NEW PHENOMENON IN SEMIMETALS AND SEMICONDUCTORS

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We have found and investigated an unusual property which exists at low temperatures when a current flows through an extremely small ohmic contact (area $\sim 10^{-10}$ cm^2) between a normal metal and a single crystal of Bi, Sb, or semiconducting BiSb alloys. We propose as a tentative explanation for this that the region of the single crystal in ohmic contact with the metal becomes superconducting.

The effect is simply demonstrated in the current-voltage curves of Fig. 1. As the current is increased to a current I_c, the resistance of the sample switches from a low resistance R_L at low currents to a high resistance R_H. The effect has no polarity with respect to bias voltage. Under certain conditions, when the current is decreased from a value $>I_c$, the transition from R_H to R_L occurs at a current $I_c' < I_c$, causing a hysteresis as seen in the figure. A portion of the hysteresis seems somewhat dependent on the sweeping speed.

The small contact areas are derived by evaporating a metal through a pinhole in an oxide layer on the cleaved surface of a single crystal of Bi, Sb, or BiSb alloys. The substrate is kept near room temperature to avoid any alloy formation during the evaporation. Al and In, at temperatures where they were nonsuperconducting, and Ag were used as the counter electrode. The effect was seen with slightly different characteristics, dependent on the metal used. The data presented here are, for the most part, of Al on Sb, because with this combination the phenomenon is easiest to observe.

The effect is strongly dependent on the temperature, as can be seen for Sb in Fig. 1. However, there exist differences between samples. For example, the aforementioned hysteresis, which depends on temperature, was not always present and is not understood at this time. Moreover, the units were very sensitive to "electrostatic shocks" causing the hysteresis to change or disappear as well as changes in R_L and R_H to occur. Some data were taken on samples which exhibited no hysteresis and had a rounded transition around I_c as the curve at 4.20°K shows in Fig. 1. The temperature dependence of I_c for one sample is shown in Fig. 2.

The effect is also strongly dependent on the magnitude of the magnetic field. The general shape of the I-V curve is the same independent of the direction of the magnetic field relative to the current direction. However, the structure at currents $\sim I_c$ is slightly different, but we treat this as of secondary importance and will not say more of this at the present time. All data reported here were for H perpendicular to the interface. It should be noted that for Sb as opposed to Bi, R_L and R_H were not strongly dependent on magnetic field in the range studied here.

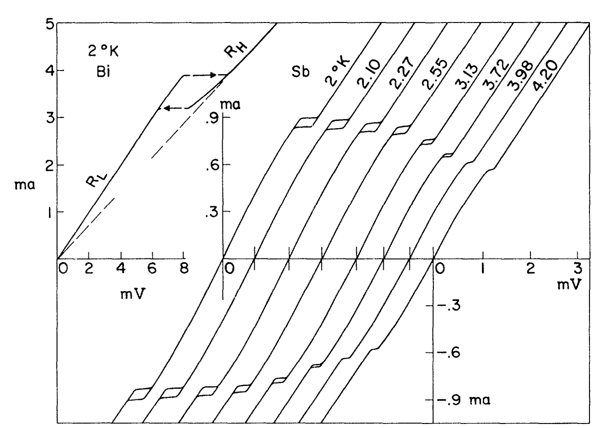

FIG. 1. Plots of I vs V for Al on Sb for different temperatures and a plot of I vs V for Al on Bi at 4.2°K.

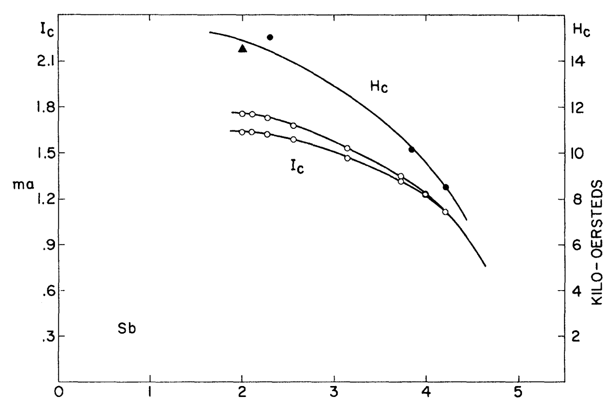

FIG. 2. I_c and I_c' (open circles) with $H=0$, vs T, and H_c vs T (closed circles) for one Al on Sb sample. One point (triangle) of H_c vs I for another Al on Sb sample.

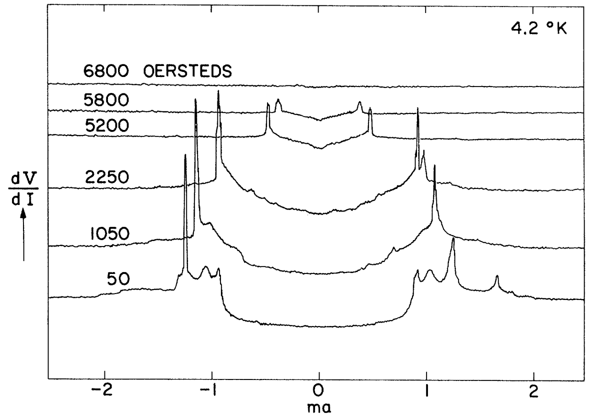

FIG. 3. A plot of dV/dI vs I for Al on Sb for different magnetic fields. The zero level of dV/dI was shifted for each curve.

Figure 3 is a plot of dV/dI vs I for different magnetic fields at a given temperature. The existence of multiple peaks in dV/dI vs I at currents near I_c indicate that the current flows through more than one pinhole. It is found that I_c is linearly dependent on magnetic field and I_c falls to zero at H_c. It is also found that there is a temperature dependence of the slope of I_c vs H such that H_c increases faster as T is lowered than $I_c(H=0)$ does. Measurements of H_c for different temperatures are plotted in Fig. 2 for the same sample that the temperature dependence of I_c is plotted.

