

RECOILLESS FRACTION ON ^{197}Au MÖSSBAUER SPECTROSCOPY

Yasuhiro KOBAYASHI¹, Hironori OHASHI², Masayuki KUROKUZU¹, Makoto SETO¹

¹*Institute for Integrated Radiation and Nuclear Science, Kyoto University, 2, Asashironishi, Kumatori town, Osaka Prefecture, 590-0494, JAPAN*

²*Faculty of Symbiotic Systems Science, Fukushima University, 1, Kanayagawa, Fukushima city, 960-1296, JAPAN*

Tel: +81-72-451-2495

Fax: +81-72-451-2656

E-mail: kobayashi.yasuhiro.3x@kyoto-u.ac.jp

The recoilless fraction is a parameter that reflects lattice vibrations and provides important knowledge in physics, chemistry, etc. However, in the commonly used ^{57}Fe Mössbauer spectroscopy, the recoilless fraction is not actively measured. This is because the recoil energy of ^{57}Fe is low, and the recoilless fraction is usually saturated at low temperature to room temperature. On the other hand, in ^{197}Au Mössbauer spectroscopy, the energy of γ -rays is high, so differences and changes in the recoilless fraction appear significantly. We attempted to estimate the Debye temperature not from the absolute amount of spectral absorption area but from its temperature dependence curve. The Debye temperature was estimated by fitting the temperature dependence curve with the calculated value of the Debye model. We estimated the Debye temperature of metallic Au with reasonable accuracy to the literature value and estimated that of Au compounds. Also, we estimated almost the same Debye temperature for samples with different thicknesses. Although this method is simple, it is helpful for ^{197}Au Mössbauer spectroscopy.

Keywords: ^{197}Au Mössbauer spectroscopy, recoilless fraction, Debye temperature

1. Introduction

The recoilless fraction is the probability that recoilless resonance of an atomic nucleus (Mössbauer effect) occurs and is also called the Lamb-Mössbauer factor. This value corresponds to the Debye-Waller factor in X-ray diffraction. The recoilless fraction reflects lattice vibrations and bonding of atoms, and its behavior can be approximately described by the Debye temperature based on the Debye model. The Debye temperatures can provide important knowledge of physics, chemistry, and so on [1, 2]. It is also important for determining the ratio of atoms belonging to each spectral component in Mössbauer spectra. In the Mössbauer spectra, the spectral absorption area appears as the product of the number of atoms ratio in each state and the recoilless fraction. When measuring unknown samples, the correct component ratio cannot be determined without the value of the recoilless fraction. In the ^{57}Fe Mössbauer spectra, the difference in recoilless fraction due to the chemical form of Fe is not significant in most cases. Especially for inorganic and metallic materials, it is often assumed that there is no difference in the recoilless fraction at each state of Fe. On the other hand, some organic compounds and biological materials have small recoilless fractions at room temperature [3, 4]. Discussing the area ratio of components in the Mössbauer spectra of these materials requires low temperatures to saturate the recoilless fraction. In ^{197}Au Mössbauer spectroscopy, many materials differ in recoilless fractions at typical measurement temperatures ($T < 60\text{K}$). In the ^{197}Au Mössbauer spectra, the recoilless fraction differs between Au^{1+} and Au^{3+} compounds [5]. In addition, it is considered that the recoilless fraction becomes small when the metallic Au becomes fine particles or clusters [6, 7]. In Au clusters, it has been reported that the recoilless fractions differ depending on the sites [8, 9]. In ^{197}Au Mössbauer spectroscopy, the recoilless fractions are essential parameters. As the elementary data for Au Mössbauer measurements, we measured the absorption area of the spectra in multiple chemical states. We studied a method for estimating the Debye temperature not from the absolute amount of spectral absorption area but from its temperature dependence curve.

The following equation describes the recoilless fraction f using the Debye model [10].

$$f = \exp \left[-\frac{3E_R}{2k\theta_D} \left\{ 1 + 4 \left(\frac{T}{\theta_D} \right)^2 \int_0^{\theta_D/T} \frac{u du}{e^u - 1} \right\} \right]$$

Here, T is the temperature, θ_D is the Debye temperature, and E_R is the recoil energy of the γ -ray emission or absorption. Figure 1 shows the temperature dependence in the recoilless fraction on the Mössbauer effect of ^{197}Au , calculated from the above equation assuming various Debye temperatures. As the Debye temperature decreases, the recoilless fraction decreases, and the inflection point of the curves of the temperature dependences also changes. We attempted to estimate the Debye temperature from these differences in the temperature dependence curve.

