

as MgS or ZnSe considered here, where the  $S^{2-}$  or  $Se^{2-}$  free atomic orbitals are either very diffuse or unbound, and local orbitals which are minimally distorted from the free atomic case would be very diffuse and overlap greatly at best. Such orbitals would be poor choices in many calculations because of their great overlaps. Therefore, we find it desirable in some cases to obtain local orbitals

which are greatly distorted from the free orbitals.

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## Direct Optical Observation of the Semiconductor-to-Metal Transition in SmS under Pressure

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A discontinuous change in the reflectivity due to the first-order semiconductor-to-metal transition has been observed in SmS at a pressure of about 6 kbar. The metallic state is characterized by a golden yellow luster which arises because of interband transitions superimposed on the Drude reflectivity. These results and the pressure dependence of the optical-absorption edge in semiconducting SmSe and SmTe are in excellent agreement with earlier resistivity measurements.

Recent resistivity measurements<sup>1</sup> under pressure on SmTe, SmSe, and SmS have revealed that these monochalcogenides undergo a pressure-induced semiconductor-to-metal transition, without involving any change in the crystal structure. This discovery has generated considerable interest in the study of their magnetic<sup>2</sup> and pressure-volume behavior<sup>3</sup> under high pressure, as well as optical studies at atmospheric pressure.<sup>1,4-6</sup> In this paper we show that the change in reflectivity under *pressure* is one of the most striking phenomena associated with the semiconductor-to-metal transition and in this respect is more spectacular than the resistivity change which can be influenced by extrinsic impurities. In particular, we present for the first time evidence for *metallic* reflectivity in SmS at hydrostatic pressures greater than 6.5

kbar. These results, together with our optical-absorption data taken under high pressure on the insulating state of SmTe and SmSe, provide strong evidence for the interpretation that the semiconductor-to-metal transition in all three compounds arises from *4f*-electron delocalization into the *5d* conduction band and that this is an intrinsic property of the material.

The measurements were made in a hydrostatic-pressure vessel equipped with sapphire windows. Plexol was used as a pressure medium. The reflectivity or absorption data could be taken over the wavelength range 0.26–2.5  $\mu$ . The maximum attainable pressure was about 14 kbar.

Figure 1 shows the reflectivity of single-crystal SmS at a fixed wavelength of 0.8  $\mu$  as a function of pressure for near-normal incidence. With in-

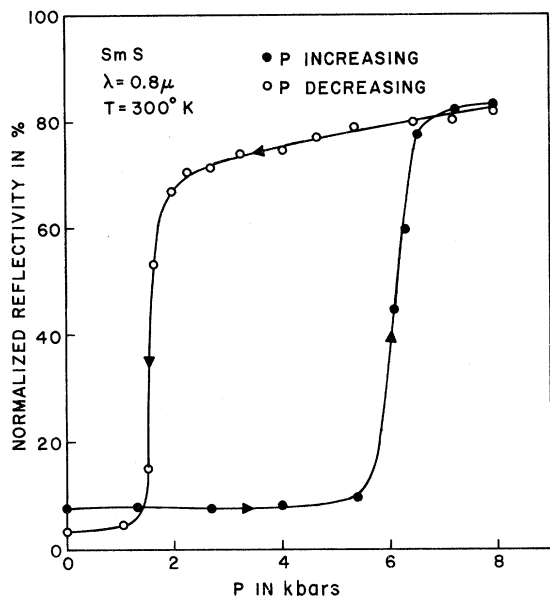


FIG. 1. Change in reflectivity at the semiconductor-to-metal transition in SmS at  $0.8 \mu$ . Note the hysteretic nature of the transition.

creasing pressure relatively little change is observed until a pressure of about 6 kbar is reached. Between 6 and 6.5 kbar the reflectivity changes by at least one order of magnitude and then remains essentially constant. The absolute value of the reflectivity in the metallic state at wavelengths greater than  $0.8 \mu$  is at least 85% of that of aluminum. The exact value is difficult to estimate because of difficulties in obtaining reproducible alignment of the crystal and the reference Al mirror inside the pressure vessel, and also because of the dependence of the reflectivity on the quality of the crystal surface. The values quoted in this paper are believed to represent the lower limit. The transition exhibits marked hysteresis and the reflectivity returns to its original value at  $\sim 1.5$  kbar. The small difference in reflectivity below 1 kbar is due to multiple cracking of the crystal during the reverse transition (see Fig. 1).

