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Articles

Valence state of Eu in its hydride under hydrogen pressure of up to 80 GPa by ^{151}Eu synchrotron-radiation-based Mössbauer spectroscopy

Ryo Masuda[1]*, Takahiro Matsuoka[2,3], Kosuke Fujiwara[4], Hirokazu Kadobayashi[5], Shinji Kitao[6], Makina Saito[7], Kaito Murakami[1], Yoshin Hara[1], Taiki Kato[1], Kenta Ebina[1], Takaya Mitsui[4]

[1] *Graduate School of Science Technology, Hirosaki University, Bunkyo-cho, Hirosaki, Aomori, 036-8561, Japan.*
[2] *Tender X-ray Diffraction and Scattering Team, NanoTerasu Research Center, Research & Utilization Branch, Japan Synchrotron Radiation Research Institute, Aoba, Sendai, Miyagi, 980-8572, Japan.*
[3] *National Institute of Physics, College of Science, University of the Philippines Diliman, Quezon, 1101, Philippines.*
[4] *Quantum Beam Science Directorate, National Institutes for Quantum Science and Technology, Kouto, Sayo, Hyogo, 679-5198, Japan.*
[5] *Japan Synchrotron Radiation Research Institute, Sayo, Hyogo, 679-5198, Japan.*
[6] *Institute for Integrated Radiation and Nuclear Research, Kyoto University, Kumatori, Sennan, Osaka, 590-0494, Japan.*
[7] *Department of Physics, Graduate School of Science, Tohoku University, Sendai, Miyagi 980-8578, Japan.*

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^{151}Eu synchrotron-radiation-based Mössbauer spectroscopy was performed to study the electronic state of Eu hydride under hydrogen pressure up to 80 GPa, which is the highest hydrogen pressure achieved at SR-based Mössbauer spectroscopy (i.e., energy domain). All the Mössbauer spectra of Eu hydride from 18.2 to 80 GPa showed a simple single-line profile without any nuclear electric quadrupole interaction or magnetic hyperfine interaction. The isomer shift of Eu hydride clearly showed an ionic Eu^{3+} state and no evidence of a Eu^{2+} state. It increases as the hydrogen pressure increases due to the enhancement of electronic density at ^{151}Eu nuclei, which could be understood mainly by the contribution of lattice contraction. The linear relation between the isomer shift and inverse volume for EuH_x (x≈3) is evaluated, which would form a basis for further Mössbauer study on the electronic states of Eu hydrides with higher hydrogen contents, i.e., x>4.

Keywords: *Europium hydride, high hydrogen pressure, ^{151}Eu Mössbauer spectroscopy, synchrotron radiation*

1. Introduction

Hydrogen is known to be absorbed by many materials and often causes significant changes in their electrical and magnetic properties. Rare-earth elements are representative hydrogen-absorbing materials, and their dihydrides and trihydrides have long been synthesized and studied under hydrogen pressures of several MPa.[1,2] In these rare-earth hydrides, systematic discussions have been conducted on the relationship between hydrogen content and changes in crystal structure and electronic state. Among them, europium (Eu) exhibits distinctive behavior. For a long time, only the dihydride phase of Eu had been confirmed, which distinguishes Eu from other rare-earth elements where trihydrides are commonly observed.

The electronic state of Eu in its hydrides has been investigated by ^{151}Eu Mössbauer spectroscopy. Early studies demonstrated that Eu in the dihydride adopts an ionic Eu^{2+} state,[3] clearly different from metallic Eu.[4]

A significant development occurred in 2011, when new Eu hydride phases were discovered under hydrogen pressures above 7 GPa.[5] Synchrotron radiation (SR) X-ray diffraction (XRD) experiments revealed that the phase crystallizes in a tetragonal I4/mmm structure above 10 GPa hydrogen pressure. This phase was regarded as a slightly distorted variant of the cubic $Fm\bar{3}m$ structure, typical of trihydrides of other rare-earth elements. Subsequent studies identified seven hydride phases below 20 GPa.[6] Furthermore, several higher europium hydrides were synthesized under extremely high hydrogen pressures up to 200 GPa by two experimental groups[7,8]. Their structural diversity has been extensively characterized by SR-XRD, demonstrating that the Eu–H system exhibits rich structural variations over a wide pressure range.

