

Structural and valence transitions of EuH_x exposed to high pressure H_2 conditions

Rare-earth metals R, including yttrium (Y) and scandium (Sc), can absorb large amounts of hydrogen (e.g., 300 mol% in YH_3 , at ambient pressure). This has led to extensive studies of their physical and chemical properties for industrial applications and academic interest.

This study [1] is conducted to establish a clear connection between the structural phases of EuH_x and the other RH_x , and to contribute to a full understanding of the interaction between hydrogen and rare-earth metals. In particular, we are interested in phase transformations and valence states of EuH_x under H_2 pressures that exceed 1 GPa to identify the known phases of other “regular” RH_x .

Systematic studies of RH_x have revealed common features in the crystal structure. RH_x crystallizes into essentially three structural phases, α , β and γ phases, depending on the hydrogen composition of $x = \text{H}/\text{R}$. The α phase is a solid solution where H atoms are distributed statistically at the tetrahedral (T) interstitial sites of the metal lattice as impurities. The β phase has an fcc structure. The β phase has been observed for dihydrides and several trihydrides RH_3 (for R = La, Ce, or Pr) [2]. In dihydrides, H atoms occupy T sites, forming an fcc fluorite structure. The γ phase possesses an hcp structure with the ideal composition RH_3 (R = Y, Nd, Sm, Gd, Tb, Dy, Ho, Er, or Lu) [2]. It is known to transform to an fcc structure at high pressures [3].

Europium hydride EuH_x has been an irregular member among the RH_x family because of its unique

structural properties. Reflecting its divalent ground state $4f^{n+1}(5d6s)^2$, the dihydride EuH_2 crystallizes into the orthorhombic $Pnma$ (PbCl_2 -type, $Z(\text{Eu}) = 2$) structure. EuH_x is the only rare-earth metal hydride for which other structural phases have not been clearly observed. When EuH_2 is exposed to high-pressure H_2 , one can expect an increase in hydrogen composition and valence changes that lead to structural phase transitions. The chemical potential of hydrogen on hydrogen solubility is significantly enhanced by high pressures exceeding 1 GPa [4]. The valence state of Eu can be changed between $4f^{n+1}(5d6s)^2$ and $4f^n(5d6s)^3$ by high pressure or by chemical manipulation. Thus, at a sufficiently high pressure, the β or γ phase may result from additional hydrogen uptake and a valence transition.

We have studied the crystal structures of europium hydride compressed in H_2 and He environments by X-ray diffraction (XRD) in **BL10XU** and DFT calculation. These systems are denoted as EuH_x/H_2 and EuH_2/He , respectively. To investigate the valence state of EuH_x , synchrotron Mössbauer spectroscopy measurements of EuH_x/H_2 were carried out in **BL09XU**.

Figure 1 shows the typical integrated X-ray diffraction diagram of EuH_x/H_2 with the crystal structures of the three new phases denoted as EuH_x -II, III and IV. At 7.2 GPa, EuH_x -I, which has $Pnma$ structure, transformed to the EuH_x -II, which crystallizes in $P6_3/mmc$ (Ni_2In -type) structure. The EuH_x -II transforms to EuH_x -III with a tetragonal $I4/m$ structure at 8.7 GPa and subsequently to EuH_x -IV

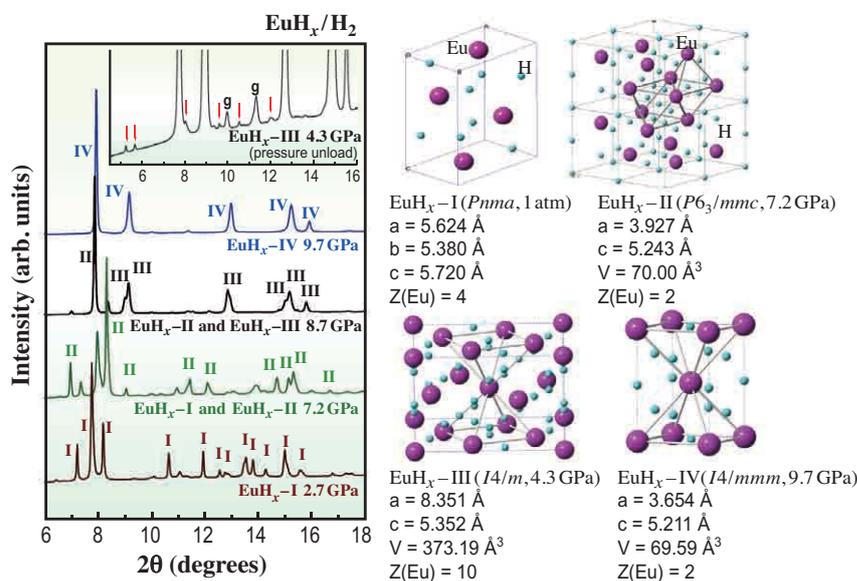


Fig. 1. Integrated XRD profiles of the EuH_x/H_2 system with crystal structures of EuH_x -I, II, III, and IV phases. The inset graph indicates the XRD profile of EuH_x -III at 4.3 GPa when pressure is unloaded. The downward arrows in the inset graph show the satellite peaks of the EuH_x -III phase. The “g” labels show the diffraction peaks of the Re-metal gasket.

