Joint 20th AIRAPT – 43th EHPRG, June 27 – July 1, Karlsruhe/Germany 2005

Band gap closing in yttrium hydride at high pressures

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Summary

High pressure infrared spectra were measured for yttrium trihydride, YH_3, prepared by hydrogenation of yttrium metal in hydrogen fluid at pressures around 1 GPa. The spectral change with an hcp-fcc structural transition was observed at about 10 GPa in agreement with X-ray diffraction results. With further increase in pressure to 23 GPa, the hydride became opaque suddenly in the whole infrared region. X-ray diffraction measurement showed that the metal lattice maintained the fcc structure across the electronic transition likely with band gap closure. The 1*s* metal theoretically predicted was probably realized in YH_3 at high pressures.

Introduction

The structural and electronic state has intensively been investigated theoretically and experimentally for rare-earth hydrides, which show metal-insulator transitions with the opening of band gap by successive hydrogenation from di- to tri-hydride. Kelly *et al*. have calculated that the small displacement or symmetry lowering of the hydrogen positions in the hcp metal lattice leads to a band gap opening and the band gap closes again with the rearrangement of hydrogen when the volume is reduced to about 85 % (Kelly, 1997). Ahuja *et al*. have predicted an insulator-metal transition in association with an hcp-fcc structural change at about 1.5 GPa (Ahuja, 1997). X-ray diffraction measurements revealed the hcp-fcc at about 10 GPa in agreement with the theoretical prediction (Palasyuk, 2005 / Machida, 2004). However, the hcp-fcc transition was not accompanied by metallization. Wijngaarden *et al*. observed that YH_3 remained transparent in the visible region at least up to 25 GPa and extrapolated the insulator-metal transition pressure to be around 55 GPa from the pressure dependence of the optical gap measured (Wijngaarden, 2000). The band gap closure or metallization of YH_3 still remains unfound.

We performed the infrared spectroscopic investigation on the band gap closing in YH_3 at pressures to 30 GPa and observed a dramatic change in transmission spectra at 23 GPa likely associated with the band gap closure.

Experimental Method

We used a diamond anvil cell (DAC) to synthesize YH_3 and measure the infrared specra under high preussre. The sample chamber was 180 μm in diameter and 64 μm thick made by drilling a hole in a tungsten gasket. A fragment of yttrium a few micronmeter thick was placed in the sample chamber with a few ruby balls for pressure measurement. The yttrium foil was handled in a glove box charged with inert argon gas to prevent oxidation of the metal surface. The DAC with the sample was then filled with a hydrogen fluid compressed to 180 MPa using a gas loading apparatus (Takemura, 2001).

The metal foil reacted with the surrounding hydrogen fluid to form an YH_3 insulator and upon leaving at 1.1 GPa for a few tens hours, the sample turned a transparent brown. Infrared spectra were measured with a microscope Fourier transfer infrared spectrometer

with reflecting objectives (magnification: 16 and numerical aperture: 0.3). The wavenumber 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 800 times (30 min) accumulation. Raw spectra unavoidably contained the absorption from the diamond anvils, which was practically eliminated by a reference spectrum of an empty DAC.

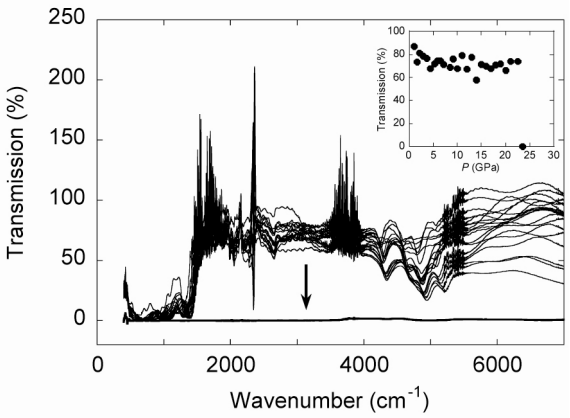

Figure 1 Transmission spectra measured at various pressures. Transmitted light was completely lost in the whole infrared region at 23.6 GPa. The insertion panel shows the variation of transmission intensity at 3000 cm^{-1} with pressure.

