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Superconductivity in the Narrow-Gap Semiconductor $CsBi_4Te_6$

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Supporting Information

ABSTRACT: Superconductivity was discovered in the narrow-gap semiconductor $CsBi_4Te_6$. A superconducting transition around 4.4 K was observed for p-type samples in temperature-dependent resistivity and magnetic susceptibility data. Stoichiometric $CsBi_4Te_6$ is not a superconductor. A remarkably high critical field of ∼10 T was estimated from the field-dependent resistivity data. The strongly anisotropic $CsBi_4Te_6$ system is monoclinic and the first member of a larger homologous series $Cs_4[Bi_{2n+4}Te_{3n+6}]$ that exhibits unconventional superconductivity, suggesting that proper doping of the homologous series may create a novel class of superconductors from semiconductors.

Reports of superconductivity in semiconductors such as PbTe,[1] GeTe,[2] SnTe,[3,4] Bi_2Se_3,[5] and $TiSe_2$[6] and even Si[7] upon doping suggest that deriving superconductors from narrow-gap semiconducting materials is a viable synthetic approach. The mechanism for the emergence of superconductivity in semiconductors is unclear;[8] however, useful insights and clues exist. For example, the narrow-gap semiconductor rock-salt PbTe ($E_g \approx 0.3$ eV) shows superconductivity ($T_c \approx 1.5$ K) upon doping with a small amount of Tl.[9] The superconductivity has been discussed in terms of modification in the density of states (DOS) near the Fermi level and the resonant scattering of carriers with the Tl virtual bound states. Systematic studies using an additional dopant such as Na into Pb(Tl)Te show that the superconductivity is remarkably enhanced when the Fermi level is aligned with these two impurity levels as the Na doping increases.[10] These effects highlight the potential of doping narrow-gap semiconductors with appropriate dopants whose energy levels can couple strongly to the band structure near the Fermi energy and possibly create sizable DOS modifications and enhancements. It is not clear whether the presence of strong spin−orbit coupling in these systems is important for the appearance of superconductivity. We envision that similar modification could occur in the DOS upon doping of more complex materials and drive them to superconductivity. Here we report the occurrence of superconductivity at 4.4 K in p-type doped samples of $CsBi_4Te_6$, a low-dimensional narrow-gap semiconductor material with a high critical field of ∼10 T.

$CsBi_4Te_6$ is a good thermoelectric material at low temperature,[11−13] with a thermoelectric figure of merit of 0.82 at 225 K. It is a narrow-gap semiconductor with $E_g \approx 0.08$ eV.[12] Large centimeter-sized crystals of $CsBi_4Te_6$ can be obtained by slow cooling of the melt after the reaction of Bi_2Te_3 with Cs vapor at 670 °C. Typical crystals have needle-like morphology and cleave easily because of their fibrous nature (Figure 1A).

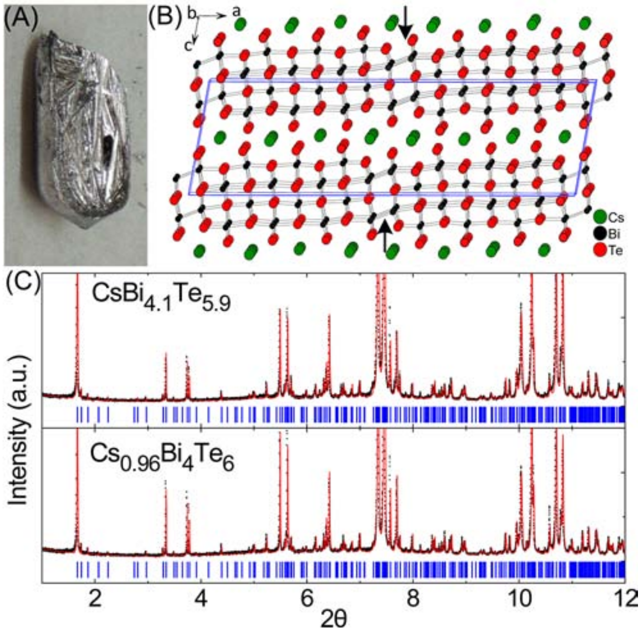

Figure 1. (A) Needle-like crystal habit of an as-grown centimeter-sized polycrystalline $CsBi_4Te_6$ ingot. (B) Layered structure of $CsBi_4Te_6$ with the Bi−Bi bond of 3.238(1) Å shown with arrows. (C) High-resolution synchrotron ($\lambda = 0.413894$ Å) powder diffraction data of the superconducting doped $CsBi_4Te_6$ samples. Red solid line shows the corresponding Rietveld fits.

