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Optical absorption in ytterbium monochalcogenides under pressure

V. Narayanamurti, A. Jayaraman, and E. Bucher
Bell Laboratories, Murray Hill, New Jersey 07974

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The pressure dependence of the lowest-lying $4f \to 5d$ absorption band in crystalline films of YbTe, YbSe, and YbS has been studied. The absorption edge which occurs at about 1.8 eV in YbTe, 1.5 eV in YbSe, and 1.1 eV in YbS at zero pressure is shown to close at a rate of 11.0, 9.8, and 6.5 meV/kbar, respectively, for pressures up to 8 kbar. The measurements predict gap collapses in all the three chalcogenides at pressures of the order of 175 kbar, in good agreement with pressure-volumes studies and qualitative changes in the reflectivity at high pressures.

I. INTRODUCTION

Recent resistivity measurements under pressure and pressure-volume studies on the Sm monochalcogenides[1,2] have revealed that these compounds undergo a semiconductor-to-metal transition at room temperature under the influence of high pressure. The large volume changes without involving any structure change and the metallic behavior at high pressures were explained on the basis of the delocalization of the $4f$ electron of the Sm ion and consequent change in the valence state from 2^+ towards the trivalent state. Further, optical-transmission and reflectivity measurements[3] were crucial in elucidating the role played by the band structure in the transition and verified that the observed pressure effects were intrinsic to the material. In particular, the optical-absorption features and the pressure dependence of the absorption edge provided key evidence to the idea that the energy gap between the localized $4f$ level and the $6s$-$5d$ conduction-band edge decreased with pressure[4] and ultimately vanished.

Since the above work on the Sm monochalcogenides, more recent pressure-volume studies[5] on YbS, YbSe, and YbTe have revealed that valence changes occur in the Yb compounds as well, but at much higher pressures (150–200 kbar). Based on some earlier optical measurements at atmospheric pressure and resistivity measurements[6] under pressure on YbTe, Francillon *et al.* suggested that a valence transition in YbTe may be expected near ~40-kbar pressure, which is in conflict with the pressure-volume data. Since no data on the pressure-induced shifts of the optical-absorption edges in the Yb monochalcogenides exist to resolve the conflict, we thought it would be worthwhile to determine the energy gap, as well as the shift in the absorption edge with pressure, in YbTe, YbSe, and YbS under hydrostatic pressure. We have made measurements up to about 8 kbar. The measured energy gaps between the localized $4f$ state and the $5d$ conduction-band edge and their pressure dependences are consistent with the results of pressure-volume studies and lend strong support to the idea of electronic collapse in Yb monochalcogenides near 175-kbar pressure. These results again highlight the importance of optical measurements in providing direct and detailed information of the energy levels involved in the metal-insulator transition in the rare-earth chalcogenides. The results will be presented and discussed in this paper.

II. EXPERIMENTAL DETAILS

Pressure measurements were made in a high-pressure cell (made from Vascomax 300 alloy) provided with sapphire windows and capable of reaching a maximum pressure of ~10 kbar. Plexol 262 was used as the pressure medium. The absorption measurements were made with a Spex model 1500 spectrophotometer, over the wavelength range of 1.1 to 0.4 μm.

For absorption measurements thin crystalline films of YbS, YbSe, and YbTe were prepared in a Denton high-vacuum evaporator provided with an electron-beam gun. The evaporations were carried out in vacuum of 10^{-6} Torr. Both sapphire and NaCl substrates were tried. The data presented in this paper were all taken with films on NaCl substrates. The crystallinity of the films was confirmed by recording their x-ray-diffraction patterns. The powder patterns, as well as the lattice parameter, were consistent with that of the bulk starting material. The choice of NaCl was dictated by the fact that in order to get meaningful data under pressure a close match of compressibility, as well as the lattice constant for the substrate and the Yb chalcogenide was very crucial. Data were taken with films of different thicknesses to check the reproducibility. As a final check, a YbS film was scraped off its NaCl substrate and was pressurized in a high-pressure diamond-anvil apparatus to make sure that qualitatively the reflectivity changes at high pressure were similar to that observed with bulk YbS.

The path length of the Plexol high-pressure medium was kept minimal as far as possible and was typically not more than 2 mm. Nevertheless, weak absorptions (~a few percent) were noticed at 1.19, 0.91, and 1.02 μm. The data were, therefore, taken as a function of pressure with and without the film to eliminate the effects of the medium. In the following, we present the normalized data.

