities. Dispersing the small particles on supports, the catalytic activity of gold increases. Au small particles supported on some materials shows high catalytic activity to oxidize CO to CO₂ at temperatures as low as 197 K [1,2].

The interaction between particles and supports may give new activity to the catalysts. Hydroxyapatite (HAp) is known as bone mineral, and it is nature-friendly. Furthermore, it is good support of nanoparticles [3]. HAp binds strongly with Au, and it avoid the fusion of the nanoparticles.

We have studied the supported Au nanoparticles catalysis using ^{197}Au Mossbauer spectroscopy to elucidate the origin of the catalytic activity. Using ^{197}Au Mossbauer spectroscopy, we can observe the signals from Au atoms without disturbance from supports. Moreover, it is sensitive to the electronic states of Au atoms. Thus, Mossbauer spectroscopy is powerful for the study of supported catalysts.

EXPERIMENTS: The supported Au nanoparticles catalysis was prepared by the deposition precipitation method and calcination. The mixed solution of HAuCl₄ and HAp was kept on pH 9 and 65°C, thus the Au ions were precipitate on HAp as Au(OH)₃. After precipitation, the specimens were washed with distilled water, and dried. These specimens were calcined for 4 hours at 600°C in air. At that time, Au(OH)₃ was degraded into Au metal, and the Au nanoparticles were firmly fixed on HAp.

^{197}Au Mössbauer measurement was conducted using a constant-acceleration spectrometer with a NaI scintillation counter. The ^{197}Au γ -ray source (77.3 keV) was obtained from ^{197}Pt (half-life; 18.3 hrs) generated by irradiation of neutron to 98%-enriched ^{196}Pt metal foil using KUR. The γ -ray source and samples were cooled to 16 K, and the spectra were recorded in a transmission geometry. The isomer shift value of a gold foil was referenced to 0 mm/s.

RESULTS: Figure 1 shows ^{197}Au Mössbauer spectra of the pure Au bulk and Au nanoparticle catalysis. Observed spectrum shows almost same shape and peak position as pure Au bulk. Thus, the electronic state of the Au nanoparticle catalysis does not have much difference from bulk. However, the different catalytic activity from bulk Au was observed on this catalysis. The activity comes from a very small percentage of the Au atoms, for example in surface, at edge and by lattice defect. And, high activity is owing to the increase of the surface area. We will study the other type catalysis to elucidate the particle-size dependence of the Mössbauer spectra and activity of the catalysis.

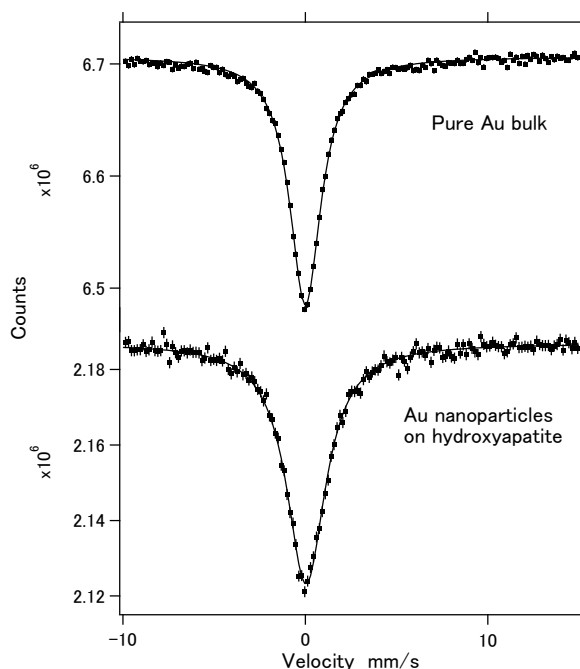


Fig. 1 ^{197}Au Mössbauer spectra of the pure Au bulk and Au nanoparticles catalysis at 16K.

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INTRODUCTION:

The Mössbauer spectroscopy is one of the most powerful methods for investigation of electronic states, magnetic properties, chemical properties, and so on. A remarkable feature of this method is to extract the information of the specific isotope. Although about one hundred of Mössbauer energy levels are known, research activities in Mössbauer studies so far are quite limited, except ^{57}Fe and ^{119}Sn . It is partly because commercially available sources at present are only ^{57}Co and $^{119\text{m}}\text{Sn}$ for the Mössbauer spectroscopy of ^{57}Fe and ^{119}Sn , respectively.

On the contrary, at the Institute for Integrated Radiation and Nuclear Science, various short-lived isotopes can be obtained by neutron irradiation at Kyoto University Research Reactor(KUR). We have already been performing Mössbauer spectroscopy of some isotopes, such as ^{125}Te , ^{129}I , ^{197}Au , by obtaining $^{125\text{m}}\text{Te}$, $^{129\text{m}}\text{Te}$ or $^{129\text{m}}\text{Te}$, $^{197\text{m}}\text{Pt}$, respectively. Moreover, complementary short-lived isotopes can be produced by high-energy γ -ray irradiation at the electron linear accelerator(KURNS-LINAC).

