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High-pressure study of YH_3 by Raman and visible absorption spectroscopy

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Raman and visible absorption spectra of YH_3 were measured at high pressures, in order to clarify the structural and electronic phase transitions. The Raman results revealed the presence of an intermediate phase at 9–24 GPa between the low-pressure hexagonal and high-pressure fcc phases. The Y-framework structure and the position of interstitial H atoms are changed on the transition to intermediate phase. The results of the absorption measurements demonstrate that the optical band gap starts to close in response to the phase transition.

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I. INTRODUCTION

In 1996, Huiberts *et al.*[1] have discovered reversible optical properties of yttrium and some other rare-earth films driven by those hydrogenations. The reversible change in YH_x between a metal (YH_2) and an insulator (YH_3) (Refs. 1–4) demonstrated potential applications as switchable mirror. The hydrogenation causes also a structural transformation from the fcc YH_2 with *ABCA* stacking sequence for the metal planes to the hcp YH_3 with *ABA* stacking sequence. In these structures, there are two interstitial sites, the tetrahedron (T) and octahedron (O) sites, for accommodation of hydrogen atoms. The hydrogen atoms occupy only the T site for YH_2, while occupy the T and O sites for YH_3. For YH_3, a structure with space group $P6_3cm$ or $P6_3$, in which H atoms on the O site (H_O) are located near the metal Y plane,[6–8] has been proposed to be consistent with experimental results of neutron diffraction,[7,8] Raman scattering,[10–14] neutron scattering,[9] and NMR.[15]

The first theoretical approach to explain the band gap opening due to hydrogenation has been done by Kelly *et al.*,[5] who predicted that the off-centering of hydrogen in the interstitial space is important for the gap opening, by an LDA calculation. However, from a fact that the YH_3 stabilized by MgH_2 retains the fcc structure in the insulating phase,[16] the gap opening is believed to be of electronic origin rather than the structural origin. Several groups[17,18] have explained the gap opening in YH_3 and LaH_3 using the strong correlation models in which the hydride is viewed as an H^- lattice embedded in the metal lattice. The model proposed by Eder *et al.* predicted a gap of roughly 2 eV for YH_3.[18] This strong correlation was indirectly supported by the recent Raman results forYH_3 by Racu and Schoenes,[14] who investigated the band width of the breathing modes of Y as a function of temperature. The band broadening sensitive to temperature was interpreted with a coupling between the breathing mode and electrons excited from H vacancy levels into 4*d* conduction band of Y.

The electronic properties and crystal structure of rare-earth hydrides can be changed by the pressurization as well as the hydrogenation. At very high pressure, the rare-earth trihydrides are expected to undergo the insulator-metal transition in association with the gap closure, which is much of interest in the sense of 1s metal realized by metallization of the hydrogen sublattice. The gap closure of YH_3 has already been studied, but the critical pressure is controversial; visible transmission measurements[19] predicted the band gap to be closed at 55 GPa, while the recent IR experiments[20] to be at 23–26 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,[21,22] 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[21] or (2) a new structure[22] that is not explained by intermediate structures observed for pure Y showing the hcp-fcc phase transition. In any case, the phase transition of YH_3 is different from that for the pure Y, which suggests that the interstitial hydrogen plays an important role for the phase transition.

In this paper, we present a high-pressure Raman and visible absorption study which was carried out for YH_3 at room temperature up to 40 GPa to clarify the phase transition and insulator-metal transition. The vibrational spectra related with Y and H are clearly measured up to 37 GPa. The Raman spectra obtained at 9–24 GPa give evidence that there is a new phase intermediate between the hexagonal and fcc phases. The results of the absorption measurements indicate that the band gap starts to close on transition from the hexagonal to the intermediate phase. The gap closure is predicted to be complete in the fcc phase.

II. 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 preindented tungsten gasket of about 0.03 mm thickness served as the sample chamber. The yttrium hydride surrounded with hydrogen was prepared in DAC with the same manner as de-

