Superconductivity in the Artificial Metals: Metallic Indium Antimonide, the Indium-Antimonide–Tin Alloys, and Metallic Indium Telluride*

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(Received 9 April 1964)

Superconductivity has been observed in metallic indium antimonide, in the alloys of indium antimonide with tin, and in indium telluride. The compounds and alloys were prepared and stabilized at atmospheric pressure in the way described by Darnell and Libby. Superconducting transition temperatures and critical magnetic fields were obtained by the eddy-current decay method used in measuring resistivities.

SEVERAL binary compounds of the post-transition metals have high-pressure polymorphs that are metals.[1–7] Extensive study of these has been severely restricted because of the high-pressure environment, i.e., the press. Recently, Darnell and Libby have removed this limitation by a cooking and freezing technique[8–10] enabling, in many cases, the recovery of the polymorph at atmospheric pressure. The first polymorph recovered in this manner was metallic indium antimonide which in the subsequent studies was found to have a crystal structure identical to white tin.[8] This form of tin is a superconductor with a transition temperature of 3.7°K. The interesting possibility therefore existed that indium antimonide is also a superconductor.

Samples were prepared in the manner already described by Darnell and Libby[8,9] with a starting material with no one impurity in excess of 40 ppm. All measurements of the superconducting transition temperature were performed with a method similar to that of Bean et al.[11] for measuring the resistivity ratio in metals. Eddy currents are set up in the sample and their decay is observed on the oscilloscope. The decay rate is a measure of the resistivity in the normal state, whereas the decay rate goes essentially to zero with the onset of superconductivity. The details of the apparatus have been described elsewhere.[12]

At 4.2°K, the sample of metallic InSb measuring about 25 mm in length and about 6 mm in diameter was still in the normal conducting state and had a conductivity somewhat less than that of tin at the same temperature. In contrast to tin the superconducting transition for the indium antimonide (II) started at about 2.1°K and was complete at about 1.6°K. This was published in a preliminary brief report[12] and later measurements by us and others[13–15] are in good agreement. The broadness of the transition suggests that the indium antimonide (II) is strained which is presumably a result of its somewhat unusual mechanical properties and method of preparation.

Because of the identical structure of the indium antimonide (II) and tin it seemed possible to form alloys between the two. This was done without great difficulty[8] and the superconducting transition temperatures were compared.[15] As might be expected, the transition temperatures of the new metallic alloys $InSbSn_1$, $InSbSn_2$, and $InSbSn_4$ lie between the transition temperatures observed for $Sn(\beta)$ and $InSb(II)$. The results are exhibited in Fig. 1 which shows the transition temperature as a function of atom fraction of $Sn(\beta)$ in $InSb(II)$. The lower curve represents the temperature at which normal conductivity started to appear at a given $Sn(\beta)$ atom fraction. The upper curve represents the temperature at which the transition to the normal state was completed for the same $Sn(\beta)$ atom fraction. The atomic volumes were calculated from the respective lattice parameters obtained from x-ray data and were found to be essentially the same for $InSb(II)$, $Sn(\beta)$, and their alloys. The variation in the superconducting transition temperature versus atom fraction of $Sn(\beta)$ suggests that these systems are solid solutions in agreement with other evidence[8] leading to the same conclusions. This seems reasonable in view of the fact that the solvent and solute atoms have nearly equal size, have the same "average" valency and form metals with identical crystal structures.

In addition to indium antimonide (II), a second compound with indium was recovered by Darnell and

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Libby in its metallic phase at atmospheric pressure: indium telluride (II), following on work of Banus *et al.* at Lincoln Laboratory[16] who reported adequate metastability for recovery of the metallic phase without cooking or quenching. Again the preparation and some of the physical properties have already been discussed in the preceding article by Darnell and Libby.[8] Indium telluride (II) also was found to have a superconducting transition temperature somewhat below tin, namely at 2.2°K. In contrast to InSb(II), the InTe(II) has a relatively sharp transition width of about 0.01°K. The sharpness of the transition might indicate that the specimens were not highly strained. Measurements in magnetic fields showed that the intermediate state extended over a fairly wide range. This may in part be explained as due to the nonideal geometry of the specimen which consisted of several cylindrical pieces about 5 mm in diameter with lengths from 1 to 12 mm. The results are shown in Fig. 2. The lower curve represents the magnetic field at which the sample became superconducting at a given temperature. The upper curve is a straight line tangent to the experimental curve at low critical fields. This is the curve an ideal superconductor would follow obeying the parabolic expression for the critical field. Extrapolation of the data to zero degrees would indicate a critical field $H_c(0)$ of about 800 G.

In the process of further experimentation, we encountered in one or two cases transition temperatures of 2.5°K. Banus *et al.*[17] had observed transition temperatures of 3.7–3.5°K. This prompted us to perform a series of additional experiments in order to explain these discrepancies.

