SUPERCONDUCTIVITY IN $TlBiTe_2$: A LOW CARRIER DENSITY (III-V)VI_2 COMPOUND

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Superconductivity has been found to occur in samples of $TlBiTe_2$ with nominal carrier densities of approximately 6×10^{20} holes per cm^3. The superconducting transition temperature is 0.14°K and the upper critical magnetic field at the absolute zero of temperature is 10 Oe. Replacing Bi with Sb produces the compound $TlSbTe_2$ which remains normal down to 0.015°K.

In 1964, Cohen theoretically predicted that suitable heavily doped semiconductors should become superconductors at low, but experimentally attainable, temperatures.[1] A series of experiments designed to check this prediction quickly led to the discoveries that two p-type degenerate semiconductors, GeTe and SnTe, and one n-type, $SrTiO_3$, are superconductors.[2] The superconducting transition temperature T_0 of these compounds is a function of carrier density and lies in the range 0.03-0.5°K for carrier densities in the range 10^{18}-10^{21} cm^{-3}.

During the five years which have passed since the above results were obtained, no new low carrier density (i.e., $<10^{21}$ cm^{-3}) superconductor has been found that does not contain one of the above three compounds.[3]

This fact leads one to conclude that superconductivity among degenerate semiconductors is indeed a rare phenomenon. We believe that our discovery of superconductivity in the $TlBiTe_2$ system is evidence that superconductivity among degenerate semiconductors is probably as widespread a phenomenon as originally envisioned.[1]

Cohen[1,2] has elucidated those normal-state parameters such as high carrier densities, large effective mass, many-valley band structure, etc. which are important for the occurrence of superconductivity in degenerate semiconductors and semimetals. He also emphasized that the actual calculation of expected superconducting properties from normal-state properties "is limited by the fact that the normal-state properties must be known very well." Thus, by and large, one is essentially left to his own intuition, or that of his colleagues, as to what materials he should investigate for the occurrence of superconductivity.

$TlBiTe_2$ and $TlSbTe_2$ have a room-temperature structure which is a rhombohedral distortion of the NaCl strucutre.[4] Mazelsky and Lubell[5] reported that $TlBiTe_2$ has a positive Hall coefficient lying in the range 0.30-0.35 cm^3/C. These facts are partly responsible for the suggestion[6] that these ternary (III-V)VI_2 compounds might behave, as far as superconductivity is concerned, in a manner analogous to the IV-VI compounds GeTe and SnTe.

Samples of $TlSbTe_2$ and $TlBiTe_2$ were prepared from a melt in a manner described elsewhere.[7] Temperatures between 1.2 and 0.015°K were produced by the magnetic cooling method utilizing potassium chrome alum as the coolant salt. The experimental arrangement of salt and sample has been previously described in detail.[8]

Superconductivity was detected from measurements of the magnetic susceptibility of the sample as a function of the absolute temperature. Data were obtained by an ac mutual-inductance technique[8] utilizing a modified Hartshorn-type bridge[9] operated at a frequency of 27 Hz using a 0.01-Oe measuring field.

Our initial observation of superconductivity in $TlBiTe_2$ was made on a rectangular bar $3 \times 3 \times 10$ mm cut from the grown ingot by a diamond cutoff wheel. Figure 1 contains plots of χ' and χ'', the in-phase and out-of-phase components of the ac magnetic susceptibility, as functions of the absolute temperature. These data were obtained in a residual magnetic field of 10^{-2} Oe. Our experimental definition of the zero-field transition tem-

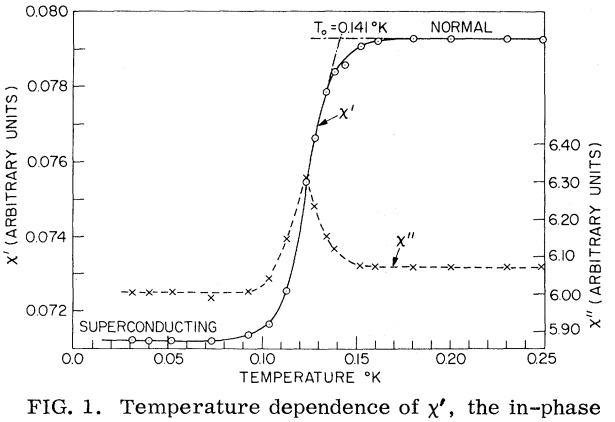

FIG. 1. Temperature dependence of χ', the in-phase component, and χ'', the out-of-phase component of the ac magnetic susceptibility with the sample in a residual magnetic field of 0.01 Oe.

