[9] See, for example, A. Mooradian and G. B. Wright, Phys. Rev. Letters 16, 999 (1966).

[10] After this manuscript was prepared, we have learned that C. B. Duke, M. J. Rice, and F. Steinrisser (to be published) have observed similar d^2I/dV^2 structure in the reverse bias of their n-type GaAs-In tunnel junctions. They attribute their results to self-energy effects from electron-plasmon interaction in the bulk volume GaAs electrode. We have observed d^2I/dV^2 structure in both bias directions corresponding to an increase in conductance. Our data, as discussed in the text, are consistent with our interpretation that the d^2I/dV^2 structure is due to surface plasmon emission in the surface layer of the bulk GaAs electrode.

MAGNETIC AND SEMICONDUCTING PROPERTIES OF SmB_6†

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SmB_6 has been found to show no magnetic ordering down to a temperature of 0.35°K. We interpret this to mean that the Sm ion is in its nonmagnetic divalent configuration at low temperatures and find direct evidence for the changing electronic configuration of Sm from trivalent to divalent with decreasing temperature in the observed semiconducting behavior at low temperatures.

SmB_6 is found to change from a metal to a semiconductor with decreasing temperatures and to show intrinsic semiconducting behavior down to 3°K. The compound prepared by two different methods shows no evidence for magnetic ordering down to temperatures as low as 0.35°K. This contrast to all the other magnetic rare-earth hexaborides[1-3] leads to the tentative conclusion that at low temperatures, where the ordering is to be expected, the Sm ion is divalent and has the $4f^6$ configuration. In that configuration the spin and orbital angular momenta cancel, and of course no ordering is expected. As will be shown below, there is an intimate connection between the semiconducting and magnetic properties which follow directly from the change of valence of the Sm ion as a function of temperature. At and near room temperature, x-ray absorption measurements[4] and magnetic susceptibility data[5] indicate that the Sm is present in both its divalent and trivalent state, with the latter being most prevalent.

The cubic CsCl-type structure of the rare-earth hexaborides admits only one site for the Sm ion. This means that thermal energy at room temperature must be sufficient to ionize an electron from its $4f^6$ environment. As the temperature is lowered, then, one might expect to find an exponential temperature dependence of various properties related to carrier concentration. Striking confirmation for such a model has been found in the temperature dependence of the resistivity shown in Fig. 1.

It has been well established theoretically that the boron framework in the hexaboride lattice acquires two additional electrons per six boron atoms to complete its covalent bonds.[6] Experimental confirmation for this model has been found by Johnson and Daane[7] who have shown that the alkaline-earth hexaborides are semiconduc-

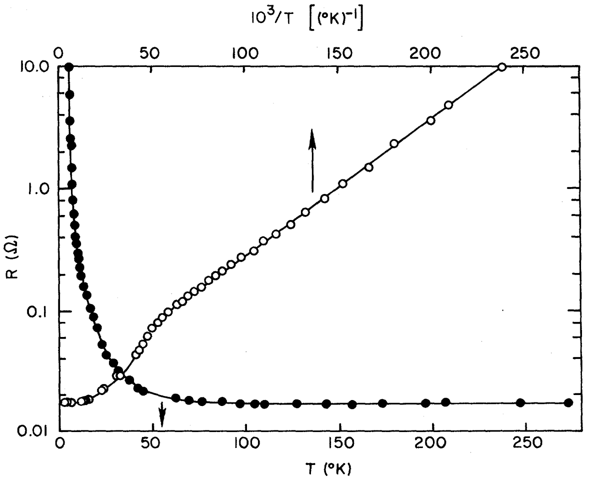

FIG. 1. Resistance of SmB_6 as a function of temperature. Closed circles: resistance versus T; open circles: resistance versus $10^3/T$.

tors. Hall-effect measurements of the hexaborides of the trivalent ions Y[7] and La[8] show, assuming that all the conduction electrons are in a single band, that there is within a few percent of one conduction electron per trivalent ion. In Fig. 1 both types of behavior, i.e., metallic and semiconducting, are evident as the temperature is lowered. We observed no major difference between the sintered and arc-melted samples, although the activation energy associated with the resistivity (0.0023 eV) differs slightly for the two samples (about 10%). At present we have insufficient data to determine whether there is an appreciable temperature dependence of the energy gap.

At 3°K the resistivity shows a sharp break and increases only by a factor of 1.3 with decreasing temperature down to 1.6°K. This may be due to the onset of another type of conduction mechanism which bears some relation to the impurity-band phenomena which have been studied so extensively in extrinsic semiconductors. At this time, however, we cannot rule out the possibility that it may be due to trace impurities of other rare-earth ions in the lot of Sm metal from which the samples were prepared (see below). To explain this sharp break with the above model, we would need about 0.2% impurities of other trivalent rare-earth ions. Preliminary Hall-effect data show that the ratio of the Hall coefficients at room temperature and 4.2°K is equal to the ratio of the resistivities at the corresponding temperatures.