The effects of impurities and of strain on the superconducting transition temperature are well known. X-ray data of our samples showed no presence of InTe(I) which according to the sensitivity of the method means less than five percent. Spectrographic analysis showed less than 50 ppm of any one impurity. The major
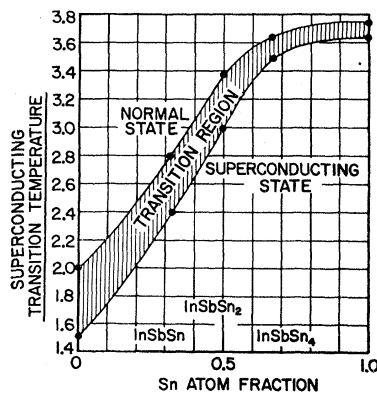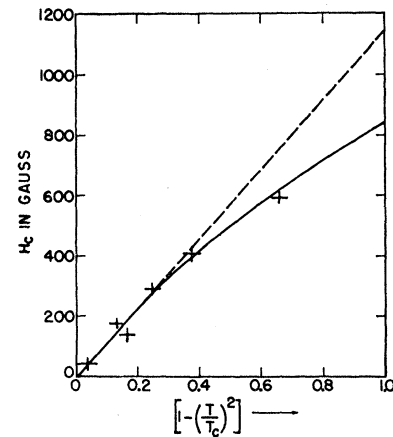

FIG. 2. Parabolic fit of critical magnetic field for InTe(II).

impurity therefore probably was InTe(I) produced by partial conversion either during the preparation or afterwards at atmospheric pressure. Therefore, a sample was prepared and examined in the following manner. First, the sample was converted in a solid-liquid-solid process in which the liquid phase was maintained for thirty minutes at 30-kbar pressure. Then the sample was slowly cooled to 77°K at a pressure of 30 kbar. After the pressure was slowly released, the sample was removed from the press and maintained at 77°K until it was placed into liquid helium. The superconducting transition temperature was found to be 2.2°K. Now, the sample was kept at room temperature for approximately three to four weeks and measured at intervals initially several hours long and later several days long. The measurements were performed as the sample converted gradually to phase I, until the conversion was so far advanced that the onset of superconductivity could no longer be detected. The transition temperatures always remained at 2.2°K giving a strong indication that the presence of phase I did not influence the transition temperature.

Next, effects of strain in the material were investigated. Most likely strain was introduced during the conversion process, since heating for a single short interval at high temperature yielded samples which gave a transition temperature higher than 2.2°K, i.e., upwards to 3.5°K. By annealing at high temperature and with repeated temperature cycling samples with a transition temperature of 2.2°K were obtained. Furthermore, wider transition widths were found to go along with higher transition temperatures. In these cases, annealing from 50 to 100°C or pulverizing reduced the transition temperature. Cracking the samples into 2-mm large pieces reduced the transition temperature by a few tenths of a degree, whereas pulverizing always resulted in a transition temperature of 2.2°K. Since these processes will tend to reduce strain it seems very likely that strain was the cause of the higher transition temperatures. The presence of residual strain in samples of elevated superconducting transition temperatures was also indicated by a slight broadening of the x-ray

FIG. 1. Superconducting transition temperature versus tin atom fraction for the InSb-Sn system.

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diffraction maxima at large angles of 2θ. It is possible that during the preparation of the "strained" samples and their treatment afterwards, a certain amount of phase I was introduced but this was felt to have negligible influence on the basis of the previous experiment.[18]

The lowering of the transition temperature with removal of strain is consistent with general behavior of all B1-type compounds.[19,20] If the transition tempera-

ture of 2.2°K can be associated with a completely strain-free sample then the critical magnetic field extrapolated to zero of about 800 G appears rather high and places InTe(II) as a candidate for type-II superconductivity. Further experiments are planned to investigate this. On the basis of an "average" valency, InTe(II) obeys the Matthias rules. In further comparison with compounds of the same structure, InTe(II) is the eleventh superconductor in the number of B1-type compounds reported as of 1 January 1963[20] and extends the range of reported transition temperatures from 5.6–17.8°K to 2.2–17.8°K.

[18] Recently, Geller et al. [S. Geller, A. Jayardman, and G. W. Hull, Jr., Appl. Phys. Letters 4, 35 (1964)] published results on the transition temperature of InTe(II) as a function of the stoichiometric ratio of In to Te. For a ratio of one-to-one they get a transition temperature of 3.2–3.45°K which is close to the value of Banus et al. We have no explanation of this except for strain since we prepared our samples very carefully and our measured lattice constants agree with those of Geller et al. within 0.02 Å for a ratio of one-to-one.

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Negative Magnetoresistance in Impurity Conduction

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(Received 24 March 1964)

Negative magnetoresistance is observed at 4.2°K in Cd-doped p-type GaAs, vapor deposited n-type GaAs, and P-doped n-type Ge. In n-type GaAs prepared by Czochralski or horizontal-Bridgman techniques, samples with carrier concentrations less than about 10^{16} show negative magnetoresistance at 4.2°K which goes through a maximum at fields less than 10 000 G and becomes positive at high fields. At concentrations greater than 10^{16} there is no clear indication of a maximum at fields up to 20 000 G. The ratio of longitudinal to transverse magnetoresistance in the impurity conduction range is a function of temperature and field, but at 1.4°K it exceeds 0.9 both for negative magnetoresistance at low fields and for positive magnetoresistance at high fields. The over-all trends of the data on GaAs and other materials require two competing processes to account for the magnetoresistive behavior. One of these is the effect of the magnetic field in reducing orbital overlap which has been demonstrated by Sladek and Keyes on n-Ge and n-InSb. A competing process which could operate in the "hopping" region of impurity conduction might be an increase in the population of a set of states of higher energy and mobility than the ground states due to a reduction in the energy separation between them.

INTRODUCTION

NEGATIVE magnetoresistance has been reported in n- and p-type InSb,[1–3] Ge doped with As,[4] Sb,[5] and Cu,[6] n-type GaAs,[7,8] B-doped Si,[9] and P-doped

Si.[10] We report here the observation of negative magnetoresistance in Cd-doped GaAs, P-doped Ge, and

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