Raman and optical absorption studies of rare-earth hydrides under high pressure

T. Kume$^1$, H. Ohura$^1$, T. Takeichi$^1$, S. Sasaki$^1$, H. Shimizu$^1$, A. Ohmura$^2$, A. Machida$^2$, T. Watanuki$^2$, K. Aoki$^2$, and K. Takemura$^3$

$^1$Department of Materials Science and Technology, Gifu University, 1-1 Yanagido, Gifu, 501-1193, Japan
$^2$Synchrotron Radiation Research Center, Japan Atomic Energy Agency, Hyogo 679-5148, Japan
$^3$Advanced Materials Laboratory, National Institute for Materials Science, Tsukuba 305-0044, Japan

E-mail: kume@gifu-u.ac.jp

Abstract. Raman and visible absorption study were performed for $\text{YH}_3$ and $\text{ScH}_3$ at high pressures, in order to clarify the structural and electronic phase transitions. The Raman results of $\text{YH}_3$ revealed the presence of an intermediate phase at 9-24 GPa between the low-pressure hexagonal and high-pressure fcc phases. The characteristic behaviour was commonly observed for vibrational properties of $\text{YH}_3$ and $\text{ScH}_3$, suggesting a common mechanism of the structural transformation. The results of the absorption measurements for $\text{YH}_3$ demonstrate that the optical band gap starts to close in response to the phase transition.

1. Introduction

In 1996, Huiberts et al.[1] have discovered switchable properties of yttrium and some other rare-earth films driven by those hydrogenations. The reversible change between the metal ($\text{YH}_2$) and insulator ($\text{YH}_3$) demonstrated potential applications as switchable mirror. The hydrogenation causes also a structural transformation from the fcc $\text{YH}_2$ to the hcp $\text{YH}_3$. The hexagonal structure of $\text{YH}_3$ and $\text{ScH}_3$ is shown in figure 1, in which the metal atoms only are displayed. The H atoms are intercalated into the two interstitial sites, i.e., octahedron (O) and tetrahedron (T) sites of the hexagonal close packed (hcp) structure. The arrangement of the interstitial spaces for O site is shown with octahedrons in figure 1. Since there are one O site and two T sites per one metal atom, the hydrogen occupies all of the interstitial sites in the case of the trihydrates. For $\text{YH}_3$ and $\text{ScH}_3$, the hydrogen atoms in O site ($\text{H}_o$) are not centered at the octahedrons but displaced near the metal basal plane. The $\text{H}_o$ atoms are believed to be displaced without ordering in the case of Sc[2] and with long-range order in the case of Y[3]. The crystal symmetries are explained with $P6_3/mmc$ for Sc trihydride and $P6_3cm$ (or $P6_3$) for Y trihydride. The dihydrides ($\text{YH}_2$ and $\text{SeH}_3$) take the face centered cubic (fcc) structure, in which the hydrogen occupies only the T sites.

Recently, several authors have reported the electronic and structural properties of rare-earth hydrides under high pressure. The energy gap closure of $\text{YH}_3$ was investigated by two research
group[4,5], but the critical pressure is controversial; visible transmission measurements [4] predicted the band gap to be closed at 55 GPa, while the recent IR experiments[5] suggested the gap closure to be at 23-25 GPa from the abrupt drop in the transmittance. Also for the structural change of YH$_3$, which sluggishly proceeds from the hexagonal to the fcc structure over a large pressure span ranging from 10 to 20 GPa[6,7], there are two interpretations. The x-ray diffraction data obtained around 10-20 GPa were interpreted with (1) the coexistence of the hexagonal and fcc structures[6] or (2) a new structure [7] that is not explained by intermediate structures for pure Y observed during the hcp-fcc phase transition. In the case of the Sc hydride, a recent x-ray diffraction experiments suggest that the intermediate phase exists around 30-40 GPa in between the low pressure hexagonal phase and high pressure fcc phase[8].

