Infrared spectroscopic study of the band-gap closure in YH$_3$ at high pressure

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Infrared vibrational absorption spectra are measured for yttrium trihydride at room temperature and pressures up to 30 GPa. The spectral change that begins near 12 GPa is interpreted in terms of a hcp-fcc structural transition, which agrees with previous x-ray diffraction measurements. For the hydrogen vibrations in the low-pressure hcp phase, the mode Grüneisen parameters are derived from the observed peak frequency shifts with pressure and the reported bulk modulus. The value of 1.91 for the octahedral-site vibration is three times larger than those for the tetrahedral-site vibrations, suggesting hybridization between the hydrogen 1s and yttrium 4d orbitals at the octahedral site. The infrared transmission spectra collapse when the high-pressure fcc phase is compressed beyond 23 GPa. The band gap abruptly closes without a structural change in the fcc metal lattice. The experimental results are in contrast to the previous theoretical calculations predicting the electronic transition either with hcp-fcc structural change or in the hcp low-pressure phase without structural change. The transition mechanism is still inconclusive.

I. INTRODUCTION

Hydrogenation causes yttrium (Y) to exhibit a metal-insulator transition. Yttrium hydride YH$_x$ gradually becomes transparent in the visible light region as the hydrogen concentration x increases from 2 to 3. The shiny mirror switches to a yellow, transparent window.[1–3] A structural change from a face-centered-cubic (fcc) to a hexagonal-close-packed (hcp) lattice accompanies the transition. Both the fcc and hcp lattices have two tetrahedral (T) and one octahedral (O) sites per metal atom. The first two hydrogen atoms selectively occupy the T sites of the fcc lattice to form a CaF$_2$ type structure (space group $Fm\bar{3}m$) and then the third one enters into the remaining O sites, which accompanies a structural change into the hcp lattice with a HoD$_3$ type structure (space group $P\bar{3}c1$) and a band gap opening of $\sim$1.8 eV, YH$_3$.[4,5] Lanthanum hydride LaH$_x$ also undergoes a transition from a metal to an insulator at a hydrogen concentration $2 \leqslant x \leqslant 3$. However, the metal-insulator transition proceeds through a fcc structure without the transition into a hcp structure.[1,3,6] A large band gap around $\sim$2 eV is a characteristic feature of rare-earth metal hydrides. Most other metal hydrides such as TiH$_x$ and VH$_x$ remain metallic over the entire hydrogen concentration.

The electronic states of rare-earth metal hydrides have been theoretically investigated. A band structure calculation provides a simplified picture of the hydrogen-metal bonds. The dihydride MH$_2$ is rather an ioniclike compound with negatively charged hydrogen atoms at the T sites, while in the trihydride MH$_3$ the hydrogen atoms that occupy the O sites form s(hydrogen)-d(metal) hybridization.[7] For YH$_3$ and LaH$_3$, three distinct theoretical models have been proposed to explain the origin of the large band gaps produced by hydrogenation. The first is essentially a band model where the *self-energy* correlation is properly evaluated to open a

gap in both hcp and fcc trihydrides.[8–12] The second is the symmetry-breaking model proposed specifically for hcp YH$_3$, which demonstrates a gap opening by introducing symmetry-lowering displacement in the hydrogen and metal positions.[13] These models achieve the band gap opening, but do not reproduce the large band gap compared to the experimentally determined value. The third is a strong electron correlation model[14,15] where the hydrogen 1s band is calculated for an H$^-$ ion sublattice embedded in the fcc metal lattice. A band gap of 1.5–2.1 eV is obtained, which is consistent with the experiments. The H$^-$ sublattice assumes an ionized hydrogen atom even at the O site. This conflicts with the band models that show s-d hybridization rather than ionic interactions. The mechanism of the metal-insulator transition by hydrogenation is even less understood.