Visual observation of the transition in the pressure vessel through an optical microscope (under white-light illumination) shows that at a pressure of about 6 kbar a few points in the crystal begin to "flash" and exhibit a yellow color. By 6.5 kbar the entire crystal exhibits a "brilliant golden yellow luster" and the first-order transition is complete.

In Fig. 2 we show the quantitative wavelength dependence of the reflectivity of SmS in the metallic (8 kbar) and insulating states. It is clear from this figure that the golden yellow color must arise from the "hole" in the reflectivity curve of the metallic

state, which has a deep minimum at about  $0.46 \pm 0.02 \mu$  ( $\sim 2.6 \text{ eV}$ ) and a weak maximum at about  $0.84 \pm 0.4 \mu$  ( $\sim 1.4 \text{ eV}$ ). Such a pronounced dip in the reflectivity has been observed experimentally in the noble metals Cu, Au, and particularly Ag and have been ascribed to bound-electron (inter-band) transitions.<sup>7</sup> Possible origins for the "bound"-electron transition in metallic SmS are discussed later. The rise in the reflectivity at wavelengths beyond the minimum indicates that the true plasma frequency probably lies in the ultra-violet. Assuming 0.7 electrons are created per  $\text{Sm}^{3+}$  and taking an average effective mass of  $\sim 0.4$  (obtained from the band-structure calculations of Cho<sup>8</sup> for the analogous EuS), one obtains a plasma frequency of  $\sim 7 \text{ eV}$  ( $\sim 1800 \text{ \AA}$ ). If, however,  $m^* = 1$ , then  $\hbar\omega_p \approx 4.5 \text{ eV}$ .

We have observed the same behavior in samples differing in dc resistivity by an order of magnitude in the semiconducting state. Although the magnitude of the dc resistivity drop associated with the semiconductor-metal transition varies, depending on the extrinsic part of the sample resistivity, the high reflectivity (under pressure) in all the samples provides strong evidence that the effects described here are intrinsic to the material.

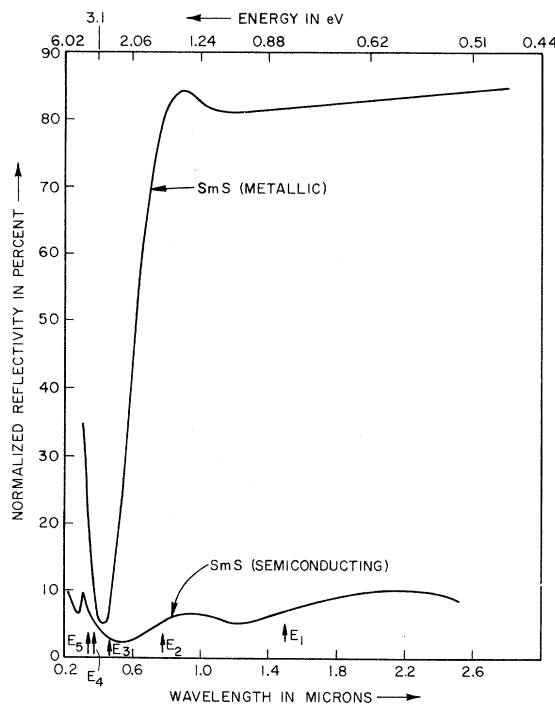


FIG. 2. Wavelength dependence of reflectivity of SmS in the semiconducting and metallic states. The arrows  $E_1$  to  $E_5$  show the positions of the peaks observed in thin-film optical-absorption and photoemission data. The reflectivity curve of metallic GdS is identical with that of the high-pressure phase of SmS (see text).