The main purpose of this research is to develop effective Mössbauer sources for various isotopes to apply many fields of researches for less common isotopes in Mössbauer spectroscopy.

EXPERIMENTS AND RESULTS:

(1) ^{161}Dy Mössbauer spectroscopy

The 25.5keV level of ^{161}Dy is known as the most useful level for Dy-Mössbauer spectroscopy. As for the Mössbauer source, ^{161}Tb with a half-life of 6.88days is effectively usable. Since ^{161}Gd becomes ^{161}Tb in β -decay process with a half-life of 3.7 minutes, ^{161}Tb source is obtainable by neutron irradiation of ^{160}Gd . Since natural Gd contains 21.86% abundance of ^{160}Gd , natural Gd is usable by waiting a few days for decay of a by-product of ^{159}Gd

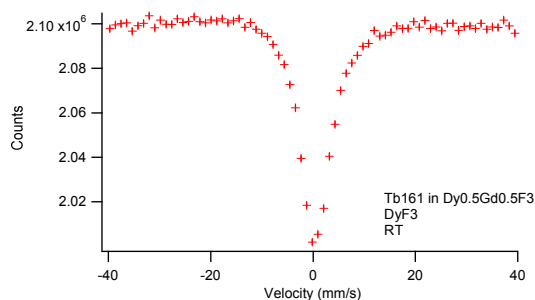


Fig. 1. ^{161}Dy -Mössbauer spectrum of DyF_3 at room temperature using ^{161}Tb source in $\text{Dy}_{0.5}\text{Gd}_{0.5}\text{F}_3$ irradiated at KUR.

with a half-life of 18.48 hours. In this study, in order to improve the source material, $\text{Dy}_{0.5}\text{Gd}_{0.5}\text{F}_3$ was synthesized[1]. After Dy_2O_3 and Gd_2O_3 was dissolved in HCl , HF was added to obtain precipitation of hydrated $\text{Dy}_{0.5}\text{Gd}_{0.5}\text{F}_3$. Anhydrous $\text{Dy}_{0.5}\text{Gd}_{0.5}\text{F}_3$ was obtained by evacuation of the hydrated compound with careful heating. The neutron irradiation was performed by pneumatic tube(Pn) for 1 hour at 5MW operation of KUR. The expected ^{161}Dy Mössbauer spectra were obtained successfully by using a Xe proportional counter. The ^{161}Dy -Mössbauer spectrum of DyF_3 at room temperature using ^{161}Tb source in $\text{Dy}_{0.5}\text{Gd}_{0.5}\text{F}_3$ is shown in Fig. 1. Since expected single-line spectrum was obtained, this source material can be widely used for many application experiments in Dy-Mössbauer spectroscopy.

(2) ^{169}Tm Mössbauer spectroscopy

The 8.4 keV level of ^{169}Tm is used for Tm-Mössbauer spectroscopy. Its low-energy feature of the γ -ray has an advantage in high recoilless fraction even at high temperature. As for the Mössbauer source, ^{169}Er with a half-life of 9.3 days is obtained by neutron irradiation of ^{168}Er (natural abundance of 26.8 %). Even when natural Er is used as a source material, a by-product of ^{171}Er with a half-life of 7.5 hours from ^{170}Er (natural abundance of 14.9 %) was reduced by waiting a few days. In this study, Er-Al alloy with about 10 wt-% Er was used as a source material[2]. The Er-Al alloy was obtained by the arc-melting method followed by solution treatment. The neutron irradiation was performed by long-term irradiation for 3 weeks at KUR. Since the fluorescent X-rays of Er with energies of 6.9 to 7.8 keV are not separated in an energy spectrum with a Xe proportional counter, the right-half of the γ -ray peak was chosen for Mössbauer measurements. The ^{169}Tm Mössbauer spectra of TmAl_2 absorber were obtained successfully as shown in Fig. 2. Therefore, this source material is applicable for various Tm Mössbauer spectroscopy.

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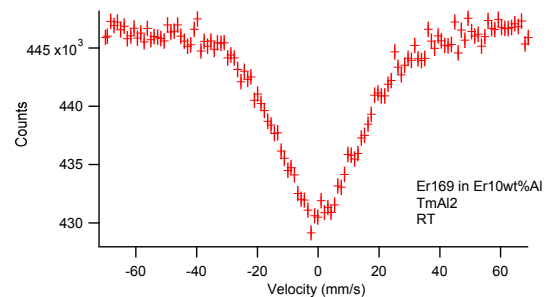


Fig. 2. ^{169}Tm -Mössbauer spectrum of TmAl_2 at room temperature using ^{169}Er source in Er-Al alloy irradiated at KUR.