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Continuous and Discontinuous Semiconductor-Metal Transition in Samarium Monochalcogenides Under Pressure

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Resistivity and lattice-constant measurements under high pressure on SmS show that a $4f \rightarrow 5d$ electronic transition in SmS occurs discontinuously at 6.5 kbar at room temperature, whereas such a transition takes place continuously over a broad pressure range in SmTe and SmSe. The pressure-induced semiconductor-to-metal transition in the Sm chalcogenides and their pressure-volume relationship are consistent with the conversion of Sm^{2+} to Sm^{3+}. Optical-absorption measurements in these materials correlate well with the resistivity data under pressure. The semiconductor-to-metal transition in Sm chalcogenides appears to fit the model recently proposed by Falicov and Kimball for a system with a localized state and a conduction band.

We recently reported the occurrence of a continuous semiconductor-to-metal transition in SmTe,[1] due to $4f$ electron delocalization induced by high pressure. In this Letter we report the discovery of a discontinuous $4f \rightarrow 5d$ electron delocalization in SmS. Both the resistivity and the lattice constant abruptly decrease at 6.5-kbar pressure at 293°K, without any change in the crystal structure. The discontinuity in the lattice constant at this pressure is consistent with the conversion of Sm^{2+} to Sm^{3+}. The occurrence of continuous and discontinuous semiconductor-metal transition in Sm monochalcogenides presents an entirely new situation from both theoretical and experimental points of view.

Samarium sulfide was prepared by a reaction of high-purity sulfur with Sm in a quartz tube and a subsequent melting in a tantalum tube, under high vacuum. The material on cooling was well crystallized, but polycrystalline, with large single-crystal regions. X-ray powder photographs confirmed both the NaCl structure and the lattice constant (5.97 Å) appropriate to SmS.[2] For resistivity as well as optical studies single crystals were used.

The material had low resistivities, in the range 0.01 to 0.001 Ω cm (at 1 atm) and when scratched or polished acquired a golden yellow color on the surface.[3] Four-lead resistivity measurements were made with bar samples. Indium metal provided excellent ohmic contacts. Resistivity measurements under pressure were carried out in isoamyl alcohol as pressure medium. Figure 1 shows the resistance as a function of pressure at 293°K. There is an abrupt decrease in resistance at 6.5 kbar which evidently represents a discon-

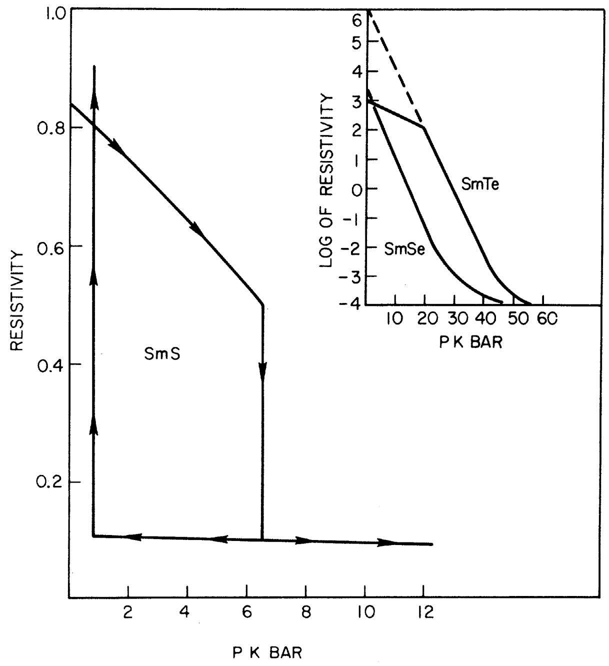

FIG. 1. Normalized resistivity versus pressure for single crystal SmS. The actual resistivity at pressures greater than 6.5 kbar is ~3–4×10^{-4} Ω cm. See text. The data for SmTe and SmSe are shown in the inset.

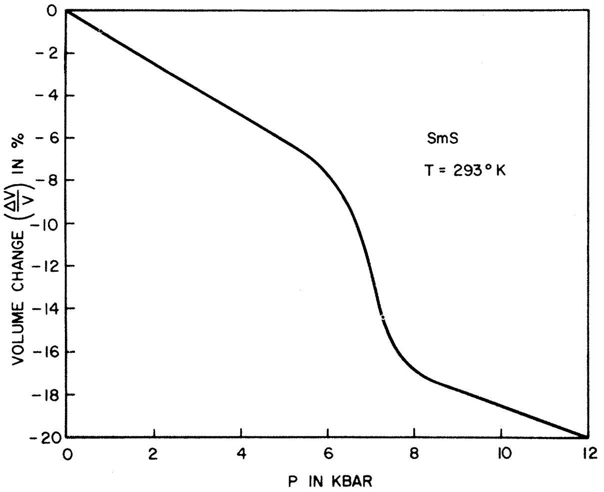

FIG. 2. Volume change versus pressure for powdered SmS (obtained from compression data). $T = 293$°K.

tinuous phase transition. The temperature coefficient of resistance was found to be positive after the transition, while before the transition it was negative.