2. Experimental Procedure

^{197}Au Mössbauer measurement was performed 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 hours) generated by neutron irradiation to 98%-enriched ^{196}Pt metal foil using Kyoto University Reactor (KUR). ^{197}Au Mössbauer measurements were performed using the helium refrigerator at 20 to 70 K. The samples and source were into 1 atm He gas, so both were in the same temperatures. The series of temperature dependence measurements were made by changing the temperature only. In spectral measurements, changes in collimation and geometry affect the background's intensity, thus changing the absorption area. We did not touch the sample and the γ -ray source in a series of measurements to avoid the geometry change. We set the single channel analyzer (SCA) slightly wider than usual and did not change the amplifier's gain during measurements. The absorption peak position of a metallic Au foil was set as 0 mm/s. The Mössbauer spectra were fitted with MossWinn program [11, 12].

We prepared Au metal, gold(III) hydroxide ($\text{Au}(\text{OH})_3$), and gold(I) sulfide (Au_2S) for the standard chemical state samples of Au. $\text{Au}(\text{OH})_3$ sample was prepared by adding Na_2CO_3 aqueous solution to a concentrated aqueous solution of HAuCl_4 and stirring [13]. For the Au_2S sample, NaHS aqueous solution was gently added to an aqueous HAuCl_4

solution while stirring to perform ligand exchange. Then, concentrated HCl was added all at once and stirred vigorously. The pH was further adjusted to around 1, and a precipitate was created by stirring for 1 hour. Both samples were vacuum dried at room temperature.

The Au particle supported on TiO₂ sample (Au/TiO₂) was prepared by mixing TiO₂ powder and HAuCl₄ aqueous solution to pH 9-10, stirring for 24 hours, filtering, drying at 100°C overnight, and then calcined at 300°C for 4 hours [14]. In this study, the amount of Au was 10wt% on the Au/TiO₂ sample. To facilitate ¹⁹⁷Au Mössbauer measurements, we use samples with more Au than practical material for Au-supported catalysts.

3. Results and Discussion

Figure 2 shows the temperature dependences in the ¹⁹⁷Au Mössbauer spectra of metallic Au, Au(OH)₃, and Au₂S. Au(OH)₃ sample contains metallic Au produced by decomposition as an impurity, which can be easily distinguished by spectral fitting. It is seen that the absorption intensity decreases as the temperature increases in all samples. We fitted these spectra and determined their absorption areas. The obtained isomer shift and quadrupole splitting are 2.8 mm/s and 1.9 mm/s for Au(OH)₃, and 2.3 mm/s and 5.3 mm/s for Au₂S, respectively at 20K. These values are consistent with previous studies [13, 15].

Figure 3 shows the temperature dependence in the absorption area obtained from the spectra (markers) and the temperature dependence of the absorption area at each Debye temperature (lines). The absorption area was normalized by the value at 20K, which was the lowest temperature that can be stably achieved with our cryostat. The sample and source were cooled in the same He gas bath and kept at the same temperature. This calculated value also includes the recoilless fraction of the γ -ray source and the samples. The recoilless fraction of the source was calculated using the Debye temperature of metallic platinum (240K) [16].

The obtained values for metallic Au and Au(OH)₃ are almost on the same line, and the Debye temperatures estimated by the least squares method are 169 K and 166 K for

metallic Au and Au(OH)₃, respectively. The Debye temperature of the obtained metallic Au is close to the literature value (165K) [16]. The obtained value of Au₂S showed a significant different curve from other samples, and estimated Debye temperature was 103K. It has been reported that the recoilless fractions of linear two-coordination Au¹⁺ compounds are smaller than that of Au³⁺ compounds and metallic Au, and this result is reasonable [5].

On this analysis, we did not use variable parameters other than the Debye temperature in these least squares methods. We obtained the Debye temperature using simple absorption area measures and least squares fitting. This analysis method is simple and useful.