High-pressure experiments are effective tools for investigating the hydrogen-metal bonding nature in rare-earth metal hydrides. The optical gap and crystal structure measured over a wide pressure span should aid in the understanding of hydrogen-metal bonds, for which theoretical studies predict site-dependent behavior. At sufficiently high pressures, an insulator-metal transition is expected to occur in association with the band gap closure. The metallic phase of rare-earth trihydrides can be characterized as a 1s metal since the hydrogen 1s electron partially occupies the Fermi level state. Experimental investigations on YH$_3$ have been conducted by optical transmission and x-ray diffraction measurements at pressures up to 25 GPa. A 1.4 eV optical gap still existed at 25 GPa and was extrapolated to be zero near 55 GPa.[16] The hcp structure transformed into the fcc structure above 8 GPa;[17,18] this contradicts the theoretical results, which predicted an insulator-metal transition in the hcp phase[13] or with a hcp-fcc structural change.[9]

We measured the infrared vibrational and transmission spectra for YH$_3$ at pressures up to 30 GPa. The optical transparency of insulating YH$_3$ allows the vibrational and elec-

tronic states to be measured using conventional infrared spectroscopy, which is advantageous for investigating the hydrogen-metal bonding state under pressure. Infrared spectroscopy may also be beneficial for observing band gap closure or metallization, which is expected to occur at higher pressures. Previous optical absorption measurements revealed that the optical gap of YH_3 already moved from the visible region.[16] Hence, near-infrared or infrared measurements are required to further explore the band gap closure.

II. EXPERIMENT AND RESULTS

We used a diamond anvil cell (DAC) to prepare YH_3 and to measure the infrared spectra at high pressure. A sample chamber was constructed by drilling a small hole in a tungsten sheet previously indented with the opposed diamond anvils. The chamber had a cylindrical shape that was 180 μm in diameter and 64 μm thick. A fragment of yttrium foil (nominal purity 99.9%), which was approximately 80 μm in diameter and a few micrometers thick, was placed in the sample chamber along with tiny ruby balls, which were used as pressure markers. To prevent the metal surface from oxidizing the yttrium foil was handled in a glovebox charged with inert argon gas. The DAC with the sample was then filled with a hydrogen fluid compressed to 180 MPa using a gas loading apparatus.[19]

The metal foil reacted with the surrounding hydrogen fluid to form a YH_3 insulator and upon leaving at 1.1 GPa for a few tens of hours, the sample turned a transparent yellow. Infrared spectra were measured with a microscope Fourier transfer infrared spectrometer with reflecting objectives (magnification 16 and numerical aperture 0.3).[20] The wave number region from 400 to 7000 cm^{-1} was covered with a liquid-nitrogen-cooled infrared detector. Each spectrum was recorded with a spectral resolution of 8 cm^{-1} by collecting the data 800 times. The raw spectra contained the absorption from the diamond anvils, which was eliminated using the reference spectrum of the empty DAC.

The wave number region of 400–7000 cm^{-1} covers the absorptions due to the hydrogen vibrations and the interband electronic excitations. The optical absorption edge should move into the infrared region at pressures above 25 GPa. The entire spectral features are demonstrated with the 5.9 GPa spectrum (Fig. 1). The raw spectrum measured for the sample involved additional extrinsic components due to the diamond absorption and was divided by the reference spectrum to obtain the intrinsic spectral feature of the sample. The absorption peaks, which were located in the low-wave-number region 400–1400 cm^{-1}, were related to the vibrations of the hydrogen atoms that occupy the interstitial sites of the hcp metal lattice. The spectrum also contained absorption peaks that were due to the pressure transmitting medium of the hydrogen solid (hydrogen fluid solidified at 5.3 GPa). The hydrogen peaks were observed up to 22 GPa and hence indicated that the sample was always surrounded by the pressure medium of hydrogen. Several peaks between 4200 and 5000 cm^{-1} were assigned to the stretching vibrations of the hydrogen molecules and their combination bands with rotational or lattice vibrations.[21] The
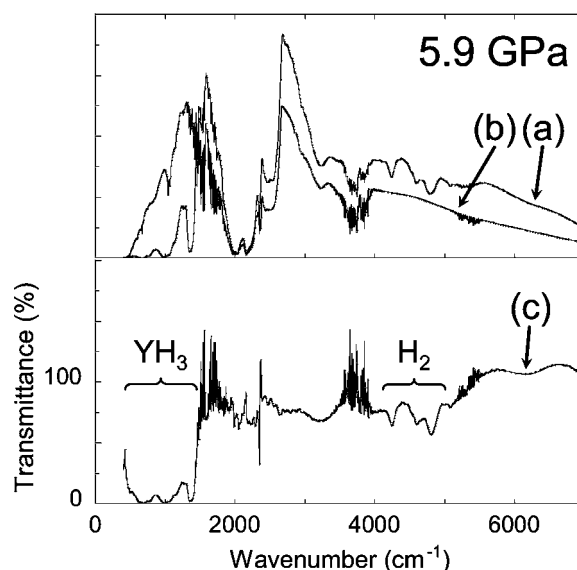

