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Heat Capacity and Resistivity of Metallic SmS at High Pressure

S. D. Bader* and N. E. Phillips*
Inorganic Materials Research Division of the Lawrence Berkeley Laboratory, and Department of Chemistry, University of California, Berkeley, California 94720

D. B. McWhan
Bell Laboratories, Murray Hill, New Jersey 07974
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The heat capacity of SmS has been measured in the metallic and insulating phases between 0.3 and 20 K. The electrical resistivity has been measured between 3 and 298 K in the metallic phase and as a function of pressure at 4.2 and 473 K. The entropy difference shows clearly the demagnetization of the $4f$ electrons in the metallic phase. The electrical resistivity increases with decreasing temperature in the metallic phase. The heat capacity and resistivity of metallic SmS are very similar to those of SmB_6, suggesting that the same underlying mechanism is responsible for the unusual properties of both substances.

An unusual class of materials that contain rare-earth ions with nonintegral valence and "soft" magnetic moments has recently been recognized.[1] Samarium sulfide exhibits the properties characteristic of these materials at pressures above 6.5 kbar but not at lower pressures and is, therefore, a particularly interesting system for further study. The first-order metal-insulator transition at 6.5 kbar and 298 K in SmS is marked by an 8% decrease in volume with no change in crystal structure.[2] There is only a factor of 5 decrease in resistivity at the transition but a factor of 10 increase in optical reflectivity at 0.8 μ.[3] The magnetic susceptibility decreases by 60%, and no evidence for magnetic ordering was found down to 1 K.[1] It has been proposed that there is a partial electronic rearrangement at the transition from an insulating phase in which Sm^{+2} ions are in the nonmagnetic $^7F_0$ ground state of the $4f^6$ configuration to a metallic phase in which, in time average, 0.7 electrons are transferred to a conduction band.[1] To account for the observed susceptibility, it was suggested that the $4f$ levels form a virtual bound state tied to the Fermi energy.[1]

We have measured the heat capacity of SmS at zero pressure and at approximately 15 kbar from 0.3 to 20 K, and we have measured the electrical resistivity as a function of pressure at 4.2 and 473 K and as a function of temperature in the metallic phase from 3 to 298 K. An unusually large temperature-proportional contribution to the heat capacity of metallic SmS was observed. The entropy change at the transition, $\Delta S = S_{\text{metal}} - S_{\text{insulator}}$, is calculated at low temperatures from the heat-capacity measurements and at room temperature from the Clapeyron equation. An estimate involving the differences in multiplet and crystal-field splittings and in Debye temperatures accounts for ΔS_{298} and shows that the entropy associated with f levels in metallic SmS disappears gradually at low temperatures. In addition, the resistivity was found to increase with decreasing temperature in the metallic phase. All of these effects are also observed[4,5] in SmB_6. In fact, the features of the heat capacity and resistivity are similar in the two materials which supports the suggestion[1] that a common model must be used to explain the unusual properties.

The heat-capacity measurements were made by the heat-pulse method using germanium thermometers which give a precision from experiment to experiment of approximately 0.1%. For the measurements in the metallic phase a clamped piston and cylinder device were used. The heat capacity of the empty cell under pressure had been determined in previous studies[6] by using a sample of

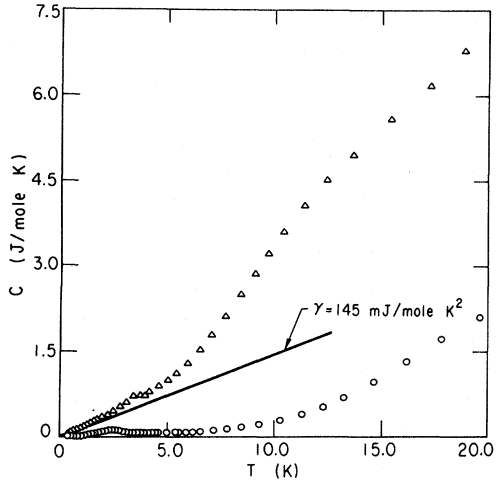

FIG. 1. Heat capacity of SmS at approximately 15-kbar (triangles), and at zero pressure (circles).

compressed diamond powder. A 4.12-g sample of SmS, which comprised 1.58% of the total weight of the cell and sample, was compressed and the transition monitored by the advance of the piston. After applying a 20-kbar load to the cell, the locking nut was tightened, and an estimated 15-kbar pressure was retained on the sample. The results of the measurements are shown in Fig. 1. The large heat capacity of the metallic phase relative to the insulating phase is evident. A plot of C/T vs T^2 shows that the limiting coefficient of the linear term in the heat capacity of the metallic phase is $\gamma \approx 145$ mJ/mole K^2.[7] A small anomaly that occurs near 3 K at zero pressure and at 15 kbar is probably associated with impurities. (Such effects have frequently been observed in rare earths and their compounds.) The anomaly obscures any linear term in the zero-pressure heat capacity, but an upper limit of approximately 7 mJ/mole K^2 can be assigned for the value of γ in the insulating phase.

