

so that

$$\begin{aligned}
 A &= 2\Xi_0 \int \frac{1}{2} \epsilon d\epsilon \left\{ 1 - \frac{\epsilon - \zeta}{[(\epsilon - \zeta)^2 + \Delta_s^2]^{\frac{1}{2}}} \right\} \\
 &\quad - 2\Xi_0 \int_{\zeta}^{\zeta + \hbar\omega_D} \frac{1}{2} \epsilon d\epsilon \left\{ 1 - \frac{\epsilon - \zeta}{[(\epsilon - \zeta)^2 + \Delta_s^2]^{\frac{1}{2}}} \right\} \\
 &\quad + 2\Xi_0 \zeta_0 (\zeta_0 - \zeta) - 2\lambda N (\zeta_0 + \eta_0) v_f^2 \\
 &= -2\lambda N \eta_0 v_f^2 \\
 &\quad + \Xi_0 \left[-\hbar^2 \omega_D^2 + \hbar^2 \omega_D^2 (1 + \Delta_s^2 / \hbar^2 \omega_D^2)^{1/2} \right. \\
 &\quad \left. - \Delta_s^2 \sinh^{-1} \hbar \omega_D / \Delta_s \right].
 \end{aligned}$$

Using (23), we have approximately

$$\begin{aligned}
 H_0^2 / 8\pi &= -2\lambda N \eta_0 v_f^2 + \Xi_0 \left(\frac{1}{2} \Delta_s^2 - \Delta_s^2 \sinh^{-1} \hbar \omega_D / \Delta_s \right) \\
 &\quad + \frac{1}{2} J N \lambda^2 u_f^2 v_f^2 + \sum_k u_k v_k (1 + N \lambda |V_1 u_f v_f|) \\
 &= \frac{1}{2} \Xi_0 \Delta_s^2 + N \lambda |V_1 u_f v_f| \Xi_0 \Delta_s \sinh^{-1} \hbar \omega_D / \Delta_s \\
 &\quad - 2\lambda N \eta_0 v_f^2 + \frac{1}{2} J N \lambda^2 u_f^2 v_f^2. \quad (C1)
 \end{aligned}$$

The last two terms can be rewritten as

$$\begin{aligned}
 &\frac{1}{2} J N \lambda^2 v_f^4 (v_f^{-2} - 1 - 4\eta_0 \lambda N / J N \lambda^2 v_f^2) \\
 &= \frac{1}{2} J N \lambda^2 v_f^4 [v_f^{-2} (1 - 4\eta_0 / \lambda J) - 1] \\
 &= \frac{1}{2} J N \lambda^2 v_f^4 (1 + 4\theta / J),
 \end{aligned}$$

from (17). Combining the first two terms in (C1), using (23) to eliminate V_1 , and using (17) to eliminate v_f , and neglecting unity compared with θ/J , we finally get Eq. (31).

Superconductivity in Indium Antimonide*

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Two samples of the metallic phase of indium antimonide were stabilized at atmospheric pressure by cooling semiconductor grade material from 100°C to 77°K at a pressure of 27 kbars, and then removing the pressure. Measurements of the magnetic moment of these samples down to 1.1°K were made using a sample-motion technique in a uniform magnetic field. Below 1.89°K, the samples exhibited bulk superconducting properties, in agreement with previous work. A high-field tail on the magnetization curves and the existence of considerable locked-in flux as the magnetic field was reduced were taken to be indications of a high state of residual strain in the sample. The slope of the critical field curve at 1.89°K was found to be $(\partial H_c / \partial T)_{T_c} = -103 \text{ G}/^\circ\text{K}$. This is consistent with values found for soft superconductors with similar transition temperatures, and implies a normal state electronic specific heat per cm^3 , which is roughly half that of white tin. White tin has the same average ionic mass as metallic indium antimonide, and presumably the same electronic density.