FIG. 1. Transmission spectra measured for (a) the empty DAC at ambient pressure and (b) the DAC containing a yttrium metal flake and solid hydrogen at 5.9 GPa. (c) The spectrum of the sample corrected for the diamond absorption is obtained by dividing spectrum (b) by spectrum (a).

structures around 2200 cm^{-1} were artificial and originated from the incomplete correction for the diamond absorption. The vibrational bands between 1500 and 1800, and 3600 and 3800 cm^{-1} were the molecular vibrations of the water vapor that contaminated the infrared beam path. Electronic absorption was not observed. The estimated optical gap was ~2.14 eV (~17 120 cm^{-1}) at 5.9 GPa,[16] and the corresponding absorption edge was still far from the infrared region.

The hydrogen concentration was estimated from the x-ray diffraction patterns and the measured infrared absorption spectra. The lattice constant vs pressure relationships measured for hcp YH_x by x-ray diffraction gave extrapolated values of 3.671 and 6.624 Å for the hexagonal a and c axes, respectively, at ambient pressure.[18] These values were consistent with the 3.672 and 6.625 Å reported for stoichiometric YH_3.[22] The infrared vibrational spectra measured at 400–1200 cm^{-1} were similar to those of $YH_{2.87}$.[23] It should be noted that the hydrogen concentration became saturated at $x \sim 2.87$ for hydrogenation in a gas pressure of 1 atm and the stoichiometric YH_3 was formed at extremely high pressures of several hundred atmospheres. Thus, a hydride sample prepared in the gigapascal pressure range is considered to have a hydrogen concentration near the stoichiometric value and is hereafter designated YH_3.

