Superconductivity in Lightly Doped Crystalline Bismuth

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Using a sensitive SQUID (superconducting quantum interference device) detector and well-shielded dilution refrigerator, we have observed a broad resistance transition below about 1 K on samples of crystalline Bi lightly doped with either tin (0.02– 0.23 at.% Sn) or tellurium (0.1 at.% Te). Between 30 mK, which is the lowest temperature available to us, and 60 mK, the resistance of samples containing 0.08-, 0.12-, and 0.16-at.% Sn actually disappears and the transition temperature increases with increasing amounts of Sn.

We have discovered that the semimetal Bi in crystalline form becomes a superconductor when doped with small amounts of Sn. The transition to the superconducting state in this p-type material is observed in the resistivity and occurs at temperatures below 0.060 K, depending on the Sn concentration and current density. We also have evidence for superconductivity in the n-type material Bi-Te and estimate its transition temperature to be slightly below 0.030 K, our lowest attainable temperature. However, only one sample of this latter material has been investigated thus far. The existence of superconductivity in these systems is of fundamental significance, since, as will discussed below, one can in principle control the transition temperature by varying the amount of dopant.

The mechanism causing the superconductivity in these low-carrier-density systems is most likely the electron-phonon interaction, but it is probably not the simplified BCS model. In the BCS theory of superconductivity, the problem basically is to solve the gap equation for a particular kernel which is the sum of two parts; one arising from the attractive phonon-induced interaction and the other from the repulsive screened Coulomb interaction. In the simplified BCS model it is assumed that both parts of the kernel have the same cutoff energy, and under this assumption one can severely underestimate transition temperatures, especially in low-carrier-density systems. The significance of this for such systems was discussed several years ago by Cohen[1] in a theoretical review of superconductivity in degenerate semiconductors and semimetals. It that review, he described in some detail the possible mechanisms for enhancing superconductivity in low-carrier-density systems and, in particular, noted that the phonon and Coulomb interactions contain resonances at characteristic frequencies which are important in determining superconductivity and which can, in principle, be shifted by varying the carrier densities. If, by doping, these resonances which appear in the structure of the kernel can be made to coincide, the transition temperature is significantly enhanced over the case in which they do not coincide. Cohen concluded that the semimetals Bi, Sb, and As, and their alloys were, in this sense, good candidates for superconductivity and should be investigated. Since that time, in spite of the extensive amount of research on Bi and doped Bi systems, there has been no observation of superconductivity prior to our work. The reasons for this are simply that the necessary technologies for obtaining sustained ultralow temperatures *and* for detecting extremely small voltages have only recently become available.

We measured the resistance of our samples by a standard four-probe method using a very sensitive SQUID (superconducting quantum interference device) as a voltage-null detector. In view of the extremely small critical current densities which we observed, the magnetic shielding of the samples (of the order of 10^{-3} G) was a significant factor in determining our ability to observe the superconductivity. For cooling to ultralow temperatures, we used a locally constructed dilution refrigerator described in detail elsewhere.[2] Although the refrigerator has been used in the past to provide cooling down to a few millikelvins, the copper mixing chamber presently in use is not capable of cooling below 0.030 K.

The resistance measurements were made on five polycrystalline samples of Bi-Sn (four of which are reported in this Letter), one single-crystal sample of Bi-Sn, and a polycrystalline sample of Bi-Te. A description of the samples is given in Table I. All of the samples were prepared from 99.9999%-pure Bi, Sn, and Te.[3] Weighted quantities of the material were first melted under high vacuum for several hours and stirred constantly to achieve a thorough mixing. This charge was then fast quenched to prevent

TABLE I. Sample characteristics. All samples were rectangular parallelepipeds on which resistances were measured with the current along the length of the samples.