In this work, we investigate vibrational and optical properties of YH$_3$ and ScH$_3$ under high pressure in order to gain an insight into the structural transformation from the hexagonal to the fcc phase, and the gap closure. For YH$_3$, the characteristic Raman spectra demonstrate the existence of the intermediate phase around 9-25 GPa and the analyses of the optical absorption spectra suggest the gap closure to be around 23 GPa. The characteristic vibrational behaviour precursor to the phase transition are commonly observed for YH$_3$ and ScH$_3$, suggesting a common mechanism of the phase transformation.

2. Experimental
The high-pressure experiments were carried out using a diamond anvil cell (DAC) with a culet of 0.3 mm in diameter. A hole of 0.1 mm in diameter drilled on a pre-indented tungsten gasket of about 0.03 mm thickness served as the sample chamber. The metal hydride (YH$_x$ or ScH$_x$) surrounded with hydrogen was prepared in DAC with the same manner as described elsewhere[7]. Raman spectra were measured at room temperature in a backscattering geometry with a triple polychromator (JASCO NR 1800) equipped with a charge coupled device detector. Radiation of 532 nm from a solid-state laser (Coherent Verdi2W) was incident with a power of 5 mW. The measured Raman spectra contain the signals from H$_2$. Therefore, we extracted the spectra of the sample by subtracting the H$_2$ spectrum multiplied by an appropriate factor so as to cancel out the H$_2$ signals. The optical absorption spectra in visible region were measured with an apparatus established elsewhere[9]. Pressure was calibrated with the ruby fluorescence.

3. Results and discussion

3.1. Raman spectra of hexagonal YH$_3$ and ScH$_3$
Figures 2 (a) and (b) show high-pressure Raman spectra of YH$_3$ and ScH$_3$, respectively. In figure 2(a), the spectrum of YH$_3$ for $P = 0$ GPa was measured after attaining the maximum pressure (37 GPa). The shape of the spectrum is the same as the previous Raman spectra [10]. For higher frequency vibrations, the Raman peaks were assigned with the aid of the previous assignments which have been carried out for the vibrational DOS[11]. The notation of O$_v$ (T$_h$) in figure 2 means that the hydrogen of O (T) site vibrates vertically (horizontally) to the $ab$ plane in the hexagonal structure. Although the direct comparison of DOS and Raman spectrum is not appropriate, the assignments can be applied for the
spectra of (a) YH

Figure 2. Pressure dependence of Raman frequencies of (a) YH and (b) ScH.

because the spectra at 9-11 GPa can be reproduced with a combination between the spectra of the hexagonal (P < 8 GPa) and the intermediate phases (11 < P < 25 GPa). At 25 GPa, the H related bands disappear, which can be explained by the transformation to the fcc phase.

Figure 2(b) shows the Raman results of Sc hydride. According to the recent high-pressure x-ray diffraction experiments [8] performed for the Sc surrounded with H2 using DAC, the specimen at about 1 GPa is composed of Sc, ScH2, and ScH3. The hydrogenation of Sc proceeds gradually with increasing pressure and the amount of ScH3 gradually increases with pressure. The present Raman spectra come from only the ScH3 because the cubic ScH2 is expected to show one hydrogen mode around 1000 cm⁻¹ and the metal Sc shows a peak around 130 cm⁻¹. As pressure increases, the Raman spectrum gradually changes. Taking into account the recent XRD experiments in which the transformation of the hexagonal ScH3 to an intermediate phase was observed around 30 GPa, we can see the disappearances of hydrogen related peaks (Ov, T6s, and T1) correspond to the phase transition to the intermediate phase.

In Figs. 3 (a) and (b), we plotted the pressure dependence of Raman frequencies of YH and ScH3, respectively. To identify the correspondence of the vibrational modes between YH and ScH3, the frequency axis for the low-frequency vibrations and the pressure axis are drawn with different scales. We note that the vibrational properties of ScH3 are similar to those of YH3, in particular for hydrogen vibrations. For example, the negative frequency shifts against the pressure are commonly observed for present case because the phonon dispersion curves were theoretically predicted to be flat and to be well separated to each other[11].