In parallel with these experimental advances, theoretical calculations have predicted the formation of higher rare-earth hydrides, including decahydrides, and numerous higher europium hydrides have been proposed.[9] For EuH_x phases synthesized at extremely high hydrogen pressures, the hydrogen content and possible magnetic ordering have been evaluated theoretically, and even magnetic ordering in the EuH_3 phase at 80 GPa hydrogen pressure has been discussed.[7,8] Since the ionic Eu^{3+} ground state has a total angular momentum J = 0 and does not usually exhibit magnetic ordering, this theoretical evaluation suggested Eu^{2+} state above 80 GPa hydrogen pressure. Nevertheless, despite the substantial progress in structural studies and theoretical predictions, experimental evidence for the electronic state of Eu above 20 GPa remains unattained. Clarifying the valence state of Eu in this pressure range represents a crucial unresolved issue.

To study the electronic state of Eu under high hydrogen pressure, SR-based Mössbauer spectroscopy[10] is particularly suitable. The incident radiation is SR in this method and the high brilliance, small beam size, low angular divergence of SR critically fits the pressure cells used in the high hydrogen pressure experiments, In fact, a diamond anvil cell (DAC) is typically employed for high hydrogen pressures, as used in references 5-8, although

*Corresponding author. E-mail: masudar@hirosaki-u.ac.jp

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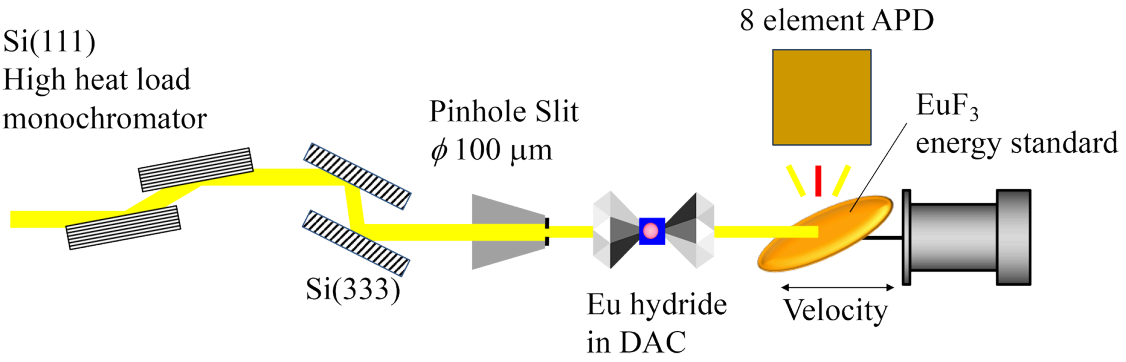

Figure 1. Schematic drawing of the measurement system for ^{151}Eu SR-based Mössbauer spectroscopy.

the sample volume confined in a DAC is extremely small. For example, the culet diameter used in reference 11 was on the order of 0.4–0.5 mm, which is much smaller than the size of conventional ^{151}Sm radioactive (RI) sources for ^{151}Eu Mössbauer spectroscopy (typically ~1 cm in diameter). Furthermore, when the cell is positioned at a distance from the source, the solid angle from the source is limited, because the γ-rays are emitted isotropically from the source. The advantages of SR-based Mössbauer spectroscopy for Eu hydrides were already shown in references 5, 6 and 11. It elucidates the Eu valence transition from Eu^{2+} to Eu^{3+} between 7 and 10 GPa hydrogen pressure.

Thus, ^{151}Eu SR-based Mössbauer spectroscopy offers a direct and experimentally feasible means to determine the Eu valence state in the previously unexplored pressure range above 20 GPa. In this article, we studied the valence state of Eu hydrides under hydrogen pressure between 18.2 GPa and 80 GPa by this method. We also discuss the influence of hydrogen pressure on the isomer shift of Eu hydrides under this hydrogen pressure region.

2. Materials and Methods

The starting material for the synthesis of Eu hydrides was EuH_x (x≈2) purchased from Kojundo Chemical Laboratory. Co., Ltd. This material was from the same batch as the raw material for EuH_2 under He pressure in reference 11. A small piece of this hydride was packed in a DAC with H_2 fluid at nearly 200 MPa using a high-pressure gas-loading apparatus installed at SPring-8. Note that the H_2 fluid serves as both the pressure medium and hydrogen source for the synthesis of higher hydrides. The culet diameter of the DAC was 0.3 mm and the hole size of the cylindrically shaped sample chamber at the SR Mössbauer experiments under GPa hydrogen pressure was typically 0.1 mm in diameter. The hydrogen pressure was determined by the fluorescence of the ruby compressed with the sample in the chamber in the DAC. Further details of the synthesis of Eu hydride samples are described in reference 5. The energy standard for ^{151}Eu Mössbauer spectroscopy was EuF_3 powder at room temperature, purchased from FUJIFILM Wako Pure Chemical Co. 1.27 mg of EuF_3 was used to make a pellet with a diameter of 7 mm. Both EuH_x and EuF_3 were non-enriched, because the natural abundance of ^{151}Eu is 47.8%.