Figure 2 shows the vibrational spectra, which are extended to the hydrogen vibrational region, measured at pressures up to 22.6 GPa. As shown in the bottom spectrum taken at 1.1 GPa, three dominant peaks were observed near 630, 940, and 1310 cm^{-1}. The peak locations and heights were consistent with those reported for hcp $YH_{2.87}$ and were assigned to one O-site and two T-site vibrations of hydrogen as the frequency increased.[23,24] Each hydrogen vibrational peak shifted to a higher frequency as the pressure increased up to 12.3 GPa. Further increasing the pressure dramatically
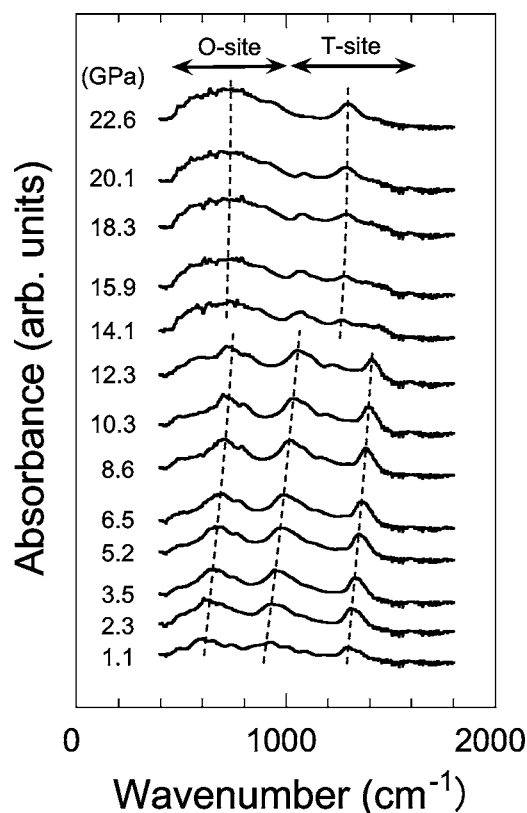
FIG. 2. Infrared vibrational spectra measured for YH_3 at pressures up to 23 GPa. The spectral features gradually change as the pressure increases above 12 GPa, which is where the metal lattice begins to transform from hcp to fcc.
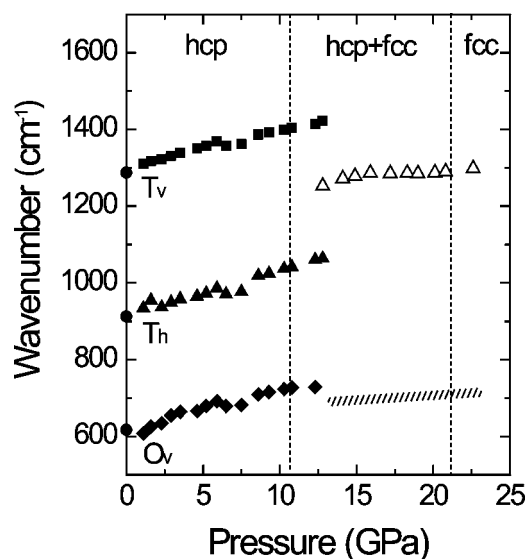

FIG. 3. Variations in the peak frequencies with pressure measured for the infrared-active hydrogen vibrations of YH_3. The frequencies of the dominant peaks in the hcp structure, one O-site, and two T-site modes, are represented with solid symbols. Solid circles represent the frequencies at atmospheric pressure reported in Ref. 23.

changed the spectral features: the vibrational peaks characteristic of the hcp structure gradually disappeared and were replaced by two dominant peaks. X-ray diffraction measurements revealed that a hcp-fcc structural transition sluggishly occurred in YH_3 between 8 and 18 GPa.[17,18] Hence, the spectral changes were attributed to the structural transition. The vibrational spectra of fcc LaH_3 were measured by neutron vibrational spectroscopy, which showed two intense broadened bands: the O-site hydrogen vibration near 530 cm^{-1} and the T-site hydrogen vibrations near 970 cm^{-1}.[25] The peaks of fcc YH_3 near 700 and 1300 cm^{-1} were assigned to the O-site and T-site vibrations, respectively.

The hydrogen vibrations show a site-dependent behavior in the peak shift with pressure. In the hcp phase, the O-site peak shifted to a higher frequency with pressure much faster than the T-site ones, especially in the low-pressure region. This probably reflects the different bonding nature at the two interstitial sites: the ioniclike bonds at the T site and the hybridized bonds at the O site. With the hcp-fcc structural transition, the O-site peak appeared at approximately the same position, but the absorption intensity markedly increased to be saturated around the peak top while the two T-site peaks merged into one peak midway between the original peaks. Both the O-site and the T-site peak positions tended to become insensitive to pressure after the transition into the fcc structure.