X-ray powder patterns of the material were recorded in a diamond-anvil high-pressure x-ray camera. At an estimated pressure of about 10 kbar, the lattice constant had decreased quite substantially (5.70 ± 0.01 Å) and the calculated $\Delta V/V$ was 16%. Since finer variation of pressure was not readily possible with the anvil camera, a compression run was made with powdered SmS mixed with AgCl. Figure 2 shows the volume change as a function of pressure. It is clear that most of the volume change occurs around a pressure of about 7 kbar at room temperature, the slight spread in data around 7 kbar presumably being due to the powdered nature of the sample used. The volume change observed in the compression data is about the same as that deduced from the x-ray studies.

Optical absorption studies were also made on single-crystal plates. The crystals exhibited a strong background absorption, but three prominent features were evident in the infrared region; two absorption peaks, one centered at 0.2 eV and another at 0.37 eV, and a gradually rising absorption edge. The sample was found to be opaque to radiation of higher photon energy.

The abrupt decrease in resistivity at 6.5 kbar and the sharp decrease in volume reflect a first-order phase transition in SmS. The high-pressure x-ray powder data reveal that this transition is isostructural, the structure remaining NaCl-type up to very high pressure (~100 kbar). The lattice constant at 10-kbar pressure reflects $\Delta V/V$ of about 16%. We attribute this large volume decrease to an electronic transition of the Sm ion from Sm^{2+} to Sm^{3+} state. It is not absolutely clear from the resistance data alone whether this transition takes place all at once at the transition pressure, because the initial slope of the resistivity versus pressure curve differs somewhat from sample to sample depending upon its resistivity; the slope is large in samples with 0.01-Ω-cm resistivity compared with samples of 0.001 Ω cm. However, the compression data indicate clearly that the compressibility before the discontinuous transition is a factor of 2 larger than the compressibility after the transition. We ascribe this high initial compressibility to a gradual conversion of Sm^{2+} to Sm^{3+} in the 0- to 6.5-kbar region, which then becomes catastrophic at 6.5 kbar.

To determine the slope of the phase boundary, the resistivity was followed as a function of pressure at 383 and at 173°K. At 383°K the abrupt transition was found to shift to a slightly lower pressure (6.4 kbar) and at 173°K to a slightly higher pressure. This indicates that the phase boundary is very steep and has a negative slope. Both at 293 and 383°K the reverse transition does not take place almost down to a kilobar pressure and then the resistivity rises very sharply indicating a reverse transition (see Fig. 1). It is impossible to reproduce the original resistivity after cycling. On examination after release of pressure the single-crystal specimens exhibited numerous cracks which run parallel to the cubic directions. The abrupt transition coupled with the large volume expansion associated with it presumably causes cracking of the specimen. Indeed this fact is a very distinctive feature of the behavior of SmS; in SmTe[1] and SmSe,[4] where the transition is continuous, no cracking is observable. Also in these latter two materials the resistivity invariably returns to the original value after each cycling.

In the inset to Fig. 1 we have reproduced the resistivity-pressure data for SmTe and SmSe for ready comparison with SmS. In the former two the resistivity decreases by about seven orders of magnitude, in the pressure range of 0 to 60 kbar. This large change in resistivity in SmTe and SmSe is to be compared with a change of about a factor of 5, observed in the discontinuous transition in SmS at 6.5 kbar. Careful measurements of the resistivity of SmSe in the high-pressure region show that within the accuracy of our measurements the transition is truly smooth (any discontinuous change in resistivity in SmSe must be an order of magnitude smaller than in SmS). In the case of SmTe and SmSe the gap for carrier activation estimated from the resistivity was found to be in good agreement with the gap derived from the optical-absorption data (0.63 eV for SmTe[1] and 0.46 eV for SmSe[4]). The features of the absorption spectra in these two materials were ascribed to electronic transitions from the $4f^6(^7F_0)$ level (hereafter called the $4f$ level) into the $4f^5 5d$ conduction-band states. Likewise the pressure variation of resistivity was associated with the shrinking gap between the $4f$ level and the bottom of the conduction band. The observed metallic conductivity at high pressure was interpreted as due to a complete delocalization of the $4f$ electron and the conversion of Sm^{2+} to Sm^{3+}. This interpretation was also found to be consistent with the pressure variation of the lattice constant reported for SmTe and SmSe.

The metallic resistivities observed in SmTe, SmSe, and SmS at high pressure are comparable and are about $3\text{-}4\times10^{-4}$ Ω cm. This strongly suggests a common origin for the semiconductor-to-metal transition in these systems. Further, in the case of SmS the x-ray data unambiguously show that Sm^{2+} to Sm^{3+} conversion takes place at the transition and this further strengthens the earlier interpretation of the results on SmTe and SmSe that $4f$ electron delocalization occurs in these compounds at high pressure.