INDIUM antimonide and several other III-V semiconducting compounds, as well as germanium and silicon, exhibit transitions into a high-pressure modification which has metallic properties.^{1,2} This transition has been studied in some detail for indium antimonide by Jayaraman *et al.*,³ who showed that the transition should occur near 23 kbars at room temperature, and that the transition pressure should depend only very slightly on temperature. It was suggested that the properties of metallic InSb should be reasonably close to those of white tin, since tin separated In and Sb in the periodic table, and these two metallic solids should have the same average ionic mass, and from elementary

considerations, the same electronic density.³ Jamieson subsequently showed that the crystal structure of this phase was very close to, if not identical with, that of white tin.⁴ Since white tin is a superconductor with a transition temperature $T_c = 3.7^\circ\text{K}$, it was interesting to speculate on the possibility that this new phase of InSb and the metallic phases of the other semiconductors would become superconducting. InSb appeared to be ideally suited for an investigation of this point, since Jayaraman *et al.* commented on the slow transition rate of this transformation in InSb at room temperature,³ and Jayaraman suggested the possibility that the metallic phase of this solid might be quenched in by cooling a transformed sample under pressure to liquid-nitrogen temperatures, and then removing the pressure.⁵ This method would appear to be feasible only for InSb, partially because of the transition kinetics, and partially because of the relatively low transition pressure.

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¹ H. A. Gebbie, P. L. Smith, I. G. Austin, and J. H. King, *Nature* **188**, 1095 (1960).

² S. Minomura and H. G. Drickamer, *Phys. Chem. Solids* **23**, 451 (1962).

³ A. Jayaraman, R. C. Newton, and G. C. Kennedy, *Nature* **191**, 1288 (1961).

⁴ J. C. Jamieson, *Science* **139**, 847 (1963).

⁵ A. Jayaraman (private communication, November 1962).

Metallic indium antimonide has been obtained at zero pressure in this manner, by Darnell and Libby,⁶ and Geller *et al.*⁷ Bömmell *et al.*,⁸ and Geller *et al.*⁷ have used what are essentially alternating-current resistivity measurements to show that the metallic phase of InSb is a superconductor with a transition temperature T_c below 2.1°K. The second authors reported measurements down to 0.4°K and concluded that the probable critical field at absolute zero was $H_0=1.1$ kG.⁷

The bulk superconducting properties of a substance are reflected more directly in the magnetic moment versus field relationship of a sample than in resistivity or alternating current measurements. These latter measurements are more directly affected by strains and inhomogeneities and can give only maximum values of T_c and the critical field $H_c(T)$. For this reason, we felt it important to make the magnetization measurements on bulk samples of metallic InSb which are described below.

The starting material was semiconducting grade n -type polycrystalline InSb obtained from Cominco Products, Inc.⁹ Cylindrical samples of this material, $\frac{3}{16}$ in. in diameter by $\frac{1}{4}$ in. long, were placed in a Carboloy cylinder, $\frac{1}{4}$ in. i.d., and silver chloride was packed on both ends and around the sides of the cylindrical sample to act as a pressure transmitting medium. Closely fitting pistons were placed in each end of this cylinder, and the assembled sample holder was placed in a low-temperature hydraulic press. The apparatus and methods which were used are identical with those elsewhere.¹⁰ The sluggishness of the room-temperature transition had been noted previously,³ and we found it necessary to increase the temperature of the sample holder to 100°C in order to run the transition to completion in 2 h at our highest available pressure, 27 kbars.¹¹ The base of the press and the sample holder were quenched in liquid nitrogen while this pressure was maintained constant. The pressure then was released, the sample holder removed from the press, and the sample removed from the cylinder and stored; all these operations taking place under liquid nitrogen. The reverse transition back into the semiconducting phase was found to occur near 220°K, and always resulted in a destruction of the sample due to the large volume change (18.5%⁴) and the resultant stored energy and brittleness of the semiconducting phase. These experimental details are almost identical with those of Darnell and Libby.⁶

⁶ A. J. Darnell and W. F. Libby, *Science* **139**, 1301 (1963).