Figure 3 plots the peak frequencies as a function of pressure. Each peak frequency monotonically increased with pressure and its rate became slower after the hcp-fcc transition. The peak frequency of the O-site mode of the fcc phase was roughly estimated from the absorption peak, which largely developed in intensity after the transition (see Fig. 2). The peak frequencies of the hcp phase below 12 GPa were fitted to a quadratic pressure (GPa) form to give the following results for the three dominant peaks:

$$\omega(O_v) = (607.0 \pm 5.8) + (15.0 \pm 2.2)P - (0.39 \pm 0.17)P^2, \tag{1}$$

$$\omega(T_h) = (924.1 \pm 6.8) + (7.40 \pm 2.6)P + (0.31 \pm 0.21)P^2, \tag{2}$$

$$\omega(T_v) = (1295.7 \pm 3.7) + (12.2 \pm 1.4)P - (0.22 \pm 0.11)P^2, \tag{3}$$

where O_v, T_h, and T_v in parentheses represent the vibrational motions of the hydrogen atom parallel to the crystalline c axis at the O site, horizontal at the T site, and parallel at the T site, respectively. The mode Grüneisen parameters were also obtained using the bulk modulus B_0 of 77.5 GPa,[18] and the relationship $\gamma_i = B_0/\omega_{i0}(d\omega_i/dP)$,

$$\gamma(O_v) = 1.91 \pm 0.03, \quad \gamma(T_h) = 0.61 \pm 0.01, \tag{4}$$

$$\text{and} \quad \gamma(T_v) = 0.72 \pm 0.01.$$

The obtained parameters showed the site-dependent behavior; the value for the O-site vibration was three times larger than those of the T-site vibrations.
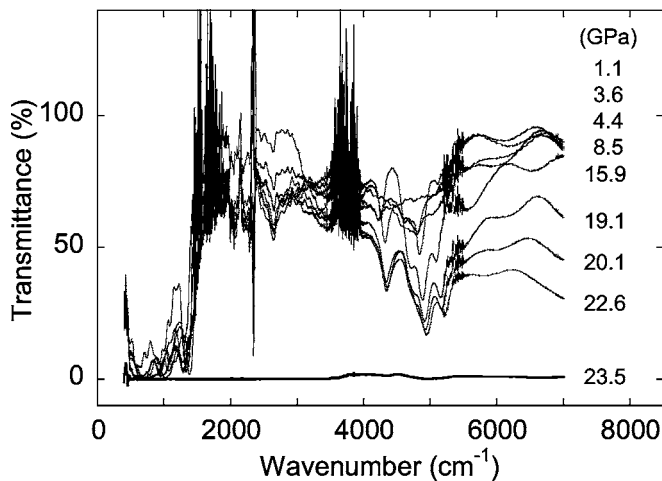
FIG. 4. The infrared transmission spectra measured for the entire wave-number region, 400–7000 cm^{-1}. The transmission spectrum collapses at 23.5 GPa and the sample becomes opaque in the infrared region.

FIG. 5. Pressure variation of transmission intensity at a fixed wavenumber of 2800 cm^{-1}. The transmission intensity abruptly drops to zero near 23 GPa and recovers when the pressure decreases to 16 GPa. The abrupt intensity drop is reproduced near 26 GPa upon the second compression. Solid and dashed lines are to guide the eye.

Figure 4 shows the transmission spectra expanded over the entire infrared region. As previously mentioned, the absorption peaks in the wave-number regions of 400–1200 and 4000–5000 cm^{-1} were due to the hydrogen vibrations of YH_3 and H_2, respectively. The absorption due to the interband electronic excitations was not observed at pressures roughly below 16 GPa. The absorption edge was still outside the high-wave-number limit of 7000 cm^{-1} or 0.87 eV. A spectrum taken at 19.1 GPa indicated that the absorption due to the electronic excitation moved into the infrared region. An absorption tail developed between 4000 and 7000 cm^{-1} and the transmission intensity rapidly decreased as the pressure further increased. The spectrum dramatically changed when the pressure increased from 22.6 to 23.5 GPa. The transmission spectrum abruptly collapsed over the entire infrared region. The optical gap closed. The spectral change was reversible. Releasing the pressure to 16 GPa caused the opaque sample to become transparent. Upon the second compression, the transmission spectrum collapsed again near 26 GPa. A preliminary infrared reflection measurement with a tungsten metal gasket as a reference was collected along with the transmission measurement during the second compression. The reflectivity, which was approximately 30% near 18 GPa, increased to 80% above 24 GPa, suggesting a transition into a metallic state.