On such measurements, there is concern about the influence of the thickness of the sample. If the sample is too thick, the absorption intensity will be saturated, and the change in the recoilless fraction will no longer match the change in the absorption area. To investigate the influence of sample thickness, we measured the spectra using different amounts of the sample. Figure 4 shows spectra measured with two amounts of the sample. The sample was Au precipitated and calcined on TiO₂ powder (Au/TiO₂). Samples of 445 mg and 867 mg in the 10 mm diameter holder were used for measurement, and the effective thicknesses estimated from the preparation values were 1.2 and 2.4, respectively. The spectra show single peak, indicating that almost all Au had been in metallic state. As seen from the vertical axis of the spectra, the absorption intensities are different from the amounts of the sample. Still, the changes in the absorption areas are highly similar. Figure 5 shows the temperature dependence in the absorption area of the sample with various thicknesses. The plot is normalized with the absorption area at 20K, as in Fig. 3. Although the samples differ in thickness by a factor of two, the measured values for both samples plot almost on the same line. This result shows that this method is not sensitive to sample thickness when the effective thickness is 2.4 or less. Although simple, this method helps measure the recoilless fraction and Debye temperature. This method can also be applied to samples with uncertain Au content.

The Debye temperatures estimated by the least squares method are 159 K and 150 K for the 445 and 867 mg samples, respectively. Although this value is somewhat smaller than the bulk Au's value (165 K), further measurements are required to conclude that this result is due to the affection from TiO₂.

4. Conclusion

We attempted to measure the Debye temperatures from the temperature dependences of the absorption areas in the Mössbauer spectra. The temperature dependence curve obtained by normalizing the absorption area by the value at 20K agreed well with the temperature dependence in the recoilless fraction calculated by the Debye model. The Debye temperature of metallic Au determined using this method agreed with the literature value of 165K. The Debye temperature of Au(OH)₃ determined using this method was close to that of metallic Au, but the Debye temperature of Au₂S was 103K. These are consistent with the trend obtained previous studies. As a result of measuring Au/TiO₂-supported fine particle samples with different thicknesses, we obtained almost the same Debye temperature regardless of the thickness. This simple method determines the Debye temperature with reasonable accuracy.

Declarations

Ethical Approval

This declaration is not applicable.

Funding

There is no special funding for this study.

Availability of data and materials

The data and materials supporting this study's findings are available from the corresponding author, Y. K., upon reasonable request.

References

- [1] R.M. Housley, N.E. Erickson and J.G. Dash, Nuclear Instruments and Methods, **27**, 29 (1964).
- [2] W. A. Steyert and R. D. Taylor, Phys. Rev., **134**, A716 (1964).
- [3] Norman A. Bell, John S. Brooks, Jacqueline K. Robinson and Stephen C. Thorpe, J. Chem. Soc., Faraday T rans., **94**, 3155 (1998).
- [4] U. Gonser and R. W. Grant, Biophys J., **5**, 823 (1965).
- [5] Jan Stanek, J. Chem. Phys. **76**, 2315 (1982).
- [6] M. P. A. Vieggers and J. M. Trooster, Phys. Rev. B **15**, 72 (1977).
- [7] Ghazal Shafai, Marisol Alcantara Ortigoza and Talat S Rahman, J. Phys.: Condens. Matter, **24**, 104026 (2012).
- [8] Tatsuya Tsukuda, Yuichi Negishi, Yasuhiro Kobayashi and Norimichi Kojima, Chem. Lett., **40**, 1292 (2011).
- [9] Norimichi Kojima, Yasuhiro Kobayashi, Yuichi Negishi, Makoto Seto, Tatsuya Tsukuda, Hyperfine Interact, **217**, 91 (2013).
- [10] Gunther K. Wertheim, *Mössbauer Effect: Principles and Applications* (Academic Press, New York,1964).
- [11] Z. Klencsar, E. Kuzmann, A. Vertes, J. Radioanal. Nucl. Chem., **210**, 105 (1996).
- [12] MossWinn - Mossbauer spectrum analysis and database software
<http://www.mosswinn.com/english/index.html> Accessed 26 February 2024.
- [13] Daisuke Kawamoto, Hiroaki Ando, Hironori Ohashi, Yasuhiro Kobayashi, Tetsuo Honma, Tamao Ishida, Makoto Tokunaga, Yoshihiro Okaue, Satoshi Utsunomiya, and Takushi Yokoyama, Bull. Chem. Soc. Jpn., **89**, 1385 (2016).
- [14] Luong Xuan Dien, Tamao Ishida, Ayako Taketoshi, Duc Q. Truong, Huynh Dang Chinh, Tetsuo Honma, Toru Murayama, Masatake Haruta, Applied Catalysis B: Environmental, **241**, 539 (2019).
- [15] C.M. Cardile, J.D. Cashion, A.C. McGrath, P. Renders, and T.M. Seward, Geochim. Cosmochim. Acta, **57**, 248 (1993).
- [16] C. Kittel, *Introduction to Solid State Physics, 7th ed.*, (John Wiley & Sons, Inc., New York, 1996).

