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DIRECT OBSERVATION OF THE PRESSURE-INDUCED SEMICONDUCTOR-TO-METAL TRANSITION IN Yb MONOCHALCOGENIDES*

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We have measured infrared absorption spectra under pressure and reflectivity spectra of YbS in the wide photon energy range from 7 meV to 30 eV. The absorption edge shifts linearly toward lower energy with pressure, and above 11 GPa it disappeared in the infrared energy region. The results are considered to correspond to the development of a f–d mixing above this pressure, which lead to an occurrence of the semiconductor-to-metal transition.

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1. Introduction

Yb monochalcogenides (YbX, X = O, S, Se, Te), which crystallize in the NaCl structure, show semiconducting properties at ambient pressure and undergo a pressure-induced semiconductor-to-metal transition without any change in the crystal structure. Pressure–volume behavior on YbS [1] suggests that Yb changes from a divalent state to an intermediate valence state with Yb^{2+} and Yb^{3+} under high pressure and YbS exhibits finally metallic properties above $\sim$ 10 GPa due to a partial f electron delocalization. The optical properties of YbX have been investigated by Narayanamurti *et al.* [2] and Syassen *et al.* [1]. However, they did not observe clearly change in

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electronic structure near the Fermi level due to the semiconductor-to-metal transition of YbX, since their measurements were performed in the near-infrared and visible region.

In this study we have investigated the optical properties of YbS under pressure down to photon energy as low as 0.15 eV in the infrared (IR) region with use of synchrotron radiation (SR) light source.

2. Experimental details

In this study YbS single crystal was used. Optical reflectivity spectra at ambient pressure were measured in the wide energy range from 7 meV to 30 eV. The measurements were performed using a Fourier-transform interferometer with conventional thermal light sources below 2.5 eV, and using SR source at the beam line BL7B of UVSOR in the Institute for Molecular Science for the energy range between 2 eV and 30 eV. The optical conductivity spectra $\sigma(\omega)$ were obtained by a Kramers–Kronig analysis of the reflectivity data [3].

Optical absorption measurements under pressure up to 11.4 GPa were carried out in IR and near-IR regions (0.15–1.4 eV). A membrane diamond anvil cell (DAC) with type II-a diamond anvil with 0.6 mm culet-diameter was used to generate high pressure. Pressure was calibrated by a ruby fluorescence measurement [4]. The sample was mounted into about 150 μm hole of a stainless steel gasket with ruby chips and Fluorinert as the pressure transmitting medium. The spectra were measured using a IR microscope optical system with SR source at the beam line BL43IR at SPring-8 [5]. The use of IR–SR source, which is highly collimated and highly brighter than the conventional IR light source, allows IR light to be focused on the specimens as small as 10 μm in the diameter without any apertures. Therefore, there are decided advantages in the IR spectromicroscopy with a DAC.

3. Results and discussion

3.1. Electronic structure in YbS

Fig. 1 shows the $\sigma(\omega)$ of YbS at room temperature in a logarithmic scale. The onset of $\sigma(\omega)$ is observed at about 1.2 eV, which indicates the $4f$–$5d$ electronic excitation across the energy gap. The many peak structures due to inter-band transition are observed above the gap energy. The inset in Fig. 1 shows the $\sigma(\omega)$ below 7 eV in a linear scale in which the four absorption peaks are mainly observed. In accordance with previous studies of YbX [1, 2], the four peaks originate from the transitions of $4f^{14}(^1S_0) \rightarrow 4f^{13}(^2F_{7/2}, {}^2F_{5/2})\ 5d(t_{2g}, e_g)$, respectively.