III. EXPERIMENTAL RESULTS AND DISCUSSION

In Fig. 1 we have plotted the absorption coefficient as a function of wavelength (in the region of 1–0.4 μm) for YbTe, YbSe, and YbS. The absorption is characterized by a rapidly rising edge starting from about 1.0 μm in YbS, 0.85 μm in YbSe, and 0.73 μm in YbTe. This edge has a width typically of 0.2 μm in YbS and 0.1 μm in YbTe, corresponding to an energy width of 0.2–0.3 eV. The data for zero pressure are consistent with the work on YbTe and YbSe by Suryanarayanan[7] and for YbS with our own earlier work.[8] The broad peak (E_1) at 0.77 μm in YbS, 0.65 μm in YbSe, and 0.59 μm in YbTe is believed to arise from the large density of states of the 5d band.[7,8] This band is expected to be split through crystal-field effects into a t_{2g} state lying lowest and an e_g state of higher energy with a 10Dq splitting of the order of 1.0 eV. Additional splittings may be expected in the excited state from the known spectra[9] of Yb^{3+}, whose 4f shell has 13 electrons which give rise to an additional doublet (^2F), separated by about 1.2 eV, due to spin-orbit effects. Thus, depending on the width of the absorptions in the crystalline state, the spectra of the Yb chalcogenides can have up to four peaks due to $4f^{14}(^1S_0) \rightarrow 4f^{13}(^2F_J)5d(t_{2g}, e_g)$ transitions. In the low-temperature spectra of YbTe and YbSe, structure corresponding to these transitions has been seen.[7] In YbS both at 300 and at 10 °K (data not shown) we see only a single additional broad peak E_2 at about 0.44 μm. The separation between E_1 and E_2 of about 1.2 eV is close to both the 10Dq and ^2F splittings expected for this material.

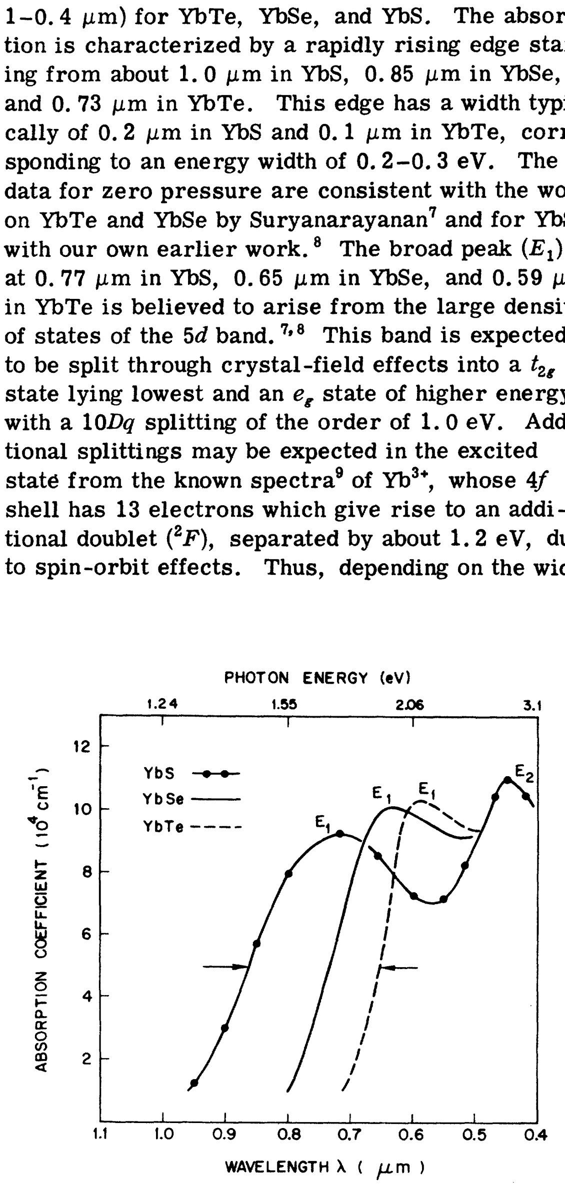

FIG. 1. Absorption coefficient as a function of wavelength for thin films of YbS, YbSe, and YbTe on NaCl substrates, at atmospheric pressure. The pressure coefficient of the absorption edge shown in Fig. 3 was measured at a value of $\alpha \sim 5\times10^4$ cm^{-1} as marked by the arrow. For a discussion of the origin of the absorption peaks E_1 and E_2, see text.

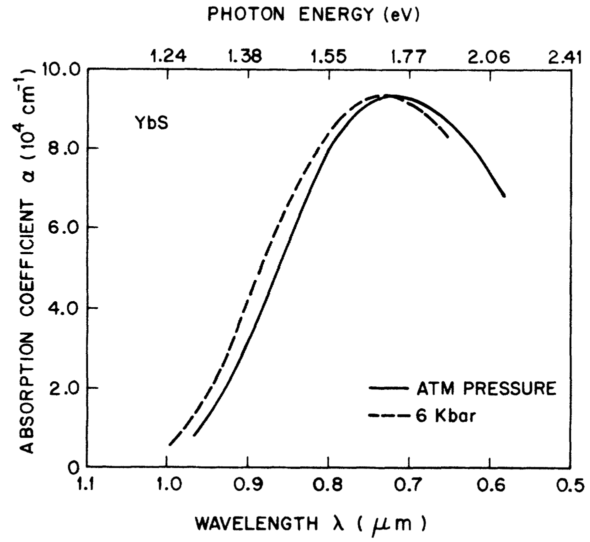

FIG. 2. Wavelength dependence of the lowest absorption band in YbS at atmospheric pressure (solid line) and at 6 kbar (dashed line).