Figures and Figure captions

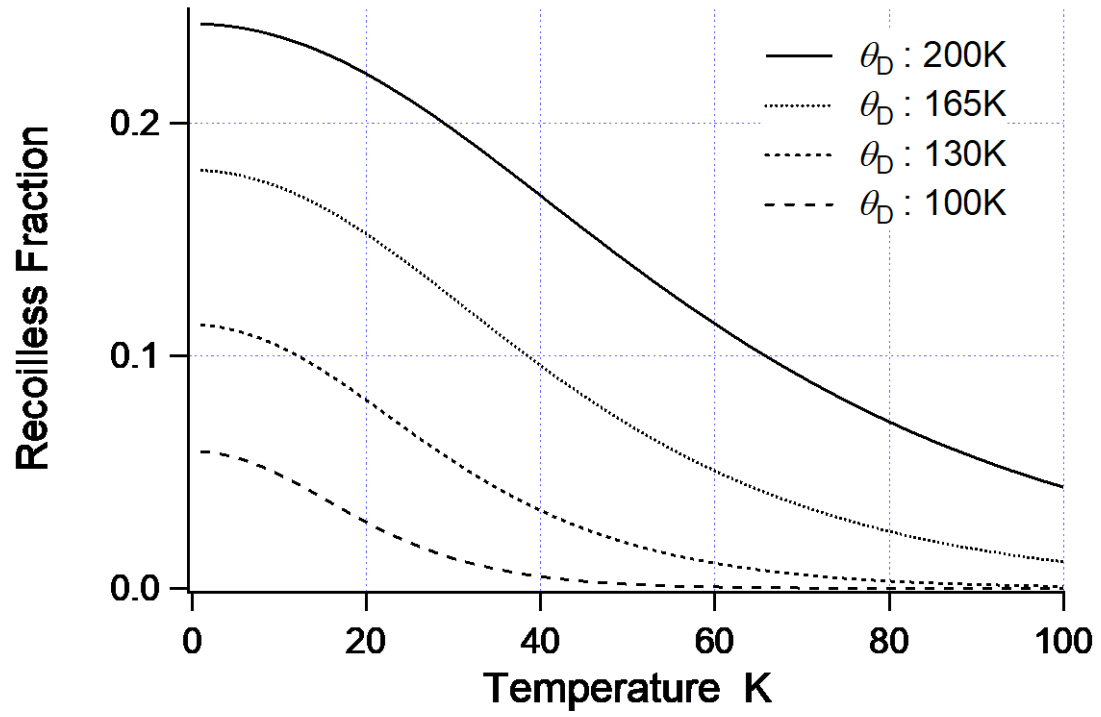


Fig. 1 Temperatures dependence of the recoilless fractions on ^{197}Au Mössbauer effect assuming various Debye temperatures.