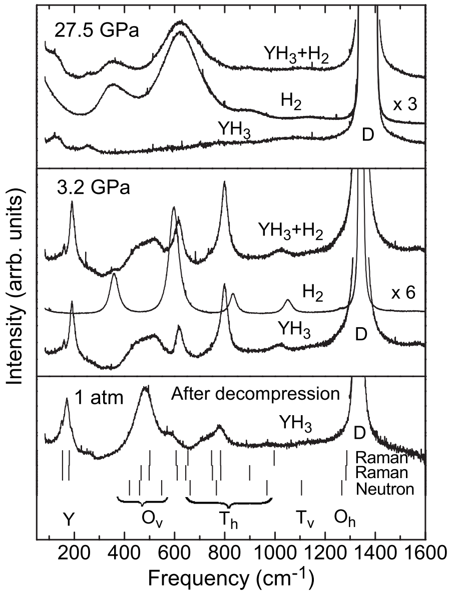

FIG. 1. Raman spectra of the sample (YH_3) and pressure medium (H_2). The top and middle panels show the examples of the extraction of Raman signals of YH_3. The bottom panel shows the Raman spectrum of YH_3 after releasing pressure to 1 atm. The previous Raman (Refs. 10 and 12) and neutron (Ref. 9) data and the assignments are also indicated. The strong signal around 1330 cm^{-1} corresponds to the signal from diamond anvil.

scribed elsewhere.[20,23] The yttrium trihydride contains vacancies at ambient condition, and then usually is represented with $YH_{3-\delta}$. It has been reported that the stoichiometric YH_3 is reached above 4 GPa when surrounded with H_2 (Ref. 19). In this paper, the yttrium trihydride is denoted as YH_3 for simplicity. 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 YH_3 by subtracting the H_2 spectrum multiplied by an appropriate factor so as to cancel out the H_2 signals (see the top and middle panels of Fig. 1). The optical absorption spectra in visible region were measured with an apparatus established elsewhere.[24] Pressure was calibrated with the ruby fluorescence.

III. RESULTS AND DISCUSSION

The bottom panel of Fig. 1 shows the Raman spectrum of YH_3 at 1 atm, measured after the high-pressure experiments to 37 GPa, together with Raman[10,12] and neutron[9] frequencies reported previously. The shape of the spectrum is the same as the previous ones.[10–14] The two peaks located below 200 cm^{-1} have been assigned to Y vibrations,[10] of which the higher frequency band is a breathing A_1 mode.[14] The H related vibrations can be assigned by following the previous assignments for phonon DOS obtained by the neutron scattering,[9] as indicated in Fig. 1. The notation of O_v (T_h), for example, means that the hydrogen of O (T) site vibrates vertically (horizontally) to the *ab* plane. In general, the direct comparison of DOS and Raman spectrum is not appropriate. Since, however, phonon dispersion curves of hydrogen modes were theoretically predicted to be flat and to be well separated to each other,[6] the assignments can be applied to Raman peaks. Although it is still difficult to assign the 600 cm^{-1} mode, we can consider this mode as the O_v mode because the Grüneisen parameter (the volume dependence of the frequency), which is indicated later, was small (0.56) compared with T modes (0.99, 0.72), as expected by considering the volume of the octahedron larger than the tetrahedron.

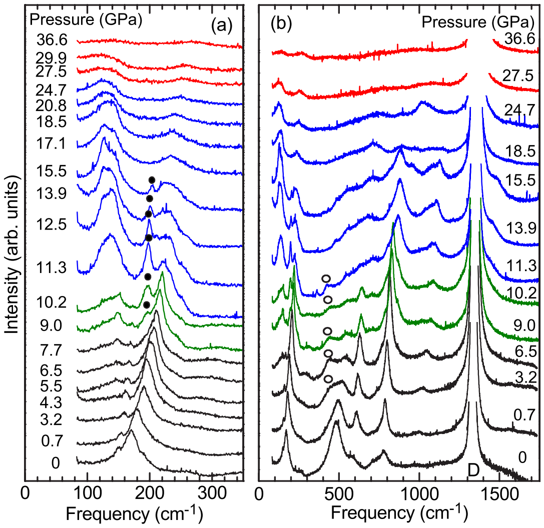

FIG. 2. (Color online) Pressure dependence of Raman spectra of YH_3. (a) and (b) correspond to the regions expanded in low frequencies (0–350 cm^{-1}) and covering whole of spectra (0–1750 cm^{-1}), respectively. The spectrum of 1 atm (0 GPa) was obtained after the high pressure experiments. The spectra characteristics of the hexagonal, intermediate and fcc phases were observed at $P<8$ GPa, 11 GPa$<P<$25 GPa, and 25 GPa$<P$, respectively. The spectra at 9 GPa$<P<$11 GPa can be explained by the coexistence of hexagonal and intermediate phases. For closed and open circles, see text. The strong signal around 1330 cm^{-1} corresponds to the signal from diamond anvil.