As seen in figure 2 (a), the spectra obtained below 8 GPa are essentially the same as the spectrum at 1 atm. In the pressure region of 9-24 GPa, several new Raman peaks are found in the low frequencies. For example, the Y related peaks at 200 cm⁻¹ cannot be explained with the coexistence of the hexagonal and cubic phases, demonstrating that there exists the new intermediate phase. The intermediate phase appears from 9 GPa because the peaks disappear, which can be explained by the transformation to the fcc phase.

Figure 3. Pressure dependence of Raman frequencies of (a) YH3 and (b) ScH3 obtained upon compression.
the O\textsubscript{v} modes (around 500 cm\textsuperscript{-1}). The common behaviors precursory to the phase transition imply a common mechanism of the transformation from the hexagonal to the intermediate phase.

3.2. Optical absorption of YH\textsubscript{3} under high pressure

Figure 4 indicates the results of optical transmission measurements of YH\textsubscript{3}. The experimental spectra are indicated with solid lines. The open circles correspond to the theoretical fitting which was carried out on the basis of the previous analyses\cite{12} under the assumption that the absorption edge is characterized by the indirect allowed transition. The optical gap energy \(E_g\) obtained as a fitting parameter is plotted as a function of pressure in figure 4 (b). The slope change is found at 10 GPa, in association with the transformation to the intermediate phase. The linear extrapolation with the present results predicts \(E_g\) to be zero around 23 GPa, in good consistency with the previous IR experiments\cite{5} in which the abrupt drop of the transmittance was observed around 23-25 GPa in the IR spectral region.

4. Conclusion

We investigated the phase transition of YH\textsubscript{3} and ScH\textsubscript{3} at high pressure by Raman spectroscopy. For the YH\textsubscript{3}, it was demonstrated that the intermediate phase exist in between the hexagonal and fcc phases. The common behaviour of the vibrational properties between YH\textsubscript{3} and ScH\textsubscript{3} suggests strongly that there is a common mechanism for the structural transformation to hexagonal to the intermediate phase. The optical absorption spectra were measured for YH\textsubscript{3} up to 20 GPa. The analyses for the absorption edge under the assumption of the indirect gap predict the gap closure to be complete around 23 GPa.

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References

[1] Huiberts J N et al. 1996 Nature \textbf{380} 231
[2] Antonov V E et al. 2006 Phys. Rev. B \textbf{73} 054107
[3] Fedotov VK et al. 2006 J. Phys.: Condens. Matter \textbf{18} 1593.
[4] Wijngaarden R J et al. 2000 J. Alloys Compd. \textbf{308} 44
[5] Ohmura A et al. 2006 Phys. Rev. B \textbf{73} 104105
[6] Palasyuk T and Tkacz M 2005 Solid State Commun. \textbf{133} 477
[7] Machida A et al. 2006 Solid State Commun. \textbf{138} 436
[8] Ohmura A et al. to be published.
[9] Kume T Fukaya Y Sasaki S, and Shimizu H 2002 Rev. Sci. Instrum. \textbf{73} 2355
[10] Racu A-M and Schoenes J 2006 Phys. Rev. Lett. \textbf{96} 017401
[11] van Gelderen P, Kelly P J, and Brocks G 2003 Phys. Rev. B \textbf{68} 094302
[12] van Gogh A T M \textit{et al} 2001 Phys. Rev. B \textbf{63} 195105

\begin{figure}[h]
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\includegraphics[width=\textwidth]{figure4.png}
\caption{Pressure dependence of (a) absorption spectra and (b) energy gap of YH\textsubscript{3}. In (a), the measured spectra and fitted absorption edges are shown by solid lines and open circles, respectively.}
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