Since it is the metal-insulator transition which is of interest to us, we shall concern ourselves with the lowest absorption band E_1 in the rest of this paper. The effect of pressure on the absorption band E_1 is shown in Fig. 2 for the case of YbS. The data for YbTe and YbSe were similar. It is clear that the effect of pressure is to uniformly shift the absorption band to lower energies (longer wavelengths). The precise value of the shift depends slightly on the wavelength. In Fig. 3 we have plotted the pressure dependence of the absorption edge. For convenience, the data were taken at near the half-height of the absorption maximum which corresponded to a value of $\alpha \sim 5\times10^4$ cm^{-1} for most of the measurements. It is clear from this figure that the pressure coefficient of the 4f-5d absorption edge, $\partial E_{fd}/\partial p$, decreases in the series YbTe to YbS from a value of − 11.2 meV/kbar for YbTe, to − 9.8 meV/kbar for YbSe to − 6.5 meV/kbar for YbS. The precise values were somewhat dependent on the choice of absorption edge, as mentioned earlier. The pressure coefficients quoted

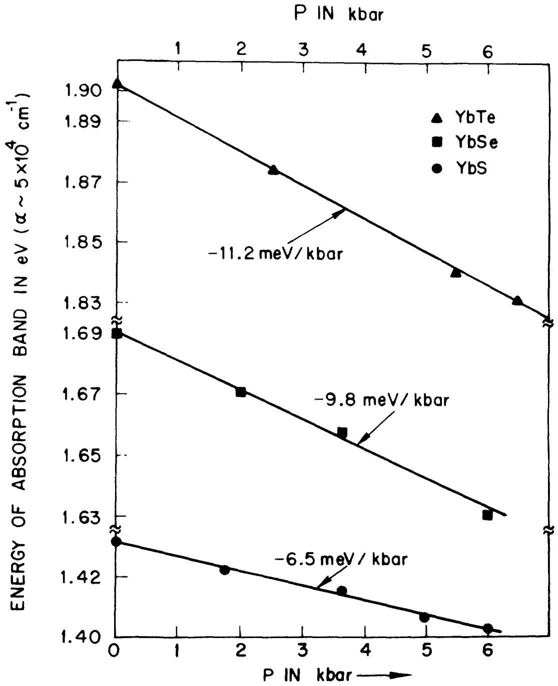

FIG. 3. Pressure dependence of the absorption edge (at a value of the absorption coefficient $\alpha \sim 5\times10^4$ cm^{-1}) for YbTe, YbSe, and YbS.

here are believed to be good to within ±10%, after taking into account the experimental uncertainties.

From the above measured values of the pressure coefficients and the 4*f*-5*d* gap at zero pressure, we conclude that the latter should vanish at pressures around 175 ±25 kbar in all three materials.[5] Thus, the optical measurements provide strong support for the idea that the anomalous pressure-volume behavior[5] of Yb chalcogenides is the result of a valence change of Yb^{2+} towards the 3^+ state. The energy separation for the 4*f*-5*d* conduction-band edge of about ~0.4 eV reported by Francillon *et al.*[5] for YbTe, which led them to predict a 4*f*-5*d* transition near 40 kbar, must be a gap between an impurity state and the conduction-band edge in YbTe. The 4*f*-5*d* conduction-band-edge energy separation in YbTe is ~1.8 eV and if the rate of closure of this gap is 11.2 meV/kbar, this gap should vanish in the 160–200-kbar region. Additional support for the correctness of our conclusion comes from qualitative reflectivity studies conducted on Yb monochalcogenides in the diamond-anvil apparatus. Metallic reflectivity analogous to that of Sm monochalcogenides at very high pressures is observed in Yb chalcogenides, but only at pressures above 200 kbar. YbTe, YbSe, and YbS become purple, copperish, and golden yellow in color respectively, at this high pressure, whereas such transitions in reflectivity are observable in the Sm compound at much lower pressures.

In summary, the optical-absorption band due to the lowest 4*f*→ 5*d* transition in the Yb monochalcogenides has been studied as a function of pressure. The measured gap and the rate of closure of this gap with pressure lead to a metal-semiconductor transition in all three compounds at pressures of the order of 175 kbar, in agreement with quantitative pressure-volume studies and qualitative observations of changes in reflectivity. The prediction of a valence transition in YbTe and 40 kbar by Francillon *et al.*[6] was based on the erroneous value for the 4*f*-5*d* gap of ~0.4 eV. The results presented in this paper stress the importance of a direct study of the pressure effects on the optical-absorption features to get a satisfactory physical picture of the metal-insulator transition in rare-earth monochalcogenides.

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