Figure 2 shows Raman spectra measured on compression process up to 37 GPa. The peak frequencies are plotted as a function of pressure in Fig. 3. The mode Grüneisen parameters (γ_i) (Ref. 26) obtained for the hexagonal YH_3 are indicated in Fig. 3. As seen in Fig. 2, the spectra obtained below 8 GPa are essentially the same as the spectrum at 1 atm. In this pressure range, the sample includes a small amount of fcc YH_2 (Ref. 22), which shows only one H band at 1142 cm^{-1} at 1 atm.[13] However, we did not observe the Raman signal from the YH_2.

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} [solid circles in Fig. 2(a)] 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 spectra at 9–11 GPa can be reproduced with a combination between the spectra of the hexagonal ($P<8$ GPa) and

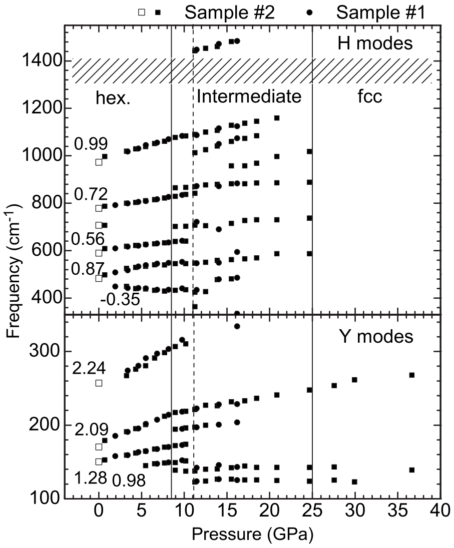

FIG. 3. Pressure dependence of Raman frequencies of YH_3 obtained upon compression. The results obtained for two different samples are indicated. The data of 1 atm shown by open squares were obtained after releasing the pressure. For the hexagonal phase, the mode Grüneisen parameters are shown in this figure. The region between the two solid lines corresponds to the intermediate phase. At pressure drawn by dashed line, the drastic spectral change was observed. The hatched area corresponds to the strong diamond signals.

the intermediate phases ($11 < P < 25$ GPa). The previous high-pressure IR experiments[20] did not identify the intermediate phase. As shown in Fig. 2, the spectra peculiar to the intermediate phase appear favorably in the Y vibrations. Since, however, the previous IR measurements did not cover the Y vibrations, it was difficult to make definitive arguments for the intermediate phase. We emphasize now the existence of the intermediate phase by means of the Raman spectroscopy. Very recently, Palasyuk *et al.*[25] have measured Raman spectra of YH_3 at high pressures up to 16 GPa. However, the Raman bands were measured in a region from 300 to 1200 cm^{-1}, corresponding to the hydrogen vibrations. Although the Raman spectral evolution of the hydrogen modes is almost the same as our results, the limitation on the spectral range and pressure range did not allow them to claim the existence of the intermediate phase.

At 25 GPa, the H related bands disappear. Taking account of the previous XRD results that the transition to the fcc phase is complete above 20 GPa,[22] we see that the present spectral changes at 25 GPa correspond to the transition to the fcc phase. The factor group analysis[13] predicted that the fcc-YH_3 has no Raman active Y mode, but one H mode which is the same mode as observed for the fcc-YH_2 at 1142 cm^{-1} under the ambient condition. Taking account of the pressure induced shift, the H band of the high-pressure fcc YH_3 will be observed around 1200 cm^{-1}, but is not detected in the present results owing to the strong diamond signal. It should be noted here that two Y bands are weakly observed above 25 GPa. This can be considered to arise from local distortions being not clearly observed by XRD measurements. Even if a vibrational mode is predicted to be Raman inactive from the symmetry of the average crystal structure, the local distortion can allow the mode being observed as a weak band. The present Raman bands can be explained with the above argument. The two Y bands of the fcc YH_3 phase are reminiscent of $YH_{2+\delta}$ (Ref. 13) and Mg stabilized YH_3,[13] in which the Y related bands are observed by a lowering of the symmetry from the fcc. For clarifying the crystal structure of the high pressure YH_3 phase, careful x-ray experiments are highly required. Unfortunately, it is difficult to definitively determine the transition pressure to the fcc phase because the Y bands remain even in the fcc phase. Since, however, the most Raman bands disappeared around 25 GPa, we believe that the transition from the intermediate phase to the fcc phase is complete around 25 GPa.