While the $4f$-$5d$ transition thus seems to occur in a continuous manner over a broad pressure range in SmTe and SmSe, the same transition takes place at a low pressure and discontinuously in SmS. The interesting questions are (1) why does the transition occur at such a low pressure in SmS and (2) why is it discontinuous? If the energy gap between the $4f$ level and the conduction band should correlate with the pressure at which metallic conductivity sets in, then a low pressure of transition strongly suggests that the $4f$ level in SmS should lie very close to the conduction band. (In SmTe and SmSe the pressure at which metallic conductivity sets in correlates[1,4] with the observed energy gap.) Earlier studies[5,6] of temperature-activated conductivity have indicated that the $4f$ level in SmS lies about 0.18 eV below the conduction band. The rising absorption and the first peak that we observe in the optical measurements are close to this estimate, and the optical data are thus not inconsistent with the small gap between $4f$ and $5d$. That the energy gap between the $4f$ level and the conduction band should decrease in going from SmTe to SmSe to SmS is also strongly indicated by the sequence of gaps observed in the Eu chalcogenides.[7]

We believe that the continuous and discontinuous nature of the transition is related to the existence of a critical interatomic distance between the Sm ions, which presumably is satisfied in SmS. The lattice constant of SmS is 5.97 Å, while in SmTe and SmSe (see Table I) the lattice parameter does not shrink to the value observed in SmS in the pressure region of our interest.

The occurrence of continuous and discontinuous semiconductor-metal transition in samarium chalcogenides seems to offer strong experimental support for the model of such transitions proposed by Falicov and Kimball.[8,9] According to this model the number of electrons n in the conduction band, as a function of temperature (or pressure), can be given by the following equation:

$$\Delta_{\text{eff}} = \Delta - 2Gn,$$

where Δ is the energy gap at zero temperature and pressure, G is a measure of the strength of the electron-hole interaction, and Δ_{eff} is a shrinking gap (with temperature or pressure). Depending upon the relative values of G and Δ, continuous and discontinuous transitions are predicted

Table I. Data on samarium chalcogenides.

Substance	Lattice constant	Resistivity (Ω cm)	Absorption edge (eV)	Pressure of transition
SmS	5.97	0.01 to 0.001	~0.2	6.5 kbar
SmSe	6.20	$3\text{-}4\times10^3$	0.46 ± 0.02	Transition continuous 0–50 kbar
SmTe	6.594	$\sim10^3$	0.63 ± 0.02	Transition continuous 0–60 kbar

by this model. Apparently in SmS, which has a smaller Δ (and lattice constant) than SmTe and SmSe, the ratio G/Δ exceeds a critical value under pressure and a first-order phase transition is observed in this material while a continuous transition is observed in the other two cases.

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Quantum Theory of Perpendicular-Field Cyclotron Resonance in Metals

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It is shown that a quantum-mechanical calculation of the surface resistance of a free-electron metal can provide a natural explanation of the broad anomaly found by Baraff, Grimes, and Platzman in their perpendicular-field cyclotron resonance experiments on potassium.

Measurements of the surface resistance of potassium in the vicinity of cyclotron resonance have shown considerable dependence on the strength of the magnetic field $\vec{B}$ oriented perpendicular to its surface.[1] The observed signal consists of a small sharp peak superposed on an anomaly[2] which is an order of magnitude broader than the peak itself. It has been known for some time that the solution of the Boltzmann equation for an isotropic electron system with a single relaxation time can give only a monotonic variation of the resistance in the region of magnetic field strength corresponding to the cyclotron frequency of the electrons.[3-5] This is because the electrons with different velocity components along the field become resonant within a large range of Doppler-shifted frequencies.[6] In an attempt to account for the potassium anomaly within a semiclassical framework, Baraff has employed a rough-surface model which incorporates a spatially varying relaxation time[7]; the narrow peak has then been interpreted as a Fermi-liquid mode which is enhanced by the anomalous field penetration corresponding to the broad signal.[8]

In this Letter we wish to propose a contrasting interpretation of the broad anomaly[9] which is not based on the assumption of different relaxation times. The essence of the present treatment is to consider the electrons from a quantum-mechanical point of view with the key hypothesis that their wave functions vanish at the surface ($z = 0$).[10,11] The electrons are considered as uncorrelated quasiparticles with an effective mass M. Scattering by phonons, impurities, etc., is described by a single isotropic relaxation time τ.[10,11] Physically, quantum effects are important for electrons which approach the surface at glancing incidence, and for which the de Broglie wavelength along the z direction is comparable with the skin depth[11]; it is precisely these electrons which contribute significantly to the surface impedance.

Since the present calculation of the surface impedance is an extension of Ref. 11 to nonzero magnetic field, we adopt the definitions from this reference except that we denote the average electric field $\bar{E}_x(z,\omega)$ as $E_x(z)$ and its Fourier component $\tilde{E}_x(k,\omega)$ as $\tilde{E}_x(k)$ so that the frequency dependence is implicit. When discussing circularly polarized radiation, it is convenient to consider the combinations $E_\pm = E_x \pm iE_y$ and $J_\pm = J_x \pm iJ_y$, which satisfy the equation

$$[k^2-(\omega/c)^2]\tilde{E}_\pm(k) = i\omega\mu_0\tilde{J}_\pm(k) + 2a_\pm, \tag{1}$$