The abrupt closing of the band gap is more pronounced in Fig. 5 where the relative transmission intensity at a fixed wave number of 2800 cm^{-1} is plotted as a function of pressure. The transmission intensity remained nearly constant as the pressure was gradually increased from 17.2 to 22.6 GPa and dropped to zero as the pressure was further increased to 23.5 GPa. The transparent sample was recovered when the pressure was decreased to 16 GPa. A rapid drop in intensity was again observed in the second compression at a pressure between 24.4 and 26.9 GPa. The transition pressure slightly shifted to a higher pressure since the sample probably suffered from some degradation during the compression and decompression cycles.
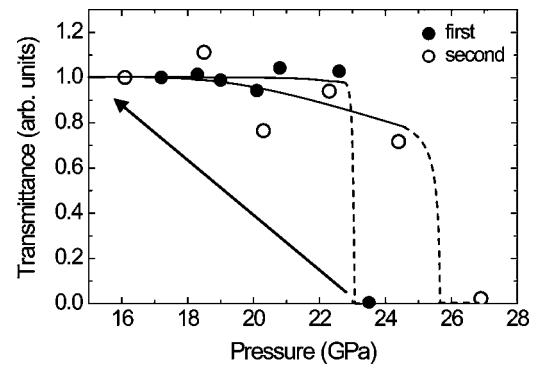
Previous visible absorption measurements showed that the energy gap remained up to 25 GPa,[16] while the present infrared measurements indicated that the gap closure was at 23–26 GPa. This discrepancy is probably explained by the sample conditions. In the visible measurement,[16] the hydride was prepared by evaporating a thin film of yttrium metal, which was 0.5 μm thick, on the top surface of a diamond anvil, and hydrogenating the film with hydrogen fluid under pressure. Thus, the thin film that evaporated on the diamond may suffer from nonhydrostatic stress during compression due to the significant mismatch in the compressibility between the hydride and diamond. However, in the present study the self-standing hydride foil was pressurized in hydrogen fluid/solid under hydrostatic or nearly hydrostatic conditions and probably underwent an insulator-metal transition at slightly lower pressures.

An x-ray diffraction measurement at 29.4 GPa, which is sufficiently above the transition pressure of 23–26 GPa, confirmed that the crystal structure did not change. Figure 6 shows an x-ray diffraction pattern measured with a monochromatized synchrotron radiation light at a wavelength of 0.049 81 nm using the high pressure diffractometer at the BL22XU of SPring-8. The details of the x-ray diffraction experiment are reported elsewhere.[18] The observed reflection peaks were well indexed with a fcc structure, showing that the fcc metal lattice was maintained across the gap-closing pressure. The fcc lattice constant at 29.4 GPa was 4.827 ± 0.004 Å and as displayed in the inset of Fig. 6, was located exactly on the compression line extrapolated from those measured for another YH_3 sample up to 23 GPa.[18] A discontinuous change in volume was not detected within the experimental error, although further measurements are necessary to examine the missing pressure span between 23 and 29 GPa.

III. DISCUSSION

The Grüneisen parameter for the *O*-site vibration is 1.91, which is three times larger than those for the *T*-site vibra-
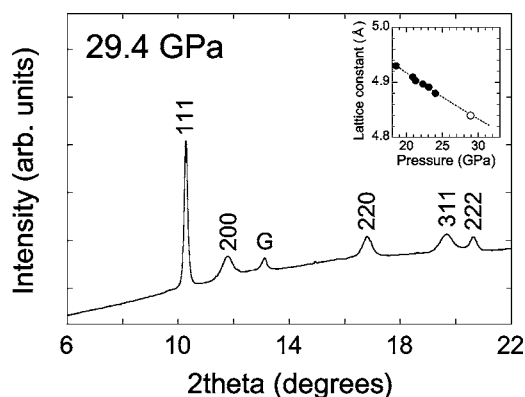
FIG. 6. An x-ray diffraction pattern measured for YH_3 at 29.4 GPa. The reflection peaks are indexed with a fcc metal lattice. G denotes the peak from the metal gasket. The inset shows the variation of the fcc lattice constant measured for another sample reported in Ref. 18 (solid circle) and the present sample (open circle). The lattice constant a at 29.4 GPa is on the compression line $a(P)$, as determined by fitting the data up to 24 GPa, $a(P)=5.128-(1.202\times10^{-2})P+(7.341\times10^{-5})P^2$.