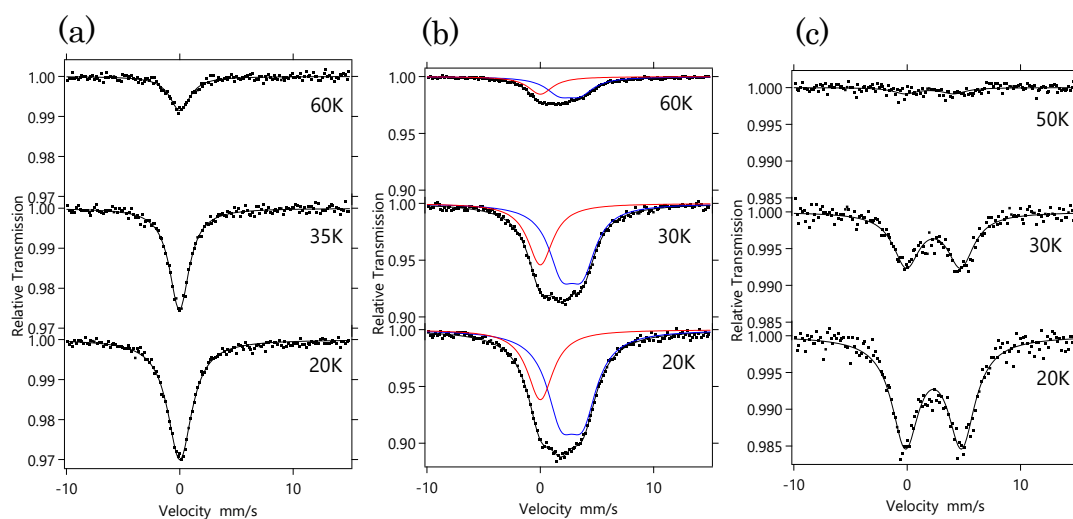


Fig. 2 ^{197}Au Mössbauer spectra of (a) metallic Au, (b) $\text{Au}(\text{OH})_3$, (c) Au_2S at various temperatures. The spectra of $\text{Au}(\text{OH})_3$ include metallic Au as impurity.

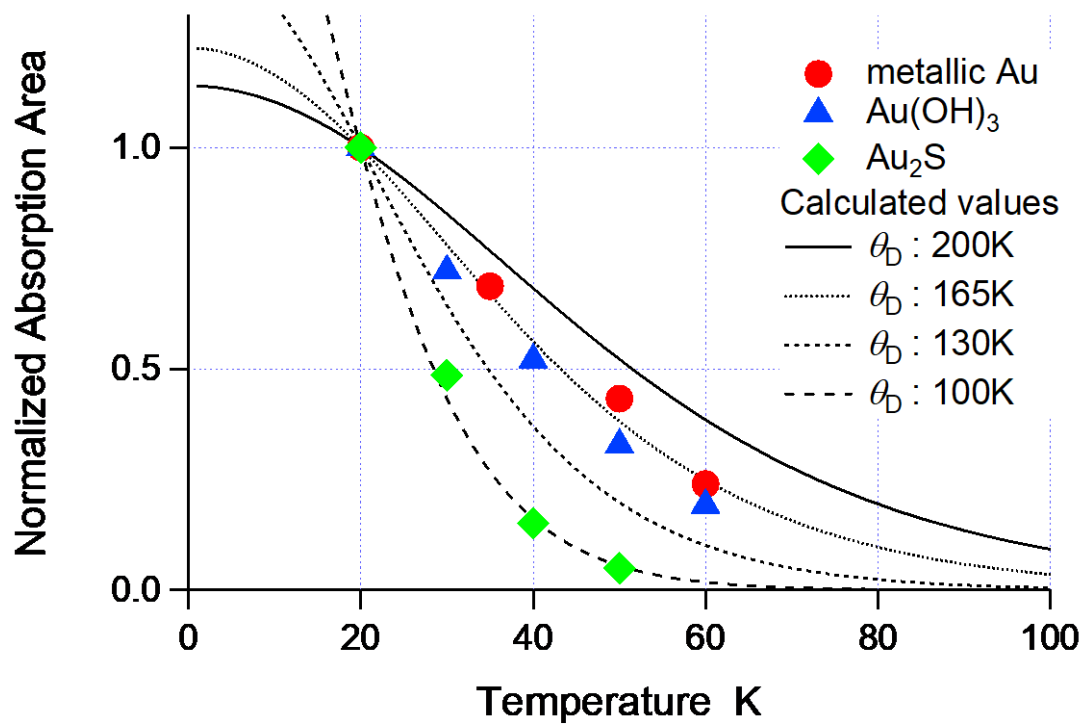


Fig. 3 The temperature dependences of the absorption area obtained from the spectra of metallic Au and Au compounds (markers), and the temperature dependences of the absorption area at each Debye temperature (lines). The absorption area was normalized by the value at 20K.