The SmB_6 was prepared from 99.9% pure redistilled Sm and 99.999% pure zone-refined B by heating pressed pellets of a stoichiometric mixture of −100 mesh B and filings of Sm. The major impurities in Sm were other rare-earth metals as 0.05% Nd, 0.03% Eu, and 0.3% Gd. The given impurity concentrations can be responsible for the flattening out of the resistivity below 3°K. After compacting at 90 000 psi, the pellets were heated to 2000°C for 3 h in sealed Ta crucibles under vacuum. Dark blue crystalline compacts which had shrunk 6.5% in diameter were obtained. For fused samples the compacts were arc melted in argon with no loss in weight. All samples were examined by powder x-ray diffraction techniques and were found to be clean within the precision of the powder method. The preparation of SmB_6 through a direct reaction of Sm_2O_3 with B in the same kind of sealed Ta crucible was not as successful.

The reciprocal magnetic susceptibility per mole between 1.6 and 1000°K is given in Fig. 2. As we pointed out in the introduction, no magnetic ordering was observed down to 0.35°K. The weaker than linear increase at higher temperatures of the reciprocal susceptibility is characteristic of Sm^{+3} and occurs also in the compounds of trivalent Sm with N, P, As, and Sb. This behavior is due to the fact that the $J = \frac{5}{2}$ and $\frac{7}{2}$ levels of the multiplets lie relatively close together resulting in an almost temperature-independent van Vleck susceptibility superimposed on the Curie-Weiss law of the trivalent Sm ion. In Fig. 2 it can be seen that at low temperatures the reciprocal susceptibility flattens out. The behavior below 10°K must be attributed to the rare-earth impurities present in the Sm. The divalent Sm should show the same temperature dependence of the susceptibility as the trivalent Eu, which shows a temperature-independent van Vleck susceptibility at low temperatures, e.g., as in the compound EuN. In the intermediate region the ratio of the divalent and trivalent Sm is changing and the reciprocal susceptibility curve reflects this fact. Direct evidence for the changing electronic configuration of Sm from trivalent to divalent with decreasing temperature has also been found by the observation that the size of the unit cell goes through a minimum near 150°K.[9]

In conclusion we would like to emphasize that the unusual properties of SmB_6 stem from the fact that the semiconducting and magnetic properties are so intimately tied together. At absolute zero the Sm ion is in its nonmagnetic $4f^6$ configuration. However, the exponential temperature dependence of the resistivity at low temperature shows that only an exceedingly small energy is required to ionize an electron into the

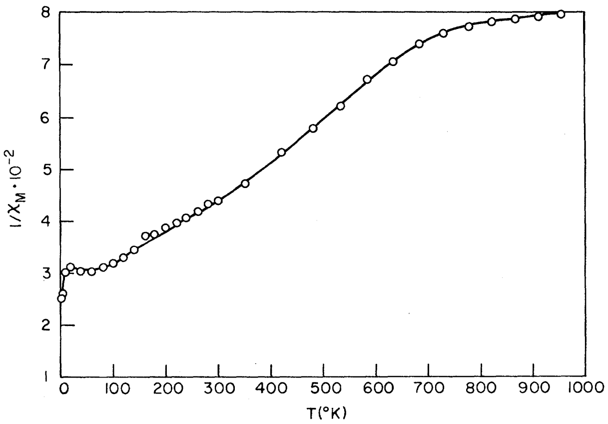

FIG. 2. Reciprocal molar susceptibility of SmB_6 as a function of temperature.

conduction band. Each time this happens, as the temperature is raised for example, a magnetic ion is formed in the lattice. At higher temperature the extra entropy associated with the magnetic ion degeneracy favors its formation and the Sm becomes predominantly trivalent. While such a model is conceptually quite clear, its quantitative application to magnetic behavior is complicated by the uncertainty of the crystal-field splittings of the low-lying levels of the trivalent Sm ion. It may be surprising that the two configurations are so close in energy but actually we were more surprised that it was possible to form polycrystalline SmB_6 so well by simply reacting the elements that its intrinsic properties were not masked.

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OBSERVATION OF LIBRATIONAL WAVES IN THE ORDERED STATE OF SOLID HYDROGEN AND DEUTERIUM BY RAMAN SCATTERING

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The Raman spectra of high purity o-H_2 and p-D_2 at liquid-helium temperatures have been obtained. Features which appear below the ordering temperature are attributed to librational waves within the $J=1$ manifold of states. On the basis of a comparison with recent theories of the ordered state, a new structure is proposed.

We have observed[1] by laser Raman scattering the theoretically predicted[2-5] librational excitations of the ordered state of solid orthohydrogen and paradeuterium. The observations agree only qualitatively with existing theories and two possible explanations for the discrepancies are proposed. The first implies that the rigid-lattice, nearest-neighbor quadrupole-interaction model is inadequate in the present case. The second alternative explanation requires a crystal structure with symmetry lower than the previously assumed[2-5] $Pa3$ space group.

The ordered state of hydrogen is one in which the molecular axes assume preferential orientations with respect to the crystalline axes, analogous to the ordering of spins in an antiferromagnet. Because the anisotropic interactions are small compared with the separation of the J levels and because the temperature is low, only the $J=1$ manifold need be considered in solid o-H_2 and p-D_2 and therefore it is the axes of the $J=1$ molecular rotational wave functions that are ordered.

X-ray and neutron data[6] have shown that the molecular centers form an fcc lattice. Theories[7] based on such a rigid fcc lattice and electric quadrupole-quadrupole intermolecular coupling predict the structure of the ground state to be $Pa3$; the neutron-diffraction data are also consistent with this space group. In this structure the axes of the dumbbell-shaped $m_J=0$ wave functions are aligned along the four fcc body diagonals. The crystal is divided into four sublattices with the oriented molecules on a given sublattice