Figure 2 indicates that H_c and I_c will probably fall to zero at some temperature T_c, in excess of 4.5°K. The general character of the phenomenon is therefore very similar to having a piece of superconductor some place in the sample. The fact that the phenomenon exists with Ag as a counter electrode eliminates the possibility of the metal being the superconductor. The dependence on magnetic field and temperature rules out a tunneling effect,[1] and hence the oxide cannot be involved. It is well known that the normal phases of Bi, Sb, and BiSb are not superconducting, and it appears that the possible strains involved are not large enough to cause phase transitions to high-pressure superconducting metallic phases.[2] Our case is probably different from the situation of Yntema et al.'s composite superconductor of compressed Bi and TiO_2 powders which was reasonably well explained on the basis of mounting thermal stress between both materials.[3] Also, it should be mentioned that Bi forms a number of alloy superconducting phases, and Sb too.[4] It, however, is unlikely to have such alloys at the interface without further heat treatment. Our fabrication process is a rather gentle vacuum evaporation of a metal such as In, Ag, or Al on a room-temperature substrate of single-crystal Bi, Sb, or BiSb alloys. The lack of structure in the dV/dI vs I curve around $I=0$ rules out effects due to induced superconductivity due to plasma pinch or high current densities.[5]

We now examine the details of the I-V characteristics. Table I gives the results. From the fact that the resistances are rather insensitive to temperature we can calculate, using values of ρ at room temperature, an equivalent diameter for a circular contact having the same spreading resistance. In all cases the diameter is ~10^{-5} cm and the critical current density J_c is ~10^7 A/cm^2 for Bi and Sb and ~10^5 A/cm^2 for BiSb alloys. The similarity of $R_H/R_L \sim 1.5$ to the ratio of the spreading resistance for a flat to hemispherical contact of $\pi/2$ leads us to believe that a small portion of the nonmetal under the contact point becomes superconducting.

We would like to propose a possible explanation to account for the superconductivity. There exists an electric dipole layer at the junction due to a difference in the contact potential $\Delta V = qNd/\epsilon$. Here qN, d, and ϵ are the charge of the dipole, the Debye length, and the permit-

Table I. Experimental parameters.

	R_L	R_H	$R_{300°K}$	d^a (cm)	J_c (A/cm^2)
Sb	~0.5	~0.75	$1\sim2$	~1.5×10^{-5}	1×10^7
Bi	~2.0	~3.0	$5\sim10$	~1.5×10^{-5}	2×10^7
Bi-Sb alloy (87-13 %)	80	130	···	~2.0×10^{-5}	3×10^5

[a]Assuming the specific resistivity $\rho=2.2\times10^{-5}$ Ω-cm for Sb, 6×10^{-5} Ω-cm for Bi, and 3×10^{-3} Ω-cm for Bi-Sb alloy.

tivity. Assuming $\Delta V = 1$ V, $d = 3\times10^{-6}$ cm, and $\epsilon = 10$ pF/cm (dielectric constant ~100), N becomes $2\times10^{13}/\text{cm}^2$, and therefore N/d approaches $10^{18}/\text{cm}^3$. It is possible that these excess carriers, either electrons or holes, make the semimetal or the semiconductor become superconducting. Our proposal is different from Ginzburg's two-dimensional surface superconductivity.[6] We are continuing to investigate this and other possible explanations.

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DEPENDENCE OF SUPERCONDUCTING ENERGY GAP ON TRANSPORT CURRENT BY THE METHOD OF ELECTRON TUNNELING

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The variation of the superconducting energy gap with transport current has been studied by electron tunneling. Thin films and a compensated geometry were used to minimize diamagnetic effects. The measurements were made near the transition temperature of the films, and are in qualitative agreement with the predictions of the Ginzburg-Landau equations.[1]

Tunneling junctions[2] were made by depositing a strip of aluminum onto a standard glass microscope slide in a conventional evaporator, oxidizing in air for ~1 h, and then depositing a cross strip of superconductor (tin or indium). The substrates were cooled to ~150°K during the latter deposition to reduce agglomeration. At the temperature of the measurements, the aluminum was in the normal state. The geometry is shown in Fig. 1. By interposing a suitable shutter into the vapor stream during deposition, the superconductor was made thicker as well as wider in the region of the contacts in order to reduce the current density at these points. SiO insulation and a lead ground plane (not shown) were added to force a uniform current distribution across the width of the film.[3] Since the films were somewhat thinner than their effective penetration depths at the operating temperatures, the current distribution was expected to be approximately uniform in the thickness direction as well. Under these conditions, the diamagnetic current density was expected to be a small fraction of the total current density at any point in the film, except perhaps very close to the film edges.

The differential tunneling conductance (dI/dV) was measured by applying a small (≈50 μV) ac voltage across the junction and measuring the ac current with a phase-sensitive detector. A feedback loop held the junction voltage constant against changes in the (low) junction impedance. The energy gap was obtained from the value of dI/dV at zero dc bias using a formula given by Giaever and Megerle.[2]

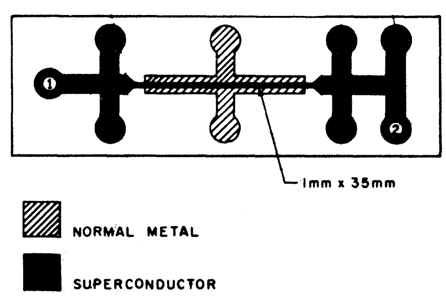

FIG. 1. Geometry of tunneling junction. Tunneling measurements are made between the normal metal and the superconductor while a transport current is passed between terminals 1 and 2.