Energy Domain Synchrotron-Radiation-Based Mössbauer Spectroscopy of EuH$_2$ under a Few GPa Pressure

FUJIWARA Kosuke, MITSUI Takaya, SETO Makoto

Magnetism Research Group, Synchrotron Radiation Research Center

Hydrogen is the smallest atom, and is stored in various materials[1]. Recently, various hydrides of rare-earth atoms have been discovered under high-pressure hydrogen conditions. These novel hydrides showed various properties. For example, LaH$_{10}$ exhibited superconductivity at over 200 K under a hydrogen pressure of more than 100 GPa[2].

Europium (Eu) metal also forms various hydrides. The structure of Eu metal is $Im\overline{3}m$, that is, body-centered cubic. It forms a dihydride EuH$_2$, whose structure is orthorhombic $Pnma$[3], under a hydrogen pressure of approximately 0.1 MPa, that is, 1 atm. This was the only Eu hydride identified in the 20th century. Recently, other forms of hydride have been synthesized under high hydrogen pressures of up to 20 GPa[3-5]. In many cases of hydride formation in metals and alloys, the typical process from one hydride to the other by increasing the hydrogen pressure is gradual hydrogen storage by the formation of a solid solution with hydrogen or the coexistence of two phases by spinodal decomposition. However, the hydrogen storage process of Eu at extended pressures is complicated: there are six hydride phases in addition to the initial $Pnma$ phase, and a tetragonal $I4/mmm$ phase is finally formed over 16 GPa. ^{151}Eu energy-domain synchrotron radiation-based Mössbauer spectroscopy (ESRMS)[6] has been performed to study the electronic state of the Eu atom in these hydride phases and it reveals that Eu was in the 2+ state in EuH$_2$, the first stage $Pnma$ hydride, and formed a 3+ state in the $I4/mmm$ hydride. Furthermore, the 2+ and 3+ states coexisted in some hydride phases.

This complicated hydride formation process might include more hydrogen storage than that in dihydrides. However, it is difficult to estimate the detailed hydrogen content because these hydrides are synthesized in a diamond anvil cell (DAC). The hydrogen content of the sample in a DAC is sometimes estimated by the volume expansion obtained through X-ray diffraction based on the general empirical rule that the absorption of one H atom into a rare-earth metal lattice induces a volume of 4±0.5 Å^3. However, when the metal stores hydrogen gradually, depending on the hydrogen pressure, the lattice expansion by hydrogen storage and lattice contraction by pressure cannot be clearly decoupled. Therefore, another method to estimate the degree of hydrogen storage is required.

When a metal stores hydrogen, its electronic states are modulated. Here, the "isomer shift" in Mössbauer spectroscopy is affected by the electronic density at the probe nucleus and thus, it might provide a useful clue about the degree of hydrogen storage. However, the isomer shift is also affected by the lattice expansion and contraction. The isomer shift δ in the velocity unit is given by the following equation[7]:

$$\delta = \frac{c}{E_\gamma} \cdot \frac{2\pi}{5} Z e^2 \left(R_e{}^2 - R_g{}^2 \right)(\rho_A - \rho_S), \qquad (1)$$

where c is the speed of light, E_γ is the energy of 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, which is often EuF$_3$ in ^{151}Eu Mössbauer spectroscopy. The electronic state of the sample under study contributes only to ρ_A. Even if there is no change in the electronic states, caused by the electron transfer between the metal and hydrogen, the isomer shift would change through the volume change in hydrogen storage. As the simplest model, we assume that the local density ρ_A is proportional to the inverse of the volume; thus, the dependence of the isomer shift on the inverse of the lattice volume is expressed as a linear function.

In this article, we report the ESRMS of Eu hydride in the pressure region of the initial $Pnma$ hydride, EuH$_2$, which is below 7 GPa at room temperature[3], to evaluate the relationship between the isomer shift and volume contraction. The existence of additional hydrogen storage in this pressure region is also discussed.

The experiments were performed at BL11XU of SPring-8, the beamline of the National Institutes for Quantum Science and Technology (QST), using the ESRMS system installed in the beamline. The samples under study were a piece of Eu metal in hydrogen fluid as a pressure medium in a DAC, or EuH$_2$ in helium fluid as a pressure medium in another DAC. Both samples were synthesized using a high-pressure gas-loading apparatus at the Japan Synchrotron Radiation Research Institute (JASRI). The energy standard for the ESRMS system was EuF$_3$ at 80 K. The details of the experimental apparatus are provided in Ref. 8.