tions, 0.61 and 0.72. The strong site dependence reflects the distinct nature of the hydrogen-metal bonds. According to a band calculation,[7] the hydrogen at the T site likely interacts as an anion with the surrounding metal atoms, whereas hydrogen at the O site forms s-d hybridization with a covalent-like bonding nature. These bonding natures originate from the mixing of the hydrogen $1s$ orbital with the t_{2g} part and the e_g part of the yttrium $4d$ orbitals at the T and O sites, respectively. Experimental data have not been reported for the high-pressure behavior of the hydrogen vibrations in metal hydrides. Thus, we cannot compare the present results for YH_3 to the high-pressure behavior of other metal hydrides. Hence, we compared the obtained mode Grüneisen parameters with those reported for representative covalent and ionic compounds. We determined a value of 1.91 for the O-site vibrations. This value is comparable to those of the optical phonons of III-V compounds such as BN and GaAs, which range from 1.0 to 1.6,[26] while the values of 0.61 and 0.72 for the T-site vibrations are comparable to those obtained for the optical phonons of a LiH ionic compound, 0.37–0.72.[27] The comparison seems very intuitive, but it approximates the result that the character of the hydrogen-metal bonding is consistent with the theoretically proposed pictures.

The hydrogen-metal bonding state of the high-pressure fcc phase can be inferred from the spectral changes, which are associated with the hcp-fcc structural transition. Both the hcp and fcc metal lattices contain two T sites and one O site per one yttrium atom, but their structures can be distinguished from the spatial arrangement of the interstitial sites. For instance, the configuration of the tetrahedral interstitial sites are linked by a face-shared configuration along the c axis in the hcp structure, but in the fcc structure they are linked by an edge-shared configuration along the [111] direction. The doublet-singlet conversion of the T-site vibrational peak in the hcp-fcc transition can be explained by the accompanying rearrangement of the T sites from the face-shared to

the edge-shared configuration. The hydrogen vibrations, which originally split into the doublet peaks in the face-shared configuration of the hcp structure, return to a degenerate singlet peak in the high-symmetry fcc structure. Neutron vibrational spectroscopy measurements reveal that the T-site hydrogen vibrations of hcp YH_3 and fcc LaH_3 show a doublet and a singlet, respectively.[25] It should be noted that the singlet peak is midway between the original doublet peaks; the peak frequencies of the doublet in the hcp phase are 1064 and 1422 cm^{-1} at 12 GPa, giving an average value of 1243 cm^{-1} very close to that of the singlet peak frequency of 1252 cm^{-1} in the fcc phase. Hence, it is concluded that the strength of the hydrogen-metal interactions does not change at the T site during the hcp-fcc transition. However, the O-site peak shows marked spectral changes since the peak increases in intensity and shifts to a lower frequency. These spectral changes are likely due to the rearrangement of the hydrogen positions at the O sites. The hydrogen atoms, which are located either on the metal plane or at the off-planar positions above or below the metal plane in the hcp phase,[4] move to the symmetric center positions of the O sites. Again neutron vibrational spectroscopy indicates that fcc LaH_3 with a hydrogen atom at the center of the O site shows that the intense peak broadens, as in high-pressure fcc YH_3.