The ^{151}Eu SR-based Mössbauer spectroscopy was performed at BL11XU of SPring-8. The schematic drawing of the typical experimental instrumentation is shown in Fig. 1. The electron bunch-mode of the storage ring was the 203 bunch mode, where the period between each electron bunch was 23.6 ns. SR from the undulator was monochromatized by a Si (111) high heat load monochromator (HHLM). After the HHLM, the SR was further monochromatized by a Si (333) double crystal monochromator to reduce the energy bandwidth to approximately 0.2 eV around the ^{151}Eu nuclear resonance. A pinhole slit of 100 μm diameter was arranged downstream of the monochromator to limit the beam size. Then the SR penetrated the Eu hydride sample in the DAC at room temperature. Downstream of the sample, the SR was incident on the pellet of energy standard EuF_3 at room temperature. The pellet was arranged at 8 degrees inclined to the beam direction. This energy standard was connected to a Mössbauer velocity transducer to control the energy of its nuclear resonance through the Doppler effect of light. Note that the velocity was calibrated by the Mössbauer laser Doppler velocity calibrator (Wissel MVC-450) and thus the velocity was relative to EuF_3 at room temperature. An array-type Si avalanche photodiode (APD) with eight elements was arranged in the same vacuum chamber together with the energy standard to detect the scattering X-rays and electrons from the standard through the nuclear resonance.[12]

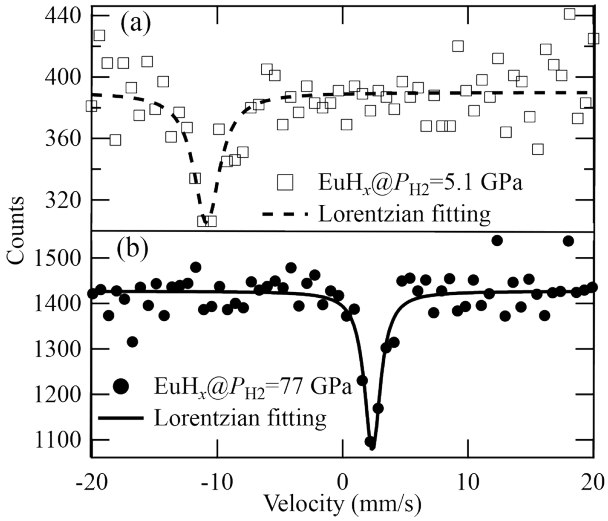

Figure 2. ^{151}Eu SR-based Mössbauer spectrum of Eu hydrides: (a) EuH_x (x~2) under 5.1 GPa hydrogen pressure and (b) EuH_x (x~3) under 77 GPa hydrogen pressure. Open rectangles and closed circles are experimental data, and the lines are the fitting curves by a Lorentzian function.

3. Results and Discussion

Although the hydrogen fluid often attacks the diamond anvil, we successfully observed the ^{151}Eu Mössbauer spectra up to 80 GPa hydrogen pressure. This is the highest hydrogen pressure achieved by SR-based Mössbauer spectroscopy. Fig. 2 (a) shows the Mössbauer spectrum of Eu hydride at 5.1 GPa hydrogen pressure. As for the typical spectra at higher hydrogen pressures, the Mössbauer spectrum of Eu hydrides at 77 GPa hydrogen pressure is shown in Fig. 2 (b). The measurement time was about half a day for one spectrum above 18.2 GPa hydrogen pressure. All the observed spectra were understood as one component

TABLE 1. The values concerning the dependence of ^{151}Eu isomer shift on the pressure.

Hydrogen pressure (GPa)	Isomer shift (mm/s)†	Volume per Eu atom (Å^3)‡	Inverse volume (10^{-2} Å^{-3})
18.2	0.84±0.21	32.3	3.09
23	1.20±0.23	31.3	3.20
50.2	1.86±0.17	27.2	3.68
52	2.22±0.18	27.0	3.71
75	2.65±0.17	24.9	4.02
77	2.41±0.15	24.7	4.05
80	2.67±0.22	24.5	4.08

†Relative to EuF_3 at room temperature.
‡Evaluated by the 3rd order Birch-Murnaghan equation of state using the parameters in reference 5.