The electrical resistivity measurements were made in a girdle die and high-pressure cryostat as described in the literature.[8] As the resistivity of insulating SmS is very sensitive to strain, independent experiments were done in which the crystal was mounted in AgCl as the pressure-transmitting medium or in a miniature Teflon cell containing a mixture of n-pentane and isoamyl alcohol. In both cases, the pressure medium is a brittle solid at low temperatures but in the latter case the initial compression at room temperature is hydrostatic. The results of increasing the pressure through the transition at 4.2 K are compared with those[9] at 473 K in the inset in Fig. 2. The change in resistance is 10^4 greater at 4.2 than at 473 K, but is smeared out because of the inhomogeneous pressure distribution at low temperatures. Even at room temperature the transition was sharp when the Teflon cell was used but was 1 kbar wide when the nonhydrostatic AgCl was used. From these curves and the transition pressure at 298 K, the slope of the phase boundary is calculated to be $dT/dP \sim -200$ K/kbar. The variation of the resistivity with temperature is shown in Fig. 2. There is a striking resemblance to SmB_6 which shows an even larger increase in resistivity at low temperatures.[4,5]

The lattice parameters of metallic SmS and SmB_6 suggest that the relative contributions of the $4f^5$ and $4f^6$ configurations are in the ratio 7:3.[1] (The isomer shift[10] and energy of the L_{III} x-ray absorption edge[11] have also been measured for SmB_6 and indicate the same ratio.) The lowest term for the $4f^5$ configuration is $^6H_{5/2}$ and in an octahedral field this term splits into a Γ_7 doublet and a Γ_8 quartet level. Inelastic neutron scattering experiments on PrS show that the Γ_7 doublet lies lowest, and a $\Gamma_7 - \Gamma_8$ separation of 165 K is obtained for SmS by scaling the PrS results as the fifth power of the lattice parameter.[12] The $R\ln 2$ entropy of the Γ_7 Kramer's doublet must disappear as $T \to 0$, and this usually occurs through magnetic

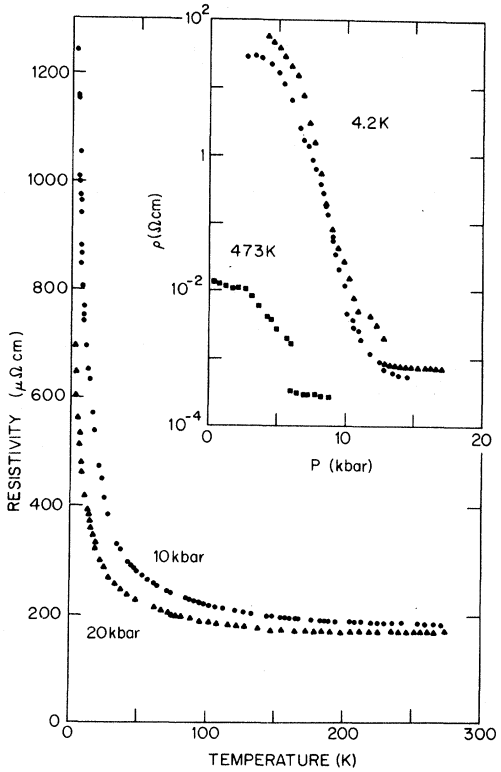

FIG. 2. The resistivity vs temperature of SmS at 10 and 20 kbar. The inset compares the insulator-metal transition as a function of pressure at 4.2 and 473 K. The pressure transmitting medium was AgCl (circles), frozen (triangles) or liquid (squares) n-pentane isoamyl alcohol.

ordering as in, for example, CeB_6[13] and $CePb_3$.[14] Integration of C/T for both the metallic and insulating phases of SmS as a function of temperature shows that ΔS increases smoothly from 0 R at 0 K to 0.54R at 20 K. This is close to 0.7Rln2 which suggests that the Γ_7 doublet in metallic SmS loses its entropy gradually, and in a temperature interval in which susceptibility measurements show no indication of magnetic ordering.

The entropy change at 298 K is calculated from the Clapeyron equation to be $(0.15 \pm 0.1)R$, substantially smaller than ΔS_{20}. The initial rapid increase in ΔS is balanced at higher temperatures by other factors such as population of higher-energy levels in the $4f^5$ and $4f^6$ multiplets and different Debye temperatures. Plausible values would be 165 K for the Γ_7-Γ_8 splitting,[12] 415 K for the $^7F_0$-$^7F_1$ splitting[15] of the $4f^6$ configuration, 266 K for the Debye temperature at zero pressure and a Grüneisen parameter of 1.5,[16] and $\gamma = 8$ mJ/mole K^2 for the conduction electrons. Such a model would give $\Delta S_{298} = 0.2R$ which is similar to the observed value of $(0.15 \pm 0.1)R$.

The unusual properties exhibited by metallic SmS and SmB_6, and which would have to be explained by a successful microscopic theory, are (1) the absence of magnetic ordering and the saturation of the magnetic susceptibility at low temperatures, (2) the apparent intermediate electronic configuration of $0.7f^5$ and $0.3f^6$ derived from volume considerations, (3) the large linear term in the heat capacity and the continuous demagnetization of the $4f$ electrons, and (4) the large rise in resistivity below 50 K. It has been suggested[1] that α-Ce also belongs in this group of materials, and $CeSn_3$ and $CeBe_{13}$ are possible additional examples—both have the Γ_7 crystal-field ground state, large linear terms in the low-temperature heat capacity, and susceptibilities that saturate at low temperatures with no indication of a divergence or magnetic ordering.[14]

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