We now discuss the crystal structure and vibrational properties of the intermediate phase, on the basis of the case of the pure Y which shows sequential transition hcp → Sm-type → dhcp→ fcc under high pressure.[27] The hcp Y ($P6_3/mmc$) possesses one Raman active shear mode with E_g symmetry, in which each hexagonal plane is vibrating perpendicular to the *c* axis.[28] This type of vibrational mode is less sensitive to the pressure. In the Sm-type structure with *ABABCBCAC* stacking, the two shear modes appear at lower frequencies than that in the hcp phase. The appearance of the lower frequency modes can be explained by the long stacking periodicity for the Sm-type structure, which folds the phonon branch of [001] direction for hcp structure. For the hexagonal YH_3, the Y band at 140 cm^{-1} with *E* symmetry[14] is understood as the shear mode because the frequency is less sensitive to the pressure. For the intermediate phase, the new strong bands at 130 cm^{-1} can be interpreted with the shear modes. Since the frequencies are lower than that for the hexagonal phase similarly to the case of Y, some complicated stacking sequences such as the Sm type are suggested. However, the recent paper[22] has ruled out the Sm-type and dhcp structures as the intermediate structure. It should be noted here that, in the intermediate region (11–25 GPa), the Raman spectral feature is successively altered; the intensities of two Y signals at 130 cm^{-1} relatively change around 14 GPa, the peak indicated with solid circle disappears at 17 GPa, and the H related spectrum (700 ~ 1200 cm^{-1}) shows drastic change at 17 GPa. These spectral changes suggest successive changes in the stacking sequence.

On the transition to the intermediate phase (~10 GPa), we should note that the vibrational bands of the H_O atoms [400–600 cm^{-1} in Fig. 2(b)] disappear or become weak. Since, if the H_O atoms are centered in the octahedron, neither fcc nor hcp structures shows Raman active H_O vibration, the disappearance of O_v band can be interpreted with displacement of H_O atoms toward the center of the octahedron. A softening behavior of O_v band [open circles in Fig. 2(b)] is possibly precursor of the centering of H_O atom. Simultaneous occurrence of the movement of H_O atoms and the stacking change of Y planes implies that the removing of H_O atoms from Y plane triggers sliding of Y planes.

Next, we discuss the vibrational properties in the hexagonal phase. As noted in Fig. 2, the peak of the Y breathing mode [170 cm^{-1} at 1 atm (Ref. 14)] becomes narrower with increasing pressure. The width of this mode originates from the decay of phonon via the interaction with electrons ex-

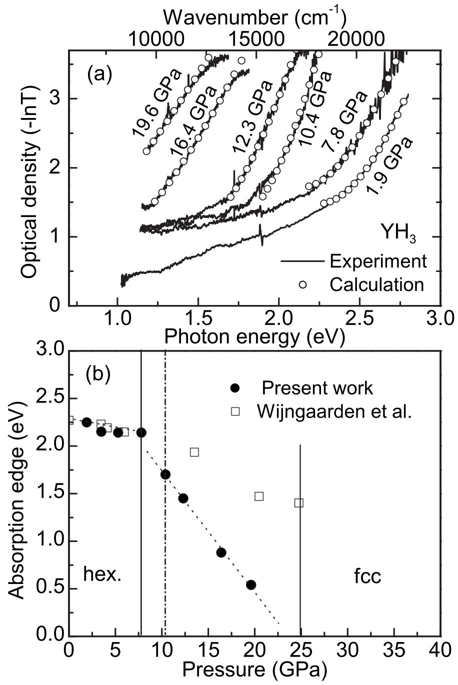

FIG. 4. Pressure dependence of (a) absorption spectra and (b) energy gap of YH_3. In (a), the measured spectra and fitted absorption edges are shown by solid lines and open circles, respectively. In (b), the optical gap energies obtained by fitting the data (see text) are plotted. The solid circles and open squares correspond to the present and previous (Ref. 19) results, respectively. The region between the solid lines corresponds to the intermediate phase.

cited from the donor level that is induced by the presence of vacancies.[14] Therefore, the unexpected narrowing can be understood as the diminishment of the decay path, resulting from the reduction of the vacancies. Peak fitting analyses indicated the decrease in the peak width from 32 cm^{-1} at 1 atm to 24 cm^{-1} at 4.3 GPa. Since the width was almost constant from 4.3 to 7.7 GPa, the YH_3 without vacancies is likely to be achieved around 4 GPa, as reported in Ref. 19. This breathing mode, for which Y vibrates around the H_O atom[14] (170 cm^{-1} at 1 atm), shows the large value of $\gamma=2.09$ (Fig. 3). It should be noted that there is another Y mode (260 cm^{-1} at 1 atm) with the larger value of $\gamma=2.24$. This volume-sensitive mode can be interpreted with the other Y breathing mode around the H_T atom.