⁷ S. Geller, D. B. McWhan, and G. W. Hull, Jr., *Science* **140**, 62 (1963).

⁸ H. E. Bömmell, A. J. Darnell, W. F. Libby, and B. R. Tittman, *Science* **139**, 1301 (1963).

⁹ The room-temperature characteristics of the sample were given by Cominco as follows: conductivity 0.005 Ω cm, Hall coefficient in 1600 G 340 $\text{cm}^3 \text{G}^{-1}$, mobility $6.8 \times 10^4 \text{ cm}^2 \text{V}^{-1} \text{sec}^{-1}$, number of carriers $1.8 \times 10^{16} \text{ cm}^{-3}$.

¹⁰ R. I. Beecroft and C. A. Swenson, *Phys. Chem. Solids* **18**, 329 (1961).

¹¹ This indicated pressure includes an unknown frictional contribution of approximately 2 to 3 kbars.

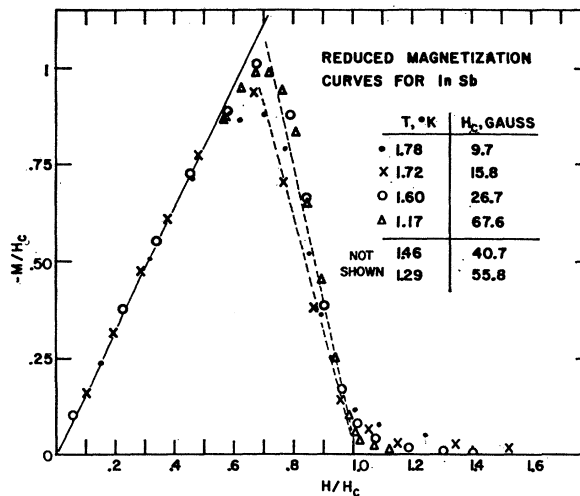


FIG. 1. Reduced magnetization curves for metallic InSb, sample InSb-II, in the superconducting state. H_c was defined as the extrapolation of the linear high-field region to zero magnetization, ignoring the tail on the curve. Data which were obtained at two other temperatures (the values of T and H_c indicated on the figure as not shown) fitted well on a similar reduced plot, and varied systematically in shape with temperature as do the plotted curves.

The magnetic moment as a function of applied field was measured for two cylindrical samples which were manufactured in this fashion. The second sample (InSb-II) was allowed to remain at 100°C for about twice the time of the first sample (InSb-I), and its superconducting properties were measured almost immediately after its removal from the sample holder. In general, the InSb-II data were more ideal than those obtained with the first sample. The magnetic moment was determined directly as a function of applied magnetic field by means of a ballistic galvanometer deflection as the sample was moved rapidly in a uniform magnetic field from one 35 000-turn coil into a second identical but oppositely wound coil.¹² Experimental results were obtained between 1.1 and 1.8°K, and these are shown for InSb-II on a reduced plot in Fig. 1. Here, the critical field H_c is defined as the extrapolation of the high-field linear portion of the magnetization curve to $M=0$. (See the dashed lines.) Data were obtained for six different temperatures for this sample, although data for only four of these temperatures are shown as typical. The slope of the linear high-field portion of the curve is roughly that which would be expected from the demagnetization factor of the cylinder involved.

The slight tail at high fields is indicative of strain in the sample. This was further emphasized by attempts to obtain data with decreasing magnetic field. In general, the magnetic moment remained positive, and showed almost completely locked-in flux. Hence, the data shown in Fig. 1 and summarized for both samples in the H_c versus T^2 curve in Fig. 2 all were obtained on

¹² D. Schoenberg, *Superconductivity* (Cambridge University Press, New York, 1952), 2nd ed., p. 53.

virgin magnetizations from zero field after the sample has been warmed to well above 2°K.