perature T_0 is depicted in the figure. A subsequent experiment on a larger section of the ingot yielded a broader transition, ~0.1°K wide, indicating that the ingot was not strictly homogenous. Weak-field Hall data obtained at 4.2°K on samples subsequently cut from the larger section yield nominal carrier-density values p^* of $(6.2 \pm 0.1) \times 10^{20}$ cm^{-3}. By definition $p^* = 1/R_0 e$ where R_0 is the weak-field Hall coefficient and e is the electronic charge.

Critical magnetic-field data were obtained by balancing the ac mutual-inductance bridge with the sample in the superconducting state and then recording the bridge output as the sample is subjected to an increasing dc magnetic field. For a given temperature, H_c(midpoint) is defined as that value of magnetic field which, for increasing values of H, produces a χ' value midway between the superconducting and normal-state values. H_c(completion) is the value of H at which χ' first becomes independent of H for increasing values of H.

By performing a series of such field "sweeps" at different sample temperatures one obtains critical magnetic field data as shown in Fig. 2. These data show that $H_{c2}(0)$ is approximately 10 Oe.

A value of 10 Oe for $H_{c2}(0)$ is rather low for a sample with a T_0 of 0.14°K; see Table I. One reason for this may be the fact that $TlBiTe_2$ has a much lower electrical resistivity than either GeTe or SnTe. This could lead to a smaller value for $\kappa(T_0)$, the Ginzburg-Landau parameter, which for alloys is approximately given by the well-known formula

$$\kappa(T_0) \cong \kappa_l(T_0) = 7.5 \times 10^3 \gamma^{1/2} \rho(T_0)$$

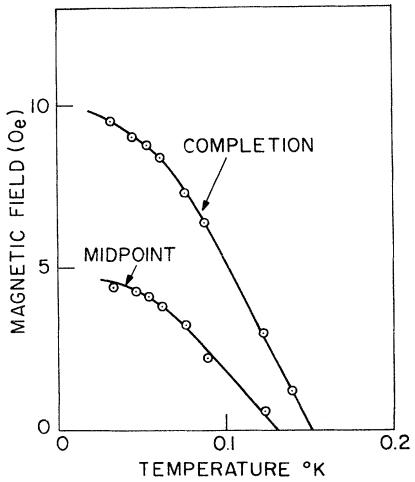

FIG. 2. Critical magnetic field curves of $TlBiTe_2$ with a p^* of $(6.2 \pm 0.1) \times 10^{20}$ per cm^3.

In this equation γ is the coefficient of the linear term in the specific heat expressed in erg/cm^3 and ρ is the normal-state resistivity in Ω cm. If γ does not change drastically as we pass from the IV-VI compounds to the (III-V)VI_2 compounds, then we see that κ for $TlBiTe_2$ would be at least eight times smaller than the GeTe values and at least five times smaller than the SnTe values. Such considerations lead one to expect that κ for $TlBiTe_2$ has a value near unity.

The paucity of published data regarding the normal-state properties of $TlBiTe_2$ precludes any comparison between Cohen's theory and experiment. The normal-state[7] data for the low-temperature electrical resistivity of $TlBiTe_2$ suggest that this material is more likely to be a semimetal than a degenerate semiconductor. Geller[10] has proposed a model to explain the occurrence of superconductivity and semiconductivity in intermetallic compounds with the NaCl structure. A value of 0.14°K for T_0 for a sample with a p^* of 6×10^{20} per cm^3 is too high to agree with the published T_0 vs p^* curve of Geller.