Bi sample	Macrostructure	Size (cm) Length	Width	Thickness	Carrier type	Carrier density[a] (10^{19} cm^{-3})
0.02 at.% Sn	Polycrystal	2.20	0.46	0.15	Hole	0.4
0.08 at.% Sn	Polycrystal	2.85	0.46	0.14	Hole	1.5
0.12 at.% Sn	Polycrystal	2.30	0.45	0.17	Hole	1.8
0.16 at.% Sn	Polycrystal	2.72	0.43	0.15	Hole	2.1
0.23 at.% Sn	Single crystal	1.40	0.31	0.28	Hole	3.5
0.10 at.% Te	Polycrystal	2.00	0.44	0.14	Electron	2.8

[a]We determined carrier densities by measuring the Hall coefficient in the high-field limit (~ 2.0 T) at. 4.2 K.

segregation of the constituents. The resulting ingots were remelted in an rf furnace and cast in a liquid-nitrogen–cooled copper mold. Finally, the samples were etched (using HCl and aqua regia) to remove any possible surface contamination. This method was used in an effort to make the samples as homogeneous as possible because of the known high segregation coefficients of Sn and Te in Bi. In spite of this, there is significant inhomogeneity in the distribution of dopant as evidenced by the broadness of the transitions shown in Fig. 1. Since we expect T_c to depend sensitively on Sn concentration,[1] if the Sn is not distributed uniformly throughout the sample different (small but macroscopic) portions of the sample will become superconducting at different temperatures. At sufficiently low temperatures, the sample will superconduct once there is a continuous superconducing path connecting the two ends of the sample. Although this is therefore essentially a percolation problem, it is an extremely complicated one requiring both a knowledge of the distribution of Sn and the dependence of T_c on Sn concentration. For this reason, we are not able to make any definitive comparisons with the theoretical work[4] which has been done on percolation in resistor networks having randomly distributed superconducting elements. In the more heavily doped Bi-Sn samples, there is evidence of Sn segregation as demonstrated by an abrupt decrease in the resistivity between 3.9 and 3.7 K, which is near the superconducting transition temperature of bulk Sn. This also occurs in the single-crystal Bi-Sn sample (which had also been etched to remove any segregated Sn from the surface) and is shown explicitly in the inset of Fig. 1. An apparent trend in going from higher to lower Sn concentrations is that the transition becomes more narrow and the amount of Sn segregation decreases. In the most lightly doped sample, 0.02 at.% Sn, the transition is, in fact, significantly sharper and there is no evidence of Sn segregation, indicating that this sample is also the most homogeneous.

The strongest evidence indicating that we are observing superconductivity in these systems is provided by the observed suppression of the transition temperature with increased current through

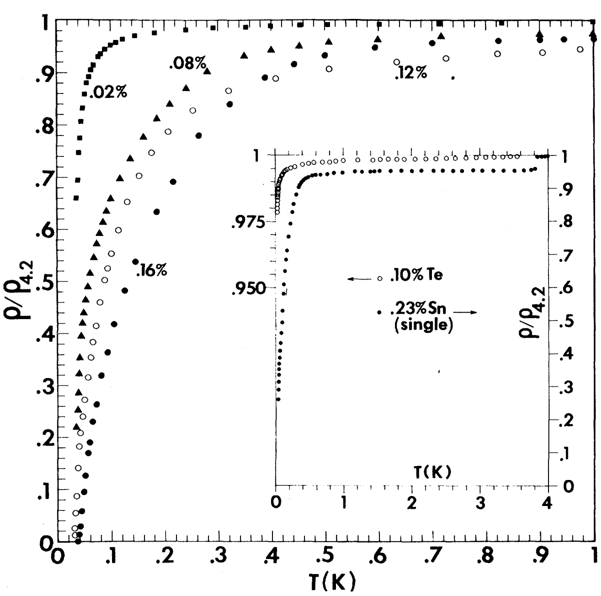

FIG. 1. Resistivity as a function of temperature normalized to resistivity at 4.2 K for different samples: solid squares, Bi + 0.02 at.% Sn; solid triangles, Bi + 0.08 at.% Sn; open circles, Bi + 0.12 at.% Sn; solid circles, Bi + 0.16 at.% Sn. In the inset, open circles, Bi + 0.10 at.% Te; solid circles, Bi + 0.23 at.% Sn. In each case the sample current is 10 μA.