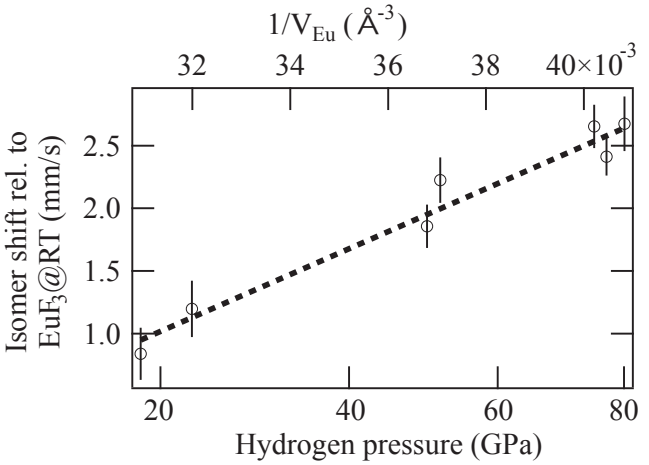

Figure 3. The relation between the isomer shift of EuH_x (x~3) and hydrogen pressure. The lower x-axis shows the pressure, and the upper x-axis shows the inverse volume corresponding to the pressure. Open circles are experimental data, and the line is a linear fitting curve of isomer shift with inverse volume.

without hyperfine splitting due to the nuclear electric quadrupole interaction or magnetic hyperfine interaction. This agrees with the previous results below 7 GPa hydrogen pressure.[5,6,11] This also agrees with the cubic-like symmetry of $EuH_{x\sim3}$ above 14.3 GPa hydrogen pressure.[5,7] Therefore, the isomer shifts of the hydrides relative to the EuF_3 at room temperature were evaluated using a simple single Lorentzian function. Note that this isomer shift evaluated in this way includes both the isomer shift due to the electronic density at the ^{151}Eu nuclei and the second-order Doppler shift due to atomic vibration. The second-order Doppler shift is expressed by the following equation in the Debye model:[13]

$$v_{\mathrm{SOD}} = -\frac{9k_{\mathrm{B}}\Theta_{\mathrm{D}}}{16Mc}\left\{1+8\left(\frac{\mathrm{T}}{\Theta_{\mathrm{D}}}\right)^4\int_0^{\Theta_{\mathrm{D}}/\mathrm{T}}\mathrm{d}x\,\frac{x^3}{\mathrm{e}^x-1}\right\}, \qquad (1)$$

where k_{B} is Boltzmann constant, Θ_{D} is the Debye temperature of the material, M is the mass of the nucleus, c is the speed of light, T is the temperature of the material. According to eq. (1), the effect of the second order Doppler shift in ^{151}Eu Mössbauer spectra in this article was at most 0.1 mm/s at room temperature. For example, v_{SOD} at 300 K is evaluated to be -0.0863 mm/s for Θ_{D}=283 K, which corresponds to EuF_3,[13] and -0.0831 mm/s for Θ_{D}=94 K, which corresponds to Eu metal.[14] Therefore, the difference of the two typical materials is 0.0032 mm/s. The difference of 1 mm/s from these values is achieved by v_{SOD} at 300 K with Θ_{D} exceeding 1700 K, which is so high that it is rarely seen in practice. Since the experimental error of the observed isomer shift was typically 0.2 mm/s, the effect of second-order Doppler shift is not discussed in the following part.

The isomer shift obtained from Fig. 2 (a) is -10.83±0.26 mm/s. This isomer shift lies between -11.28±0.11 mm/s for EuO and -7.8±0.2 mm/s for metallic Eu, which has Eu^{2+} metallic core[15], indicating that the Eu at this hydrogen pressure was in Eu^{2+} state. This isomer shift agrees well with those of Eu hydrides below 7 GPa hydrogen pressure in reference 11. As for the higher pressures above 18.2 GPa, the pressure dependence of the isomer shift is shown in Table 1 and Fig. 3. The isomer shifts lie between 0 mm/s for EuF_3 and 3.0±0.2 mm/s for $EuRh_2$, which has Eu^{3+} metallic core[15] and thus show the Eu^{3+} state under hydrogen pressures up to 80 GPa. It gradually increases as hydrogen pressure increases, and no signal implying the valence transition to any magnetic Eu^{2+} states was detected. The isomer shift was expressed in the following equation[13]:

$$\delta = \frac{c}{E_\gamma}\cdot\frac{2\pi}{5}Ze^2\,(R_{\mathrm{e}}^2 - R_{\mathrm{g}}^2)\,(\rho_{\mathrm{A0}} - \rho_{\mathrm{S}}), \qquad (2)$$

where E_γ is the energy of the nuclear resonance, Z is the atomic number of the element of the probe nuclide, e is the elementary charge, R_{e}^2 is the square of the nuclear radius of the nuclear excited state concerning the resonance, R_{g}^2 is the square of the nuclear radius of the nuclear ground state concerning the resonance, ρ_{A} is the electronic density at the probe nucleus of the sample under study, and ρ_{S} is the electronic density at the probe nucleus of the energy standard material. Therefore, the electronic density of the sample (in our case, Eu hydrides) is in linear relation to isomer shift. Since no obvious structural change was reported between 10 and 80 GPa hydrogen pressure, i.e., the crystal structure maintains cubic or slightly distorted tetragonal,[5,7] this gradual increase of isomer shift reflects the increase of electronic density at the nucleus, which is attributed to the electron transfer between Eu and H or volume contraction by pressure. First, we consider the influence of electron transfer. Contrary to ^{57}Fe Mössbauer spectroscopy, the increase of isomer shift in ^{151}Eu Mössbauer spectroscopy indicates the increase of electron density at the nucleus. This is because the nuclear radius of the first excited state of ^{151}Eu is larger than that of the ground state.[15] If we assume that the 6*s* electrons in Eu contribute to the electron transfer between Eu and H, the increase in isomer shift corresponds to the increase of 6*s* electrons. This is somewhat contradictory because it is natural that the high hydrogen pressure promotes the interaction between Eu and H, and the 6*s* electrons of Eu approach H. Therefore, the important contribution to the isomer shift is volume contraction. The volume per Eu atom can be calculated by the 3rd-order Birch-Murnaghan equation of state:

$$P(V) = \frac{3B_0}{2}\left[\left(\frac{V_0}{V}\right)^{\frac{7}{3}} - \left(\frac{V_0}{V}\right)^{\frac{5}{3}}\right]\left\{\left[1+\frac{3}{4}(B'_0-4)\left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}}-1\right]\right]\right\}, \qquad (3)$$

where P and V are pressure and volume, respectively, B_0 is the bulk modulus, V_0 is the volume at ambient pressure, and B_0' is the pressure derivative of the bulk modulus at 0 GPa. Here, we used the following parameters: B_0 = 69 GPa, V_0 = 38.8 Å^3, and B_0' = 4.[5] Thus, the inverse volume was calculated, and the axis for it is shown as the upper x-axis in Fig. 3. The relation between the isomer shift and the inverse volume is rather linear and expressed by the following relation: (Isomer shift in mm/s) = 4.3 (±0.8) (mm/s)+(1.7±0.02)×10^2/ (volume per Eu atom in Å^3). This linear relation also supports the absence of a critical structural phase transition.

This relation between isomer shift and volume at EuH_x (x≈3) is useful for the studies on hydrides with higher hydrogen contents under higher pressure by Mössbauer spectroscopy, because reported hydrides with the higher hydrogen contents show a volume expansion accompanied by structural changes. The deviation from this relation indicates the change in the electronic configuration of Eu. In fact, the isomer shift decreases due to both volume expansion and a decrease in 6*s* electrons, and thus the obtained relation helps us to estimate the contribution of volume.

4. Conclusions

Electronic states of EuH_x synthesized under high hydrogen pressure up to 80 GPa were successfully studied by ^{151}Eu SR-based Mössbauer spectroscopy. The spectra showed that the isomer shift corresponds to the Eu^{3+} state, and no signal of the magnetic Eu^{2+} state was observed, at least at room temperature. This result disagrees with the theoretical prediction in references 7 and 8 that Eu hydrides show magnetic ordering above ~80 GPa hydrogen pressure. The change in isomer shift of EuH_x to hydrogen pressure was understood as the effect of volume contraction rather than electronic transfer between Eu and H. The linear dependence of the isomer shift on the inverse volume was evaluated, which would be useful to further study on higher hydrides under higher hydrogen pressures.

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