The discovery that $TlBiTe_2$ is a low carrier density superconductor has, we feel, more significance than just adding another material to the ever-growing list of superconductors. The low-temperature studies of R_0 and ρ (T), which this work engendered, have shown that the normal-state properties of this compound are distinctly different from those of the IV-VI compounds such as SnTe and PbTe. This raises questions about

Table I. Selected superconducting semiconductors. P^* is the nominal carrier density, T_0 is the superconducting transition temperature, $H_{C2}(0)$ is the extrapolated value for the upper critical magnetic field, $\rho_{4.2°K}$ is the normal-state resistivity at 4.2°K, and $\kappa(T_0)$ is the derived value of the Ginsburg-Landau parameter.

Sample	P^* (10^{20} per cm)	T_0 (°K)	$H_{c2}(0)$ (Oe)	$\rho_{4.2°K}$ ($\mu\Omega$)	$\kappa(T_0)$
$TlBiTe_2$	6.2	0.141	10	7.8[a]	•••
SnTe	12.8	0.104	22	36[b]	3.9[c]
	16.9	0.174	60	44	5.6[c]
GeTe	8.6	0.080	~20		•••
	9.3	0.172	130	~60	6.1
	11.8	0.250	270		9.3

[a]Ref. 7.

[b]A. Sagar and R. C. Miller, in Proceedings of the International Conference on the Physics of Semiconductors, Exeter, England, 1962 (The Physical Society, London, England, 1962).

[c]See bibliography cited in Ref. 2.

the true carrier density in $TlBiTe_2$ and its relationship to T_0. Furthermore, the three sets[5,7,11] of normal-state measurements on $TlBiTe_2$ cited do not agree with one another. This could be due to variations in stoichiometry, but it might also reveal the presence of an order-disorder phenomenon[7] which controls the properties of $TlBiTe_2$ in its normal and superconducting states.

The value of $T_0 = 0.14°K$ for $\rho^* = 6.2 \times 10^{20}$ cm^{-3} is almost an order of magnitude larger than what this carrier concentration would be expected to produce in SnTe. While this value for T_0 is also at variance with the reported data for GeTe, for which the T_0-vs-p^* data decrease rapidly for p^* values less than 12×10^{20}, it suggests, albeit weakly, that the low carrier density samples of GeTe be re-examined using grown rather than sintered samples.

Clearly, further work is needed before one can pass judgement on the applicability of the many-valley model of Cohen[1] or the "ionic-type" model of Geller.[10] Both models have been invoked to predict superconductivity in low carrier density compounds of the NaCl structure.

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INVESTIGATION OF THE FERMI SURFACE OF V_3Si BY MEANS OF POSITRON ANNIHILATION*

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Measurements of the angular correlation of annihilation radiation from oriented single crystals of V_3Si are reported, exhibiting marked anisotropies. These anisotropies are interpreted as hole pockets in the Fermi surface and are compared with the predictions of the linear chain model.

In this Letter we report the first experimental results relating to the Fermi surface of V_3Si, a high-temperature superconductor ($T_c = 17°K$). V_3Si has a β-W crystal structure as do all known superconductors with high T_c (Nb_3Sn, Nb_3Al, etc.). It was suggested[1] that the high T_c as well as other anomalous properties[2] may be due to the linear chain structure of the vanadium and niobium atoms in such a lattice, producing planar Fermi surfaces perpendicular to the ⟨100⟩ directions of the chains. An augmented plane wave (APW) calculation for V_3X compounds was carried out by Mattheiss,[3] while the linear chain model was studied in detail in a series of papers by Friedel, Labbe, and Barišić.[4] The effect of interchain interactions has recently been investigated,[5] indicating that highly planar sections of the Fermi surface can persist ("torn out" planes). To date, no standard Fermi surface measurements (as de Haas–van Alphen, etc.) have been performed on high-T_c materials. Kohn suggested some time ago that the predicted planar Fermi surface could be observed by positron-annihilation techniques. Such an experiment on V_3Si was reported by Mihalisin and Parks,[6] who failed to observe any anisotropy in the angular-correlation curves.

If positron annihilation in a metal is treated in the independent-particle approximation,[7] the probability that the two annihilation photons carry