Figure 4 indicates the results of the optical transmission measurements. In Fig. 4(a), the absorption spectra $[-\ln(T)]$ experimentally obtained for various pressures are indicated with solid lines. The absorption edge is found to shift to lower energies as pressure increases. According to the previous paper,[3] the absorption edge of the hexagonal YH_3 has been analyzed using the following forms for $\alpha(\omega)$ near the optical gap

$$\alpha(\omega) \propto \frac{(\hbar\omega - E_g)^\nu}{\hbar\omega} \tag{1}$$

in which for direct allowed (forbidden) transitions $\nu=1/2$ ($\nu=3/2$) and for indirect allowed (forbidden) transitions $\nu=2$ ($\nu=3$). The actual analyses have been performed using the other forms as

$$\ln T(\omega) = \ln T_0 - C\frac{(\hbar\omega - E_g)^\nu}{\hbar\omega}, \tag{2}$$

where the constants $\ln T_0$, C, and E_g are determined from a fit to the spectra near the absorption edge. In the previous paper,[3] it was possible to fit the data equally with $\nu=3/2$, 2, or 3 and with $2.3<E_g<2.7$ eV for the polycrystalline YH_3 film. On the other hand, for the epitaxial film, the best fit was obtained with the indirect allowed transition ($\nu=2$) and $E_g=2.659$ eV.[3] In the present paper, we also analyzed the absorption edges under the indirect allowed transition regime ($\nu=2$). The fitted absorption curves are presented with open circles in Fig. 4(a). We find that the calculated absorption edge reproduces well the experimental one for all the spectra. Although the band structures are not well known for the high pressure phases above 10 GPa, the agreement of the fitted curve is fairly well. Figure 4(b) shows the pressure dependence of the optical gap E_g obtained as the fitting parameter. We find that the value of E_g starts to decrease more rapidly in response to the transition to the intermediate phase at 10 GPa. As seen in Fig. 4(b), the linear extrapolation with the present results predicts E_g to be zero around 23 GPa.[29] In the recent IR experiments,[20] the abrupt change was observed in the transmittance around 23–25 GPa; the IR light which was well transmitted up to 22 GPa abruptly dropped in intensity in the whole range studied (≤ 0.87 eV). The abrupt change can be explained as follows. From a fact that the absorption edge of the high pressure phase can be explained with the indirect gap, the optical absorption is to be very weak around the absorption edge. Therefore, it is difficult to identify the absorption edge by the IR experiment even if the energy gap is in the IR region. However, once the band gap collapses, the free carrier rapidly increases. Thus, the abrupt drop in the IR transmittance can be considered as a result of the abrupt increase in the free-carrier absorption and/or reflection due to the gap closure.

As described in the Raman results, the hydrogen position in the octahedron site is likely to shift toward the center around 10 GPa. According to the theoretical prediction by Kelly *et al.*,[5] the band gap of YH_3 is highly sensitive to the position of hydrogen. Since, however, the present pressure dependence of E_g shows a small jump around 10 GPa, the energy gap is likely to be less sensitive to the position of the hydrogen. In the Raman results, the narrowing of the Y breathing mode against pressure seems to be compatible with the previous interpretation based on the strong correlation model for the temperature dependence of the Y band width.[14] To understand the present behavior of E_g of YH_3, it may be needed to adopt the strong correlation model proposed by Ng *et al.*[17] and Eder *et al.*,[18] who regarded YH_3 or LaH_3 as Kondo insulators with large band gap. However, it is difficult to discuss the drastic change in E_g in the intermediate phase because the structure is not determined. To fully understand the pressure-induced insulator to metal transition of YH_3, the more detailed structural information is much important as well as the theoretical investigation.

IV. SUMMARY

We observed the Raman spectra peculiar to the new phase intermediate between the low-pressure hexagonal and high-pressure fcc phase. The phase transition to the intermediate phase results from the simultaneous occurrence of the change in the stacking of the metal Y plane from *ABA* to a longer period sequence and the displacement of H_O atom toward the center of the Y octahedron. From the visible absorption measurements, it turned out that the band gap in the intermediate phase narrows more rapidly with increasing pressure than in the hexagonal phase. The analyses for the absorption edge under the assumption of the indirect gap predicts the gap closure to be complete around 23 GPa, in good consistency with the previous IR experiments.[20]

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[29] The present gap energy is lower than that in the previous paper (Ref. 19). This disagreement seems to arise from the sample thickness; the previous sample was 0.5 μm thick, in contrast to the present sample of 2 μm. We believe that the thicker sample provides the more accurate results because the more steeply rising feature is obtained in the absorption edge.