Both sets of data shown in Fig. 2 extrapolate to $T_c=1.88(\pm 0.01)^\circ\text{K}$. This is in agreement with the previous results.^{7,8} The relatively smaller uncertainty in the present measurement is understandable in terms of the difference between bulk and resistive determinations. To verify this point, a quantity of flux was trapped in a specimen by first increasing the field well above H_c and then decreasing it to zero at a temperature well below 1.8°K. The sample was warmed slowly and its magnetic moment determined as a function of temperature. A large decrease in the magnetization occurred near 1.88°K, but ever smaller amounts of residual magnetization remained until the limit of the sensitivity of the apparatus was reached near $2.07(\pm 0.03)^\circ\text{K}$. Thus, the wide transitions observed earlier are due to quite small amounts of the sample which remained superconducting well above the value of T_c which we obtain for the bulk of the sample.

Very little significance can be placed in the lower temperature data shown in Fig. 2. The superconducting transitions were not reversible in any sense, and the rather great concavity of the H_c versus T^2 plot is undoubtedly due to strains. Near T_c , however, the data shown in Fig. 2 are linear and can be interpreted to give

$$(\partial H_c / \partial T)_{T_c} = -103(\pm 5)\text{G/deg.}$$

This implies a value of H_0 of the order of 100 G, which is a factor of ten less than that reported for the alternating current measurements.⁷ Again, this is understandable in terms of the ever greater significance of the strain-induced tail on the magnetization curves as the temperature is reduced. The ratio of (H_0/T_c) is approximately 55 G/°K, and is in fair agreement with data obtained for soft superconductors with transition temperatures below 2°K (Ga, Cd, Zn).¹³ If the BCS¹⁴ or parabolic relationship for the critical field is used to calculate the electronic specific heat coefficient for the normal state, a value of $\gamma=550(\pm 60)$ ergs/cm³-°K² is obtained. This result is to be compared with similar

¹³ Ref. 12, p. 224.

¹⁴ J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

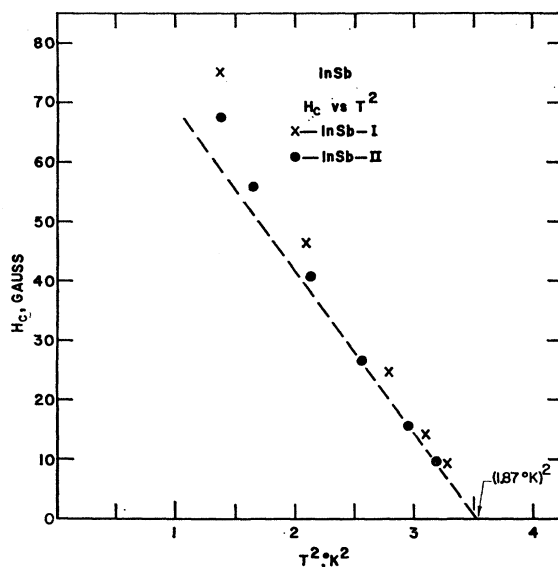


FIG. 2. A plot of H_c versus T^2 for the InSb critical field data for the two different samples which were run.

data for white tin, where $H_0/T_c=82$ G/°K and $\gamma=1080$ ergs/cm³-°K².¹⁵ This factor of two in electronic specific heat (or density of states at the Fermi level) merely emphasizes that the electronic structure of the intermetallic compound InSb is quite different from that of the pure element tin, even though the density,⁴ the average ionic mass and the number of electrons/cm³ are roughly the same for the two metals.

In conclusion, our magnetic critical field measurements on the metallic phase of InSb can be interpreted as being consistent with those which would have been obtained for an ideal soft superconductor with a transition temperature near 2°K. The magnetization curves, Fig. 1, and a plot of H_c versus T^2 as obtained from them, Fig. 2, show evidence of internal stresses in the samples, and the low-temperature data cannot be used in any thermodynamic calculation. Although this metal has the general characteristics of white tin (crystal structure, macroscopic density, density of electrons), its superconducting properties appear to be quite different.

¹⁵ W. S. Corak and C. B. Satterthwaite, Phys. Rev. **102**, 662 (1956).