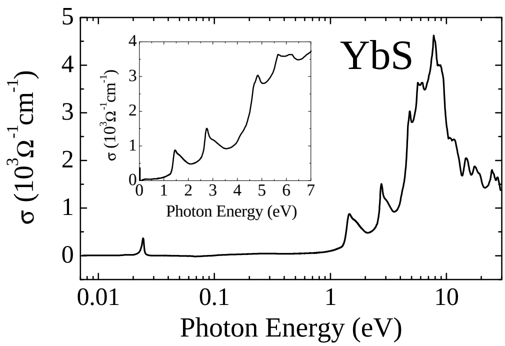

Fig. 1. Optical conductivity spectrum (σ) of YbS at room temperature. Inset shows σ below 7 eV in a linear scale.

3.2. Pressure dependence of absorption edge structure

To the next, we have measured the optical transmission spectra of YbS to investigate the pressure dependence of the absorption band due to $4f$–$5d$ excitation. The transmission spectra of YbS under several pressures are shown in Fig. 2. In the spectrum at ambient pressure, the threshold derived from the $4f$–$5d$ absorption edge was observed around 1.2 eV. The threshold energy shifts toward lower energy with increasing pressure and above 11 GPa the transmitted signal intensity disappeared in this energy region, which indicates the semiconductor-to-metal transition.

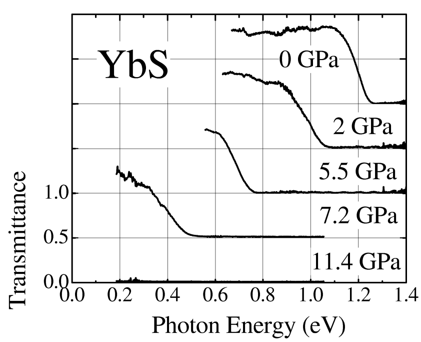

Fig. 2. The transmission spectra of YbS measured at several pressures.

To determine a pressure dependence of the absorption edge in YbS, optical density (OD) as a function of photon energy were obtained from the transmission spectra (Fig. 3(a)). The absorption band is corresponding to the optical excitation $4f^{14}(^1S_0) \rightarrow 4f^{13}(^2F_{7/2})5d(t_{2g})$. Fig. 3(b) shows the pressure dependence of the absorption edge, which was taken at a level of $\mathrm{OD} = 1$ at each pressure. It is clearly seen that the absorption edge shifts

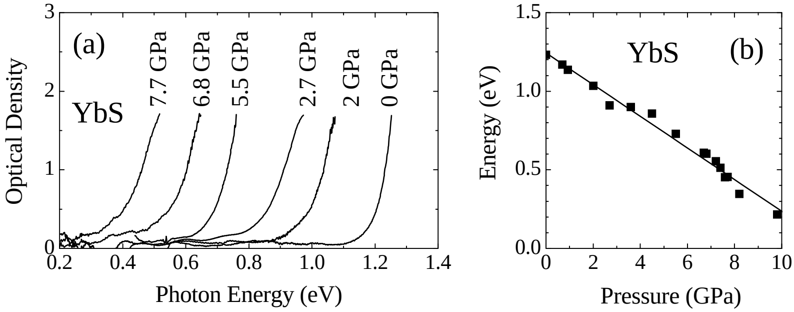

Fig. 3. (a) Absorption spectra (optical density versus energy) of YbS obtained from the transmission spectra at each pressure. (b) Pressure dependence of the absorption edge defined at OD = 1 in YbS. The solid line represents the fitted curves to the experimental data.

linearly toward lower energy with pressure. The data points can be fitted by linear relation with a slope of $dE/dP = -100\,\mathrm{meV/GPa}$ as indicated by the solid line. Since the $4f$–$5d$ excitation energies decrease at the rate, the onset of $4f$–$5d$ mixing should begin to develop near 12 GPa, which lead to a semiconductor-to-metal transition in almost agreement with the pressure–volume study [1].

In conclusion, we have extended the energy range of the optical measurements under high pressure in YbS down to 0.15 eV in the IR region with use of SR light source (SPring-8). The decreasing rate of the gap with pressure is $-100\,\mathrm{meV/GPa}$. The results may indicate that f–d mixing should begin to develop near about 12 GPa, which lead to an occurrence of the semiconductor-to-metal transition.

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