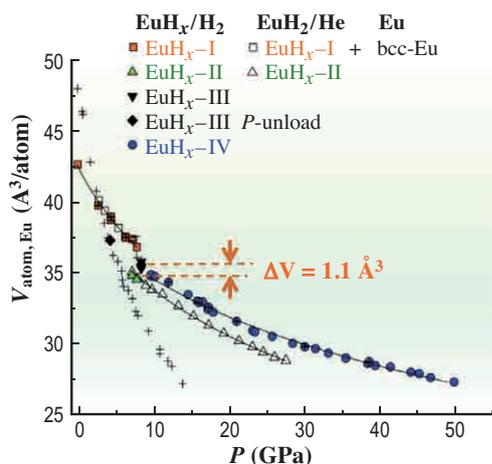


Fig. 2. Pressure dependence of $V_{\text{atom, Eu}}$. Solid lines are guides for eyes. The volume data of pure bcc-Eu were taken from Ref. 5.

with the $I4/mmm$ structure. In the EuH_2/He system, the $\text{EuH}_x\text{-I}$ to $\text{EuH}_x\text{-II}$ transition was observed at 7.2 GPa where the same transition was observed in the EuH/H_2 system. However, the $\text{EuH}_x\text{-II}$ phase was found to be stable up to 28 GPa. Here, it is clear that the transition $\text{I} \rightarrow \text{II}$ is a thermodynamic effect by external pressure and that $\text{II} \rightarrow \text{III} \rightarrow \text{IV}$ transformations are induced by the reaction between the sample and surrounding high-pressure H_2 .

To investigate the hydrogen composition x in $\text{EuH}_x\text{-III}$ and $\text{EuH}_x\text{-IV}$, we compared the atomic volume per Eu, i.e., $V_{\text{atom, Eu}}$, values at the transition pressures. $V_{\text{atom, Eu}}$ is calculated from the refined unit cell parameters and plotted as a function of pressure in Fig. 2. We observed a volume expansion of 1.1 \AA^3 in EuH_x/H_2 at 8.7 GPa, where $\text{EuH}_x\text{-II}$ and $\text{EuH}_x\text{-III}$ coexist. We make a rough estimate for it on the basis of the empirical observation that the absorption of a H atom into a rare-earth metal lattice induces $4 \pm 0.5 \text{ \AA}^3$ atomic volume expansion ΔV in the host metal lattice at ambient pressure. At high pressures, the anticipated volume expansion should be less than that at ambient pressure. Assuming that the volume expansion results only from the absorption of hydrogen atoms, the increase Δx in hydrogen composition in the $\text{II} \rightarrow \text{III}$ transition can be estimated to be at least 0.2.

We investigated the valence states of EuH_x/H_2 by synchrotron Mössbauer spectroscopy measurements. Figure 3 shows the typical Mössbauer spectra of EuH_x at 2.7 and 14.3 GPa. The velocity scale was calibrated relative to the single line of EuF_3 at ambient pressure. The isomer shift at 2.7 GPa, where the sample is in the $\text{EuH}_x\text{-I}$ phase, was -10.50 mm/s relative to $\text{Eu}^{3+}:\text{EuF}_3$, indicating the divalent state. At 14.3 GPa, the isomer shift changed to 0.71 mm/s , showing that $\text{EuH}_x\text{-IV}$ was in the trivalent state. This is clear

evidence for the hydrogen-induced valence transition of EuH_x .

We compare the $\text{EuH}_x\text{-IV}$ phase with other rare-earth metal hydrides. The fcc structure is a bct structure whose c/a ratio is $\sqrt{2}$. $\text{EuH}_x\text{-IV}$ with $c/a = 1.425$ is a slight (0.8%) distortion of fcc. Because of its trivalent character and the small distortion from the fcc structure, $\text{EuH}_x\text{-IV}$ corresponds to the β phase observed commonly for other RH_x . This is the first observation of the β phase and the trivalent state for EuH_x . Henceforth, EuH_x is no longer an irregular member of the rare-earth metal hydride family.

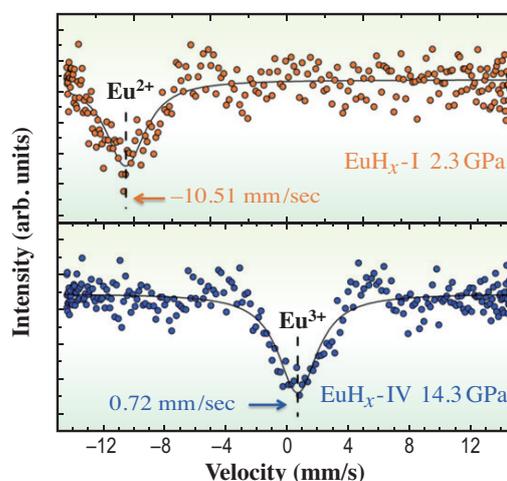


Fig. 3. High-pressure Eu-Mössbauer spectra of $\text{EuH}_x\text{-I}$ at 2.3 GPa and $\text{EuH}_x\text{-IV}$ at 14.3 GPa. Solid lines show the fit of the experimental data. The velocity scale was calibrated relative to the center of a single line of EuF_3 under ambient conditions. [1]

Takahiro Matsuoka* and Katsuya Shimizu

KYOKUGEN, Center for Quantum Science and Technology, Osaka University

*E-mail: matsuoka@cqst.osaka-u.ac.jp

References

- [1] T. Matsuoka, H. Fujihisa, N. Hirao, Y. Ohishi, T. Mitsui, R. Masuda, M. Seto, Y. Yoda, K. Shimizu, A. Machida and K. Aoki: *Phys. Rev. Lett.* **107** (2011) 025501.
- [2] P. Vajda, in Handbook on the Physics and Chemistry of Rare Earths, ed. by K.A. Gschneidner and L. Eyring (Elsevier Science B.V, Amsterdam **20** (1995) 207.
- [3] M. Tkacz and T. Palasyuk: *J. Alloys Compd.* **446-447** (2007) 593.
- [4] H. Sugimoto and Y. Fukai: *Acta Metall.* **40** (1992) 2327.
- [5] K. Takemura and K. Syassen: *J. Phys. F Met. Phys.* **15** (1985) 543.