The typical ESRMS spectra of the two samples are shown in Fig. 1. The measurement time was typically half a day for each spectrum. All observed spectra were understood by one Eu^{2+} component without hyperfine splitting, which agrees with Refs. 3 and 5. The isomer shifts of both samples increased with increasing pressure. The results of this experiment and those from previous literature are compared in Fig. 2. The volume of the Eu hydride lattice was estimated using the 3rd order Birch–Murnaghan equation of state:

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

where P and V are the pressure and volume, respectively; B_0 is the bulk modulus; V_0 is the reference volume; and B_0' is the derivative of the bulk modulus with respect to pressure. We used

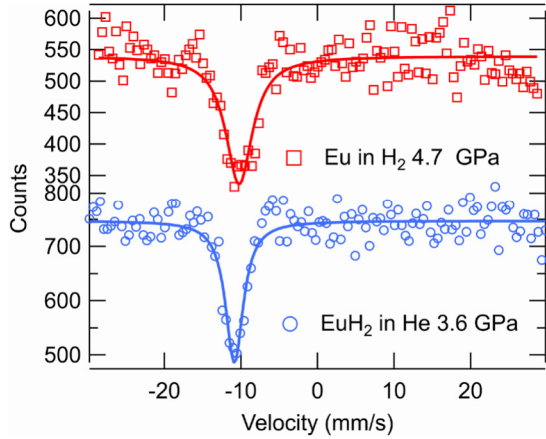the following parameters[3]: B_0 = 39.9 GPa, V_0 = 42.6 Å^3, and B_0' = 4.

Fig. 1 Typical ESRMS spectra of Eu hydrides, reproduced from Ref. 8. Open symbols are experimental data and the lines are the fitting curve by the Lorentzian function.
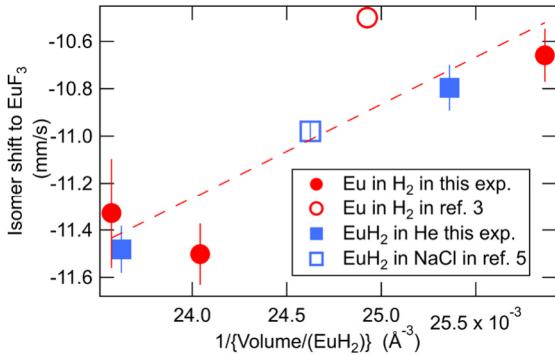

Fig. 2 Relation between the isomer shift of samples and the inverse of the volume of EuH$_2$ lattice, reproduced from Ref. 8. Filled symbols are the experimental data and the open symbols are those in Refs. 3 and 5. Circles represent the data of Eu metal in the H$_2$ fluid pressure medium and squares represent that of EuH$_2$ in the inactive pressure medium. The line is obtained by fitting the linear function using the data in this experiment and refs.

When the pressure increases, one sample, the Eu metal in the hydrogen fluid as the pressure medium, might store more hydrogen, while the other, the EuH$_2$ in the helium fluid as the pressure medium, would never store more hydrogen. Therefore, if there was some gradual hydrogen storage by increasing the hydrogen pressure, there might be some difference between their isomer shift trends. However, we cannot observe a clear systematic difference between the isomer shifts shown in Fig. 2. This result implies that there is little or no gradual hydrogen storage in this pressure range.

According to the semi-empirical model of isomer shift by Miedema[11], hydrogen absorption causes a decrease in the isomer shift in the Eu^{2+} region[12, 13]. In Fig. 2, we cannot observe a decreasing trend of the isomer shift with the increase in the inverse volume, although there is a non-negligible dispersion of isomer shifts from the fitting curve by the linear function in Fig. 2: (Isomer shifts in mm/s) = $(4 \pm 1) \times 10^2$ ((mm/s) · Å^3) × (Inverse volume in Å^{-3}) − 21 ± 3 (mm/s). This also

supports the absence of gradual hydrogen absorption.

As described in the beginning of this report, there are various hydride phases under a hydrogen pressure higher than that used in this experiment. If we assume that the electronic structure is not strongly modified in these hydride phases at which Eu shows a 2+ state, the effect of volume on the ^{151}Eu isomer shift in these phases would be similar to that in this experiment. Therefore, we can investigate the existence of gradual hydrogen absorption at higher hydrogen pressures using the linear dependence of the isomer shift on the inverse volume obtained in this experiment.

Acknowledgments

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