We now turn to the structure observed in our reflectivity curves in the semiconducting and metallic states. From the band-structure calculations of Cho<sup>8</sup> for the analogous Eu chalcogenides, one expects the lowest conduction band (above the filled  $3p$  valence band and  $4f$  states) to be a  $5d$  ( $T_{2g}$ -like) band at the  $X_3$  point in the Brillouin zone. The next higher-lying band is an admixture of  $6p$ - $6s$  states at the  $\Gamma$  point. Additional, higher levels are made up of  $5d$  ( $E_g$ -like) states which in the isolated-ion case would lie at a value of  $10Dq$  above the  $T_{2g}$  state. The ordering of levels discussed here is in good agreement with optical-absorption experiments on thin films,<sup>5,6</sup> though the width of the experimental absorption peaks and their location may be modified by exciton effects,<sup>9</sup> which are neglected here for simplicity.

Therefore, in the semiconducting state the optical-absorption data are expected to show strong peaks arising from  $4f^6 \rightarrow 4f^5 5d$  transitions with an oscillator strength<sup>10</sup>  $\sim 0.2$ . Transitions from  $4f$  to  $6p$ - $6s$  are electric dipole forbidden, and the only other expected strong transitions are the charge-transfer bands involving the promotion of a  $3p^6$  valence electron to the  $5d$  conduction states. Additional structure in the case of Sm chalcogenides,<sup>5</sup> due to the multiplet splitting of the excited  $4f^5$  configuration into  ${}^6H_J$  and  ${}^6F_J$  states, may arise. In Fig. 2 the reflectivity features at  $E_1$  and  $E_2$  in the insulating state at  $1.5 \mu$  and  $0.77 \mu$  are believed to arise from transitions  $4f^6({}^7F_0) \rightarrow 4f^5({}^6H_J) 5d$  ( $T_{2g}$ ) and  $4f^6({}^7F_0) \rightarrow 4f^5({}^6F_J) 5d$  ( $T_{2g}$ ), respectively, in agreement with optical-absorption data on thin films. The structure at  $E_3$  ( $0.48 \mu$ ) and  $E_4$  ( $0.4 \mu$ ) is ascribed to  $4f^6({}^7F_0) \rightarrow 4f^5({}^6H_J$  or  ${}^6F_J) 5d$  ( $E_g$ ) transition, as expected from a  $10Dq$  splitting<sup>5</sup> of  $\sim 1.6$  eV ( $E_3 - E_1$  or  $E_4 - E_2$ ).<sup>11</sup> Finally, the location of the charge-transfer peak  $E_5$  is expected to be at about  $3$ - $4$  eV from photoemission work on the rare-earth monosulfides.<sup>12</sup>

In the high-pressure phase, the data are characterized by metallic reflectivity in the yellow region of the spectrum. This is to be expected, once the  $4f$  state merges with the  $5d$  conduction band in the collapsed phase, releasing  $10^{22}$  free carriers per  $\text{cm}^3$ . The dielectric constant beyond the yellow region is large and negative. At higher energies the magnitude of the dielectric constant decreases considerably as the plasma frequency is approached. This decrease is, however, interrupted by a strong band-to-band transition at about  $2.6$  eV. In GdS, which is metallic at atmospheric pressure and exhibits a golden yellow luster, we have measured the reflectivity and have found a deep hole similar to that of the high-pressure phase of SmS. In GdS the golden color and the strong rise in photoemission beyond  $2.8$  eV has been attributed<sup>12</sup> to transitions from the  $3p$  valence band into  $5d$  states lying

above the Fermi level. It therefore appears reasonable to ascribe the golden yellow color of the high-pressure phase of SmS to an intense  $3p \rightarrow 5d$  charge-transfer transition. It is possible that the  $5d(t_{2g}) \rightarrow 5d(E_g)$  transition also contributes to this; the latter transition becomes allowed in the metallic phase owing to  $4f$ - $5d$  hybridization. Furthermore, from the known volume change<sup>1</sup> of SmS under pressure, we estimate that this splitting should increase to a value of about  $2.5$  eV from its value of  $1.6$  eV in the insulating state.

The above-mentioned analysis could be further quantified by a detailed Kramers-Kronig fit to the data. This is difficult in our case without a firm knowledge of the plasma frequency. We, however, have measured  $n$  and  $k$  directly by ellipsometry for the metallic GdS (which has a reflectivity almost identical to the metallic phase of SmS) in the range  $0.36$ - $0.58 \mu$ . The absorption coefficient appears from these measurements to be of the right order of magnitude to explain our reflectivity data on the high-pressure phase of SmS.

