SUPERCONDUCTIVITY IN SEMICONDUCTING $SrTiO_3$

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Recently there has been some discussion of the possible existence of superconductivity in semiconductors.[1-3] The relevance of several material parameters has been discussed by one of the authors[1,2]; of these, the criteria of high charge carrier concentration, large effective mass, many valleys, and large dielectric constant are met in reduced strontium titanate,[4-6] so that a search for a superconducting transition in this substance seemed appropriate.

This note is to report the finding of superconducting transitions in three samples of reduced strontium titanate.[7] The transitions in two of the specimens, TiR2a′ and VR8, were detected by four-lead dc resistance measurements, as shown in Fig. 1. As noted, the transitions occurred within a range of less than 0.1°K at about 0.25°K and 0.28°K, respectively. The normal resistance in each case was gradually restored by increasing the dc magnetic field intensities 300-1200 Oe and 200-2400 Oe, respectively. The magnetic susceptibility of a third specimen, HR6, was measured in an effort to ascertain whether the superconductivity was a bulk effect, and in fact such evidence was obtained.

Because of the large penetration depth and short mean free path expected in strontium titanate, a value for the Landau-Ginzberg parameter[8,9] $\kappa > 10^2$ was estimated, and the predicted extreme type II superconductivity was observed. At very small measuring fields a large diamagnetism was observed, and estimates made on the basis of sample shape, coil filling factor, and mutual inductance indicate that the effect corresponds approximately to perfect diamagnetism. When a static magnetic field of a few millioersteds was superimposed on the ambient field, the susceptibility dropped rapidly to zero as shown in Fig. 2, indicating an extremely small H_{c1}. The difference between H_{c1} and H_{c2} seems to be of the order of a thousand oersteds for this material which is consistent with the estimated value for κ. It was found also that the magnetization at fields greater than H_{c1} was nearly irreversible, i.e., little change in the susceptibility occurred on lowering the static field after H_{c1} had been exceeded. In a subsequent experiment a portion of sample HR6 was powdered to a particle size of 0.1-0.01 mm, and coils were placed so as to reduce the ambient field at the specimen to

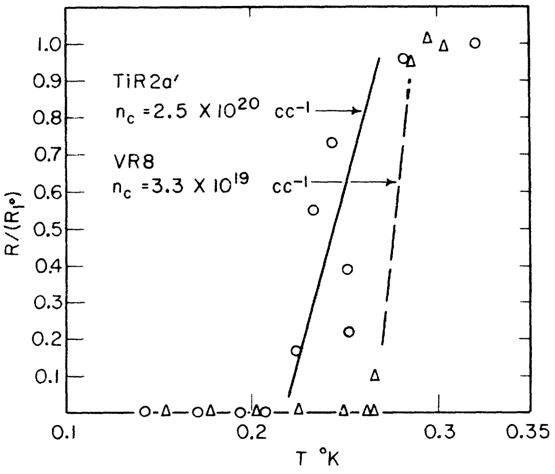

FIG. 1. The ratio of sample resistance at temperature T to that at 1°K, as a function of temperature.

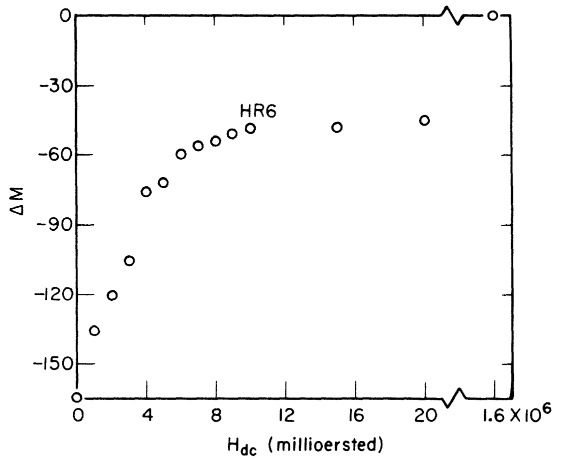

FIG. 2. The change in mutual inductance induced by specimen HR6, $n_c = 2.6 \times 10^{19}$ cc^{-1}, as a function of applied field.

10 millioersteds or less. Again a susceptibility approximating complete diamagnetism was observed. The first critical field was 0.4 ± 0.1 Oe. The susceptibility of the powder specimen was very nearly reversible in fields up to several kilo-oersted.

The reduced samples were prepared from single crystals of $SrTiO_3$, and subsequently lapped and cleaned to remove surface material. Two of the samples were reduced by prolonged heating in a vacuum of 10^{-5} to 10^{-7} mm Hg. Sample TiR2a′ was reduced in the presence of titanium metal, and VR8 by vacuum alone. The third sample, HR6, was reduced in a dynamic flow of hydrogen at 950°C. Samples TiR2a′ and VR8 were quenched more rapidly than HR6 after reduction, and thus may be more strained which could alter the transition temperatures of these samples.[1,2] The resistivities and Hall coefficients of the specimens were measured over the temperature range 2°K-300°K. All three samples were degenerate at liquid helium temperatures.

X-ray diffractometer measurements on single-crystal specimen HR6 showed the material to be a good single crystal of the perovskite structure. The same sample when powdered was shown to be of one phase, viz. perovskite; the sensitivity for the detection of second phases was better than $\frac{1}{2}$%. Special care was taken in looking for the phases Ti and TiO.

The superconducting transitions were observed by cooling the specimens by thermal contact through Apiezon N grease with single crystals of chromium potassium alum in an adiabatic demagnetization apparatus, and the magnetic susceptibility was observed in a similar way, except that copper wires were interposed between the specimen and the cooling salt to avoid interference with the specimen mutual inductance coils. The rate of temperature increase at 0.25°K during the resistance measurements was typically 3 millideg/min.

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[7] Since submittal of the original manuscript, many samples have been measured with carrier concentrations as low as 7×10^{17} per cm^3. Superconducting transitions have been found in all samples, and at the low carrier concentrations T_c is found to increase with n_c approximately as expected (cf. references 1 and 2). This behavior at low and high carrier concentrations has been discussed and interpreted already by the authors in postdeadline papers presented at the meeting of the American Physical Society, Philadelphia, Pennsylvania, 24 March 1964 (unpublished).

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STABILITY OF THE NÉEL GROUND STATE IN A TWO-SUBLATTICE FERRIMAGNET*

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Most literature dealing with ferromagnetic resonance and related topics assumes that the static magnetization vector associated with each magnetic sublattice of the crystal is spatially uniform. Since it is now known that such a configuration is not always the ground state,[1-3] it is worth while to re-examine the conditions under which the assumption *is* valid.

A convenient approach to this problem is to consider the spin-wave (magnon) spectra $\omega_k(\vec{k})$ associated with the *assumed* Néel ground state.[4] A necessary condition that this configuration be stable is that $\omega_k^2 \geq 0$ for *all* allowed values of $\vec{k}$. Since the spin waves form a complete set, any