Results

The infrared spectra were measured up to 23.6 GPa on compression. Figure 1 shows the transmission spectra of YH_3 measured at various pressures. Several peaks in the range of 400-1400 cm^{-1} and 4000-5300 cm^{-1} are due to absorption by hydrogen atomic vibrations in YH_3 and hydrogen molecular vibrations, respectively. The structures around 2200 cm^{-1} are not intrinsic, originating from incomplete correction for the absorption due to the diamond windows. The vibrational bands of water molecules contaminated in the infrared beam path appear in the range of 1500-1800 cm^{-1} (bending vibrations) and 3600-3800 cm^{-1} (stretching vibrations). The absorption peaks of YH_3, for instance, at 3.5 GPa were located at 647, 952 and 1326 cm^{-1}, and idntified to the vibrations of hydrogen atoms occupaying the interstitial sites of the metal lattice. The observation of the hydrogen vibrational peaks was experimental evidence for the formation of trihydride YH_3.

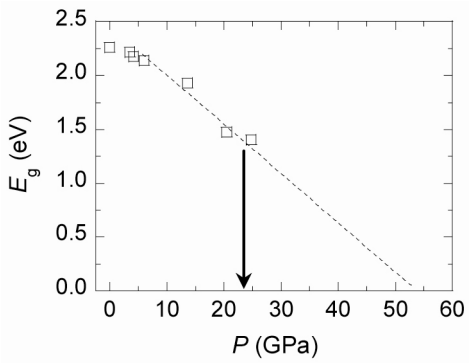

Figure 2 Pressure dependence of the energy gap measured by the visible absorption measurement (Wijngaarden, 2000). Arrow shows the electronic transition pressure observed by the present infrared absorption measurement.

A dramatic spectral change occurred while the pressure increased from 22.5 to 23.6 GPa. The transmission intensity dropped to zero for the whole infrared region measured. The abrupt change was pronounced in the pressure variation of transmission intensity at a fixed wavenumber. As displayed in the insertion panel, the intensity at 3000 cm^{-1} drops to zero at 23.6 GPa. The optical absorption due to the interband excitation seems to develop into the infrared region. The intensity at a high wavenumber region around 6000 cm^{-1} gradually decreases with increasing pressure above 18 GPa. The entire feature of the absorption edge was still out of the measuring range. However, about 50 % reduction at 7000 cm^{-1} at 22.5 GPa allows approximate determination of the gap energy of 1 eV.

Discussion

We compare the results of the infrared measurement with those of the visible experiment. The optical gap determined from the visible absorption is plotted as a function of pressure in Fig. 2 (Wijngaarden, 2000). Above 6 GPa, the optical gap decreased linearly with pressure to 1.4 eV at 25 GPa. The band-gap closure was not observed and predicted to occur aroud 55 GPa where an extrapolated gap vanished. In contrast, the present results indicates that the

band gap closes abruptly at 23 GPa about a half of the transition pressure estimated on the assumption of the continuous decrease of tha gap with pressure.

The spectral change at 23 GPa was not accompanied by structural change. The X-ray diffraction pattern taken at 29 GPa sufficiently higher than the transition pressure provided no signal for structural change. The YH_3 remains the fcc metal lattice. In addition, the fcc lattice constant is just on the extrapolated line of those measured previously up to 23 GPa for another YH_3 sample, indicating no discontinuous change in volume. These structural features are essential for discussion on a possible mechanism for the electronic transition.

Two possible senarios are presented. One is an electronic transition without any structural change. The electrons bound at H^+ cores would be delocalized to move freely when the Coulomb core potential is sufficiently screened by the surrounding electrons that densify upon compression. This type of insulator-metal transition is driven by the cooperative motion of electrons and may abruptly occur at a critical pressure as observed for YH_3. The other is the transition with the rearrangement of hydrogen atoms. The H^+ cores may be displaced from the initial positions in the fcc metal lattice when Coulomb repulsions increase beyond an critical point as a result of the lattice contraction upon compression. This has theoretically been demonstrated for hcp YH_3. The displacements of hydrogen atoms leads to the opening of a large band gap and vise versa. The hydrogen positions should play a key role in the observed electronic transition transition.

Conclusion

The high pressure infrared measurement on YH_3 revealed an abrupt and dramatic spectral change at 23.0 GPa. The transmittance went zero in the whole infrared region likely in association with the closing of the band gap. The electronic transition was not accompanied by structural change in the metal lattice and would be interpreted in terms of the delocalization of 1*s* electrons or the symmetry change in hydrogen positions.

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