the sample. A typical plot of the resistivity as a function of the current density is illustrated in Fig. 2 for the 0.12-at.%-Sn Bi sample. Note that the current densities in this figure are much lower than those used in Fig. 1. At a fixed temperature, we observe the resistivity to increase with increasing current density, indicating that the superconducting path is gradually destroyed. The higher the temperature the smaller is the critical current density which the sample can support and still remain superconducting. The superconducting transition also shifts to higher temperature with increasing content of Sn. For example, from the data shown in Fig. 2, we estimate the critical temperature[5] for the 0.12-at.%-Sn Bi sample at approximately 34 mK while for the 0.16-at.%-Sn sample, which is the most heavily doped polycrystalline sample investigated at present, the superconducting critical temperature is near 60 mK.

As mentioned earlier, we have also investigated a polycrystalline sample of Bi + 0.10 at.% Te and found evidence suggesting that it too will superconduct at sufficiently low temperatures. It is important to note that Te is itself not a superconductor so that any segregation of Te in Bi will not result in an abrupt resistivity drop at higher temperatures as observed in the comparably doped Bi-Sn samples. Other than that difference, the data for Bi-Te shown in the inset of Fig. 1 are very similar to the Bi-Sn data. The transition is apparently broad, beginning around 1.0 K, and we estimate that complete superconductivity would occur by about 25 mK.

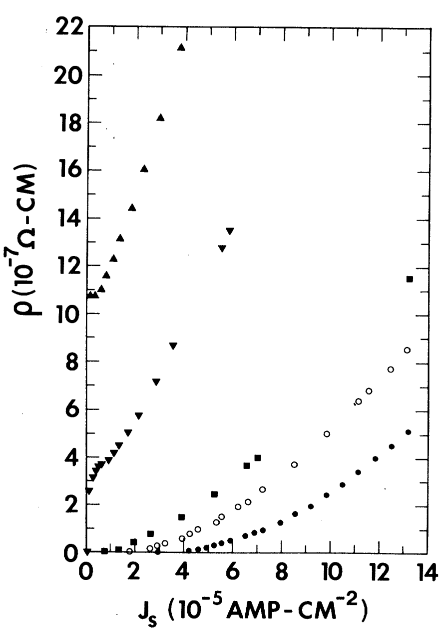

FIG. 2. Resistivity as a function of current density for the 0.12-at.%-Sn Bi sample at various temperatures: solid circles, 0.028 K; open circles, 0.030 K; inverted solid triangles, 0.034 K; solid triangles, 0.037 K.

In conclusion, we have observed that crystalline Bi becomes a superconductor when lightly doped with Sn or Te, materials which increase, respectively, the hole or electron carrier densities. Although previous measurements[6] on high-purity Bi indicate that Bi itself does not show any tendency towards superconductivity down to about 30 mK, our present results suggest that further investigations be made to search for superconductivity in pure Bi at still lower temperatures. Any such investigations must, of course, employ methods in which the samples are magnetically shielded. Further investigations are also needed in other similar low-carrier-density systems such as Sb (and perhaps even As) with various dopants. Any future studies of superconductivity in doped semimetal systems must also involve an effort to fabricate more homogeneous samples. We believe that our data show a strong dependence of superconductivity on carrier density (the broad transition implies that some parts of the sample become superconducting at temperatures as high as 1 K), but just what the nature of that dependence is and how it compares with the theory of Ref. 1 will rely on our ability to produce homogeneous samples. The best measure of homogeneity will most likely be the sharpness of the transition.

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[1]M. L. Cohen, in *Superconductivity*, edited by R. D. Parks (Marcel Dekker, New York, 1969), Vol. 1.

