CSF Electron Tubes.
[14]S. Mango, Ö. Runolfsson, and M. Borghini, Nucl. Instrum. Methods 72, 45 (1969); D. A. Hill, J. B. Ketterson, R. C. Miller, A. Moretti, R. C. Niemann, L. R. Windmiller, A. Yokosawa, and C. F. Hwang, Phys. Rev. Lett. 23, 460 (1969); A. Masaike, H. Glattli, J. Ezratty, and A. Malinovski, Phys. Lett. 30A, 63 (1969).

PRESSURE-INDUCED METAL-SEMICONDUCTOR TRANSITION AND 4*f* ELECTRON DELOCALIZATION IN SmTe

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The pressure variation of resistivity and optical absorption in SmTe has been studied. A continuous pressure-induced semiconductor-to-metal transition is observed, which we ascribe to the promotion of electrons from the 4*f* level into the conduction band as the gap between them shrinks with pressure and finally vanishes. The gap deduced from the saturation resistivity ratio $\rho(P)_{sat}/\rho(0)$ is in good agreement with the gap of 0.62 ± 0.02 eV obtained from infrared absorption data.

The monochalcogenides of Sm, Eu and Yb crystallize in the NaCl structure[1] and are found to be semiconductors.[2,3] Because of their interest as magnetic semiconductors the Eu chalcogenides have received the most attention in recent years and quite extensive optical absorption measurements[4] and some pressure work[5,6] have been reported on them. Similar studies are conspicuously absent in the case of Sm and Yb compounds. This Letter reports the discovery of a continuous pressure-induced transition in SmTe from semiconducting to the metallic state, as the pressure is increased from 0 to 55 kbar. We ascribe this semiconductor-to-metal transition to the promotion of electrons from the 4*f* level into the conduction band as the gap between them shrinks with pressure and finally vanishes. The energy gap deduced from resistivity measurements is good agreement with our optical absorption data. We believe that the pressure behavior described for SmTe will prove to be the general pattern for the semiconducting rare-earth monochalcogenides.

Samarium telluride was prepared by reacting Sm metal chips in Te vapor at about 900°C for 48 h and subsequently melting the sample in a tantalum tube. The ingot thus obtained was polycrystalline, with fairly large-sized single crystals. The NaCl structure[1] and the lattice constant appropriate to SmTe were verified from the powder x-ray diffraction data. For resistivity measurements, single-crystal samples were cut from selected regions in the ingot. Ohmic contacts were provided with indium and the standard four-probe technique was used to measure the resistance. The room-temperature resistivity was approximately 10^3 Ω cm. For optical absorption studies, a polished single-crystal plate approximately 15 mm^2 in area and 0.1 mm in thickness was used.

High-pressure resistivity measurements were carried out under hydrostatic conditions up to about 45 kbar using *n*-pentane–isoamyl alcohol mixture as pressure medium, and up to 55 kbar using AgCl as pressure medium, in a piston-cylinder device. The two sets of measurements were in good agreement in the region of their overlap. The data on resistivity versus pressure are reproduced in Fig. 1. It will be seen that the resistivity decreases by almost seven orders of magnitude and saturates at about 55 kbar. The logarithm of resistivity versus pressure exhibits two straight-line regions, with a break in slope at about 20 kbar. The pressure coefficients $d\ln\rho/dp$ are -0.10 and -0.46 $kbar^{-1}$. These slopes yield -2.6×10^{-3} and -11.9×10^{-3} eV/kbar for the pressure coefficient of the carrier activation energy. At low pressures the temperature coefficient of resistivity is strongly negative and varies strongly with pressure. At the highest pressure it becomes positive, showing thereby metallic behavior.

Figure 2 shows the optical absorption as a function of photon energy. The principal absorption edge is centered at about 0.62 ± 0.02 eV (~2 μm). There is a subsidiary absorption at longer wavelengths centered at about 3 μm (0.38 eV). A weak absorption band centered at 0.22 eV (~5.6 μm) with a half-width of 0.02 eV was also observed (not shown in Fig. 2) in our scanning between 5 and 15 μm.