Next, plausible mechanisms for the band gap closure or the metallization observed in the fcc phase are discussed. This transition is characterized by the abrupt closing of the band gap without a structural change in the metal lattice. An entirely electronic transition and structural change relevant to the hydrogen position are the possible causes of the abrupt gap closure. The present experiment lacks positional information on the hydrogen atoms and cannot figure out definitely the transition mechanism. Two metallization processes have been proposed for YH_3 based on the band structure calculations. One is a band gap closing while the hydrogen atoms rearrange into the symmetric interstitial sites. The higher-symmetry transition is predicted to occur in the hcp phase when the volume is reduced to 85%.[13] The other is metallization with a structural conversion from the hcp to fcc lattice, which would occur at a relatively low pressure around 1.5 GPa.[9] The present infrared measurement reveals that the band gap closure occurs in the high-pressure fcc phase, which is inconsistent with either theoretical prediction. Thus, an alternative explanation is required to explain the gap closing mechanism.

The atomic positions of hydrogen should play a key role in the insulator-metal transition with the band gap closing. X-ray diffraction measurements confirm that the fcc metal lattice remains through the transition. There are two possible scenarios for the hydrogen positions, especially at the O sites of the fcc YH_3. The first scenario is that the hydrogen atom occupies the center of the O site in both the insulating and metallic fcc phases. The insulator-metal transition proceeds without a structural change under pressure. Such an insulator-metal transition is often interpreted in terms of band overlap. CsI is an example of metallization by a continuous closing of the band gap.[28] From the band structure calculations for hcp YH_3 and fcc LaH_3,[8,14] a band overlap is speculated at high pressure. The lattice compression in-

creases the *s-d* hybridization at the *O* site or in the transfer integral between the adjacent hydrogen atoms.[8,14] In either case, the valence and conduction bands broaden as the pressure increases to eventually close the gap. However, the band overlap model predicts a continuous closing of the energy gap, which is inconsistent with the experimental observations. Hence, an additional mechanism such as cooperative motion of the electrons would be necessary to explain the mechanism. The second scenario is displacement of the hydrogen positions; the hydrogen atom at the *O* site moves from the center position during the transition. The off-symmetric displacement of the *O* site hydrogen atoms has been shown to dramatically change the electronic state in hcp YH_3.[13] However, the symmetry lowering explains a band gap opening. Thus, this is not the gap closing mechanism. The band gap closing observed for the fcc YH_3 is still not understood. High-pressure neutron diffraction measurements will be helpful for investigating the role of the hydrogen atoms and clarifying the transition mechanism.

The metallic phase of YH_3 is a potential candidate for a 1*s* metal. As speculated from the band structure calculations, the Fermi level would be located in the 1*s*-4*d* hybridization band. This band picture provides a very different electronic property than in fcc YH_2 with a Fermi level in the 4*d* conduction band. The electrons move via the hydrogen atoms in YH_3, but they move solely along the metal lattice in YH_2. Among the peculiar behaviors expected for a 1*s* metal, transport phenomena, which include superconductivity, are the most interesting. The strong electron-phonon coupling may realize a high-temperature superconductor and a significant isotope effect on its transition temperature. The insulator-metal transition is expected for other rare-earth trihydrides such as ScH_3 and LaH_3. The metallization of YH_3 extends the candidate materials for 1*s* metals and provides insight into light element metals such as metallic hydrogen.

IV. CONCLUSION

YH_3 undergoes structural transition at 12 GPa and electronic transition at higher pressures. Insulating YH_3 with a hcp metal lattice transforms into an insulating fcc phase near 12 GPa. The hydrogen vibrations demonstrate a site-dependent behavior as the peak frequency shifts with pressure, reflecting different hydrogen-metal bonding natures at the tetrahedral and octahedral interstitial sites. The band gap closure occurs at 23–26 GPa in the high-pressure fcc phase without a structural change in the metal lattice. These experimental results are in contrast to the theoretical results predicting the electronic transition either with hcp-fcc structural change or in the hcp low-pressure phase without structural change. The transition mechanism is still inconclusive.

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