We have also made visual observations on the pressure-induced metal-semiconductor transition in SmSe and SmTe, using a diamond-anvil apparatus. SmSe was observed to change to a bright copper color, while SmTe showed a deep purple color in its high-pressure phase. These colors are the same as metallic GdSe and GdTe. This shift to longer wavelengths is consistent with the decrease in the energy of the  $3p \rightarrow 5d$  transition and of the  $10Dq$  splitting as the lattice constant increases in going from the sulfide to the selenide. Quantitative optical-absorption measurements under hydrostatic pressure on SmSe and SmTe (up to  $7$  kbar) reveal that the  $4f \rightarrow 5d$  absorption edge in the insulating state closes at a rate of  $11 \pm 1$  meV/kbar with increasing pressure. This rate is in excellent agreement with earlier resistivity measurements under pressure<sup>1</sup> and provides additional strong evidence that the semiconductor-to-metal transition is due to  $4f \rightarrow 5d$  collapse and not due to impurity effects.

In conclusion, we have shown for the first time that the pressure-induced metal-semiconductor transition in SmS at  $6.5$  kbar is accompanied by a spectacular change in optical reflectivity. The high-pressure phase is characterized by metallic reflectivity starting from the yellow region of the spectrum, which we attribute to bound-electron transitions at  $\sim 2.6$  eV. The plasma frequency in the semiconducting state must lie in the infrared beyond the region shown in Fig. 2, where the reflectivity would rise in accordance with the Drude formula. In SmSe and SmTe, metallic reflectivity has been observed (at much higher pressures), while in the insulating state the energy gap decreases at a rate of  $\sim 11$  meV/kbar, in excellent agreement with earlier resistivity data.

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## Electron Energy-Loss Spectra of ZnS, ZnSe, and ZnTe

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A study has been made of the electron energy-loss spectra of the three IIB-VIA compounds ZnS, ZnSe, and ZnTe. These spectra have been obtained both by electron-reflection and electron-transmission techniques. The electron-reflection measurements were made from freshly cleaved single-crystal surfaces of all three compounds in an ultrahigh-vacuum atmosphere. Changes in these spectra were observed as the surface was slowly contaminated. The electron-transmission measurements were made only on ZnTe using flash-evaporated thin films. The quality of these films was established by means of x-ray-diffraction, optical-reflectivity, and optical-absorption measurements. The peaks observed in these spectra have been interpreted in terms of interband transitions, surface plasmons, and bulk plasmons. The results are compared with optical-reflectivity measurements and x-ray-induced electron-emission measurements.

### I. INTRODUCTION

The usefulness of electron energy-loss measurements in providing information concerning the higher-energy-level structure of solids has been shown in several studies.<sup>1-4</sup> Recently we reported on a study of CdS, CdSe, and CdTe<sup>5</sup> using techniques of both reflection-electron energy loss (REEL) and transmission-electron energy loss (TEEL). This paper represents an extension of this investigation to the IIB-VIA zinc compounds ZnS, ZnSe, and ZnTe.

There exist several studies of the higher-energy bands in the zinc compounds using different techniques such as optical reflectivity, electron energy loss, photoemission, and x-ray-induced electron

emission. Optical-reflectivity measurements have been made by Cardona and Harbeke<sup>6</sup> and by Baars<sup>7</sup> on ZnS; by Balkanski and Petroff<sup>8</sup> on ZnS and ZnSe; by Freeouf *et al.*<sup>9</sup> on ZnS, ZnSe, and ZnTe; and by Cardona and Greenaway<sup>10</sup> on ZnTe. Transmission-electron energy-loss measurements have been made on thin films of ZnS, ZnSe, and ZnTe by Tomoda and Mannami<sup>11</sup> and on ZnTe films by Gauthé.<sup>12</sup> X-ray-induced electron-emission measurements have been made on all three compounds by Vesely and Langer<sup>13</sup> and photoemission measurements have been made by Shay and Spicer<sup>14</sup> on ZnTe, and by Vesely, Hengehold, and Langer<sup>15</sup> on ZnTe and ZnSe.

The results reported in this paper were obtained