In order to explain the resistivity and optical

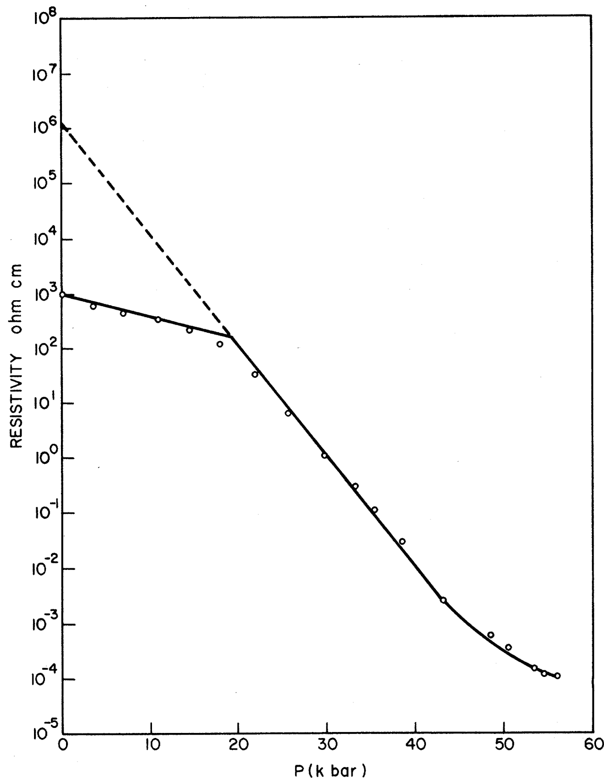

FIG. 1. Resistivity-pressure data for SmTe.

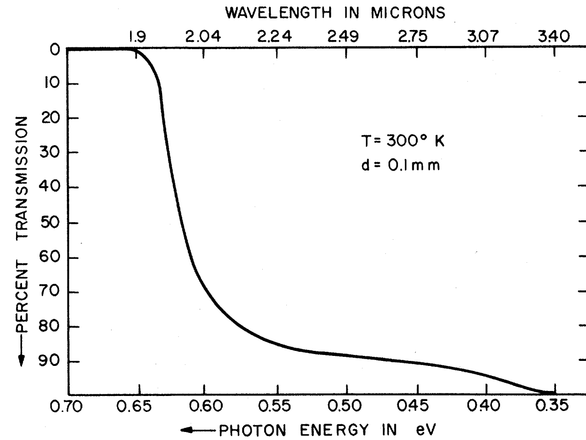

FIG. 2. Transmission spectra of single-crystal SmTe between 0.35 and 0.7 eV. Beyond 0.65 eV the sample is opaque up to the highest energy of our measurement (~3.0 eV). At longer wavelengths a weak absorption band centered at 0.22 eV (~5.6 μm) was observed.

absorption in SmTe we propose the following model: The principal absorption edge centered around 0.62 eV represents transitions from the $4f$ level to the conduction-band states. The subsidiary absorption arises due to transitions from a trap level which lies about 0.38 ± 0.02 eV below the bottom of the conduction band. The weak absorption band represents transitions from the $4f$ level to the trap level. Figure 3 illustrates the proposed model.

The logarithmic decrease in resistivity is due to carrier activation into the conduction band, as the latter moves towards the trap level and the deeper lying $4f$ level. The activation energy for carrier excitation was determined as 0.36 eV from resistivity-temperature data taken at 20 kbar. The activation energy decreased progressively with pressure at higher pressures, consistent with the dE/dP quoted above. These experiments and the agreement between the E_g determined from resistivity and optical experiments (see later) show that the Fermi level is essentially locked to the $4f$ level. If we assume that the latter does not move in energy with pressure, the pressure coefficient of -11.9×10^{-3} eV/kbar deduced from the resistivity data above 20 kbar should be ascribed to the rate of motion of the lowest lying conduction-band minimum towards the $4f$ level. This pressure coefficient is almost the same as that reported[5] for EuTe from the shift in absorption edge with pressure. The initial pressure coefficient of -2.6×10^{-3} eV/kbar is explicable if we make the assumption that the trap level is tied to one of the upper lying conduction bands and moves downwards in energy with a pressure coefficient of -9.3×10^{-3} eV/kbar. Since the trap level would then be moving at rate of -9.3×10^{-3} eV/kbar, the effective pressure coefficient would initially be only -2.6×10^{-3} eV/kbar. However when the trap level is within a few times kT of the vicinity of the $4f$ level, the full pressure coefficient (-11.9×10^{-3} eV/kbar) of the lowest conduction band would be-

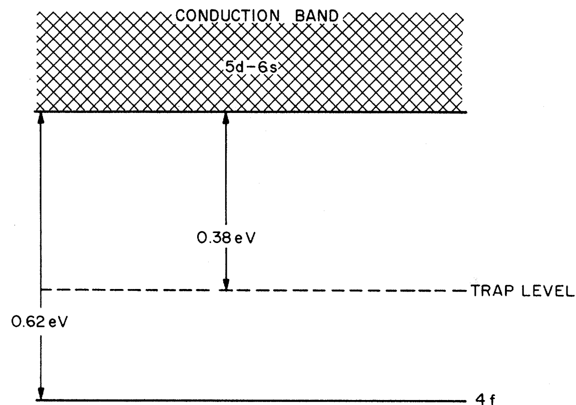

FIG. 3. Proposed model to explain the optical and resistivity data.

come effective.