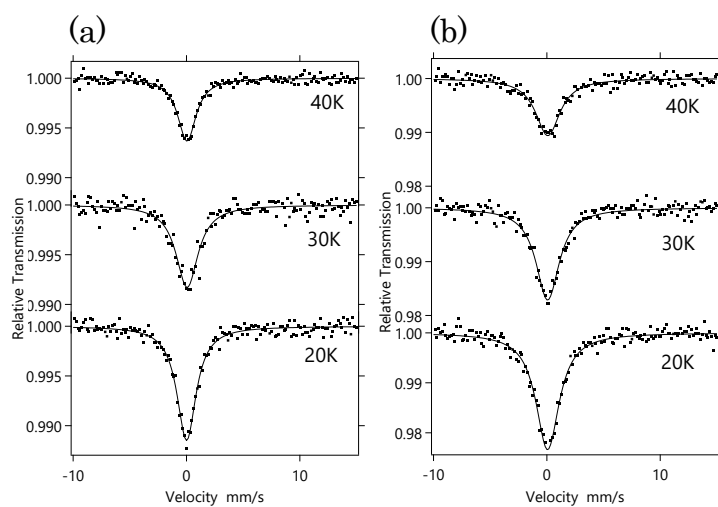


Fig. 4 ^{197}Au Mössbauer spectra of Au/TiO₂ samples (a) 445 mg, (b) 867 mg at various temperatures.

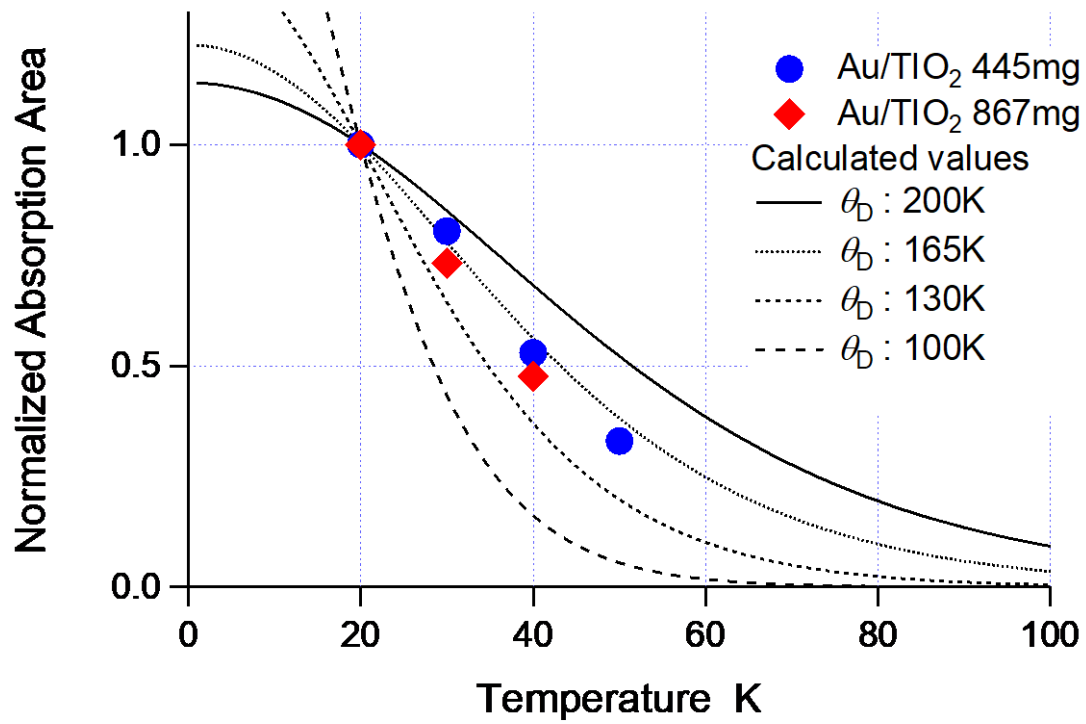


Fig. 5 The temperature dependences of the absorption area obtained from the spectra of different thickness Au/TiO₂ samples (markers), and the temperature dependences of the absorption area at each Debye temperature (lines). The absorption area was normalized by the value at 20K.