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[3]All of the samples except the Bi-Sn single crystal

were prepared from material supplied by Cominco American Inc., Spokane, Washington. The single crystal was prepared by a zone-leveling technique (from materials supplied by Johnson-Matthey & Co., Ltd., London, England) as described by C. Uher, H. J. Goldsmid, and J. R. Drabble, Phys. Status Solidi (b) 68, 709 (1975).

[4]J. P. Straley, Phys. Rev. B 15, 5733 (1977).

[5]We define the critical temperature as the highest temperature at which the SQUID detector (sensitivity of about 10^{-14} V) does not indicate any voltage. The critical temperature is then obtained by extrapolating to zero current density.

[6]C. Uher and W. P. Pratt, Jr., Phys. Rev. Lett. 39, 491 (1977).

[7]Uher, Goldsmid, and Drabble, Ref. 3.

Friedel-Type Oscillations in One-Dimensional Antiferromagnetic Insulators

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An impurity spin in one-dimensional spin-$\frac{1}{2}$ X-Y and antiferromagnetic Heisenberg models is shown to induce decaying spatial oscillations of magnetization for finite magnetic field. The wavelength of oscillation changes with magnetic field. Since these systems can be described mathematically in terms of a degenerate gas of pseudofermions, their response to impurity perturbation is similar to the response of an electron gas to a localized static charge.

It is known that the spin-$\frac{1}{2}$ X-Y and antiferromagnetic Heisenberg models with nearest-neighbor interaction in one dimension can be transformed into a problem of noninteracting (for X-Y) or interacting (for Heisenberg) fermions of zero chemical potential by using the Jordan-Wigner transformation.[1,2] This transformation has been used by many authors in the prediction and study of Peierls spin instability[3] in the compressible one-dimensional spin-$\frac{1}{2}$ X-Y model[4] and antiferromagnetic Heisenberg model,[5] and their Fermi-gas–like thermodynamic behavior.[6] In the present work this transformation is used to show the Friedel-type spatial oscillations of the pseudofermion density around an impurity in the one-dimensional spin-$\frac{1}{2}$ X-Y and antiferromagnetic Heisenberg models. The impurity magnetic atom has a spin-$\frac{1}{2}$ magnetic moment; however, it has an exchange integral J_1 with its two neighbors which differs from J, the nearest-neighbor exchange integral among the host spins. It is found that the magnetization induced at the ith site for large R_i is

$$\frac{\pi}{2}\left(\frac{J-J_1}{J}\right)\left(\frac{h}{J}\right)\frac{\sin(2k_F R_i)}{2k_F R_i},$$

where R_i is the distance of the ith site from the impurity, and k_F is a wave vector which depends on the ratio of the magnetic field h to the exchange integral J. This asymptotic oscillatory behavior disappears for zero magnetic field because of a particular momentum dependence of the pseudofermion scattering-matrix elements of the impurity perturbation. The physics behind this oscillation is the same as that behind the Friedel oscillation in a degenerate electron gas.[7] It arises because of the singular response of the Fermi gas in the ground state to perturbations with wave vector equal to twice the Fermi wave vector ($2k_F$).

Consider the case of the X-Y model. The Hamiltonian of the X-Y model containing an impurity at the origin is

$$H = J\sum_i (S_i^x S_{i+1}^x + S_i^y S_{i+1}^y) + h\sum_i S_i^z + (J_1 - J)\sum_{\Delta=\pm 1}(S_0^x S_\Delta^x + S_0^y S_\Delta^y), \tag{1}$$

where h is the magnetic field in energy units and S_i^x, S_i^y, S_i^z are the three components of the spin operator ($S=\frac{1}{2}$) at the ith site. By using the Jordan-Wigner transformation[1]

$$S_i^+ \equiv S_i^x + iS_i^y = (2)^{i-1}\exp(i\pi\sum_{j<i} C_j^\dagger C_j)C_i^\dagger,\quad S_i^- \equiv S_i^x - iS_i^y = (2)^{i-1}C_i\exp(-i\pi\sum_{j<i} C_j^\dagger C_j),$$
$$S_i^z = \tfrac{1}{2} - C_i^\dagger C_i, \tag{2}$$