Our assumption that the trap level in SmTe is tied to one of the possible upper lying conduction bands is not unreasonable and this type of behavior has been seen in CdTe[7] and GaSb.[8]

The room-temperature resistivity at atmospheric pressure and the optical absorption results reveal that the density of trap sites is smaller by an order of magnitude compared with the density of electrons at the $4f$ level. We obtain an extrapolated resistivity at one atmosphere of 10^6-10^7 Ω cm (see the dashed line in Fig. 1). From the temperature dependence of the resistivity at atmospheric pressure we deduce a carrier activation energy of about 0.35 eV. This is consistent with the position of the subsidiary weak infrared absorption which places the trap level at about 0.38 ± 0.02 eV below the bottom of the conduction band.

Using the extrapolated resistivity from Fig. 1, the saturation resistivity ratio is found to be slightly higher than 10^{10}. From this, the energy separation ΔE between the conduction band and the $4f$ level can be estimated, using the expression $\rho(P)/\rho(P_0) = \exp(-\Delta E/kT)$, as 0.60 ± 0.02 eV. This is in good agreement with 0.62 eV determined from optical absorption measurements.

The observed positive temperature coefficient of resistivity at the highest pressure indicates that metallic conductivity has been reached under pressure. Thus SmTe shows a continuous pressure-induced transition from semiconducting to the metallic state. Evidently this is a consequence of the merging of the conduction band with the $4f$ level at the highest pressure and consequent delocalization of one $4f$ electron per Sm, when the energy separation between the two goes to zero. In this event a substantial decrease in the lattice constant is to be expected since the Sm^{2+} would essentially become Sm^{3+} and the atomic volume of the latter is substantially smaller. From the resistance data, it is clear that this transition occurs continuously and one might therefore expect the lattice constant to decrease smoothly but anomalously with pressure. Rooymans[9] has reported an isostructural transition in SmTe at about 60 kbar,[10] in which the lattice constant a contracts from 6.5 Å at 30 kbar to 6.2 Å at about 60 kbar. Although a discontinuous transition has been presumed to occur by this author, his data points, in fact, seem to indicate that the transition may be occurring over a broad range of pressure, as is expected on the basis of the present work. Also, a recent high-pressure x-ray diffraction study[11] of $Tm^{2+}Te^{2-}$ has indicated that a continuous pressure-induced isostructural transition is probably occurring in which Tm^{2+} becomes Tm^{3+}. The metal-semiconductor transition in SmTe under pressure is a continuous transition and our results seem to be consistent with a model involving delocalization of the $4f$ electron into the conduction band states derived from $5d$-$6s$, as the latter moves down in energy and crosses the $4f$ level. Among the various models that have been proposed to explain metal-semiconductor transitions, the one proposed by Falicov and Kimball[12] appears to be particularly appropriate to describe the behavior of SmTe. For not only does this model allow for a continuous transition but also it describes the behavior of a semiconductor whose gap is shrinking.

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[1]A. Iandelli, in *Rare Earth Research,* edited by E. V. Kleber (MacMillan, New York, 1961), p. 135.

[2]F. J. Reid, L. K. Matson, J. F. Miller, and R. C. Himes, J. Phys. Chem. Solids 25, 969 (1964).

[3]R. Didchenko and F. P. Gortsema, J. Phys. Chem. Solids 24, 863 (1963).

[4]Review by J. O. Dimmock, IBM J. Res. Develop. 14, 301 (1970).

[5]P. Wachter, Solid State Commun. 7, 693 (1969).

[6]M. R. Oliver, J. A. Kafalas, J. O. Dimmock, and T. B. Reed, Phys. Rev. Lett. 24, 1064 (1970).

[7]A. G. Foyt, R. E. Halsted, and W. Paul, Phys. Rev. Lett. 16, 55 (1966).

[8]B. B. Kosicki, W. Paul, A. J. Strauss, and G. W. Iseler, Phys. Rev. Lett. 17, 1175 (1966).

[9]C. J. M. Rooymans, Ber. Bunsenges. Phys. Chem. 70, 1036 (1966).

[10]F. Hulliger, Helv. Phys. Acta. 41, 945 (1968).

[11]A. Jayaraman, E. Bucher, and D. B. McWhan, in *Proceedings of the Eighth Rare Earth Research Conference,* edited by T. A. Henrie and R. E. Lindstrom (U.S.G.P.O., Washington, D. C., 1970), Vol. 1, p. 333.

[12]L. M. Falicov and J. C. Kimball, Phys. Rev. Lett. 22, 997 (1969).