$CsBi_4Te_6$ crystallizes as highly anisotropic needles in the monoclinic space group $C2/m$ with $a = 51.9205(8)$ Å, $b = 4.4025(1)$ Å, $c = 14.5118(3)$ Å, and $\beta = 101.480(1)°$, and it has a unique layered structure composed of $[Bi_4Te_6]$ anionic layers with Cs^+ ions residing between the layers (Figure 1B). The layers are assembled from parallel anionic $[Bi_4Te_6]$ rods that are joined with Bi−Bi bonds at 3.238(1) Å. This creates infinite slabs that alternate with layers of Cs^+ ions to form the structure (Figure 1B). The $[Bi_4Te_6]$ rod is the secondary building unit of the compound, and it can vary in width to form different structures, like $Cs_2Bi_{10}Te_{15}$, which is related to $CsBi_4Te_6$ and belongs to the same homology.[14−16]

$CsBi_4Te_6$ prepared at the stoichiometric composition is not superconducting (Figure 2A).[17] p-type doping in this material

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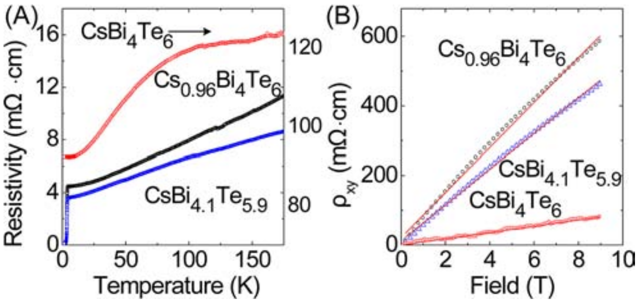

Figure 2. (A) Temperature-dependent resistivity of $CsBi_4Te_6$, $Cs_{0.96}Bi_4Te_6$, and $CsBi_{4.1}Te_{5.9}$ at zero field. (B) Field-dependent Hall resistivity measurements of superconducting p-type $Cs_{0.96}Bi_4Te_6$, $CsBi_{4.1}Te_{5.9}$, and non-superconducting $CsBi_4Te_6$ samples.

can be achieved by controlling the Bi/Te ratio, where a Bi-rich composition, i.e., $CsBi_{4.1}Te_{5.9}$, yields a p-type material. Only upon doping of $CsBi_4Te_6$ by either changing the Bi/Te ratio (p-type $CsBi_{4.1}Te_{5.9}$) or creating Cs vacancies (p-type $Cs_{0.96}Bi_4Te_6$) do the samples start to exhibit superconductivity. It is noteworthy that Bi_2Te_3 becomes superconducting under physical pressure with T_c = 4.3 K at 71 kbar.[18] High-resolution synchrotron powder diffraction data and Rietveld analysis (Figure 1C) of the doped samples confirmed the phase purity.[19] Figure 2A shows the temperature dependence of the resistivity of $CsBi_4Te_6$, $Cs_{0.96}Bi_4Te_6$, and $CsBi_{4.1}Te_{5.9}$ samples. The resistivity increases with temperature, which is characteristic for metallic (heavy doping) or semimetallic systems. The superconducting transition temperature is around 4.4 K, and the transition is observed in both magnetic susceptibility and resistivity measurements (Figures 2A and 3). Field-dependent Hall resistivity measurements at 5 K on the superconducting samples verified the hole doping with carrier density of 0.96(1) × 10^{19} cm^{-3} for $Cs_{0.96}Bi_4Te_6$, 1.21(1) × 10^{19} cm^{-3} for $CsBi_{4.1}Te_{5.9}$, and 6.93(1) × 10^{19} cm^{-3} for $CsBi_4Te_6$ (Figure 2B). We found that the surface of the crystals is very sensitive upon exposure to ambient conditions, where the resistivity below T_c does not go all the way down to zero. Zero resistivity values below T_c were found only after mounting of the electrical contacts in an Ar-filled glovebox and protecting the sample with epoxy glue.[19,20]

Temperature-dependent resistivity data[20] at zero field show an approximate temperature width of 0.4 K at T_c (Figure 3A). The resistivity data for $Cs_{0.96}Bi_4Te_6$ (Figure 3B) and $CsBi_{4.1}Te_{5.9}$ show systematic suppression of the superconducting transition by the application of magnetic field.[19] The upper critical field $H_{c2}(T)$ curve obtained from the field-dependent transition temperatures shows a remarkably high critical field of 9.7(5) T using the Ginzburg–Landau (GL) law[21] and 8.2(6) T using the Werthamer–Helfand–Hohenberg (WHH) theory[22] (considering the strong spin–orbit coupling; see Figure 3C). The remarkably high critical field value obtained by either GL or WHH theory suggests that the $CsBi_4Te_6$ system is a type-II superconductor.[23] The estimated critical field $H_{c2}(0)$ is much higher than those of other chalcogenide superconductors, such as 5 T observed for $Cu_xBi_2Se_3$.[24]

Magnetic characterization of the superconducting transition in $Cs_{0.96}Bi_4Te_6$ and $CsBi_{4.1}Te_{5.9}$ is shown in Figure 3D. T_c is approximately 4 K with an applied field of 1 G. The superconducting transition in the magnetic susceptibility is relatively broad, presumably because of the highly anisotropic crystal structure of $CsBi_4Te_6$ and the random orientation of the crystals in the polycrystalline ingot.[19] The superconducting volume fraction measured at 1.2 K and in the zero-field cooled mode was about 14% for $Cs_{0.96}Bi_4Te_6$ and 20% for $CsBi_{4.1}Te_{5.9}$ of that expected for full diamagnetism ($1/4\pi$). This represents a conservative lower limit to the true superconducting volume fraction because the diamagnetic magnetization is still decreasing steeply at the temperature where the field is applied for the ZFC measurement. Additionally, the highly anisotropic morphology of the crystal and the strong tendency to cleave along the [Bi_4Te_6] slab direction (*ab*-plane) can yield a polarized susceptibility that is not representative of the overall volume, thus giving an underestimated volume fraction.[20]

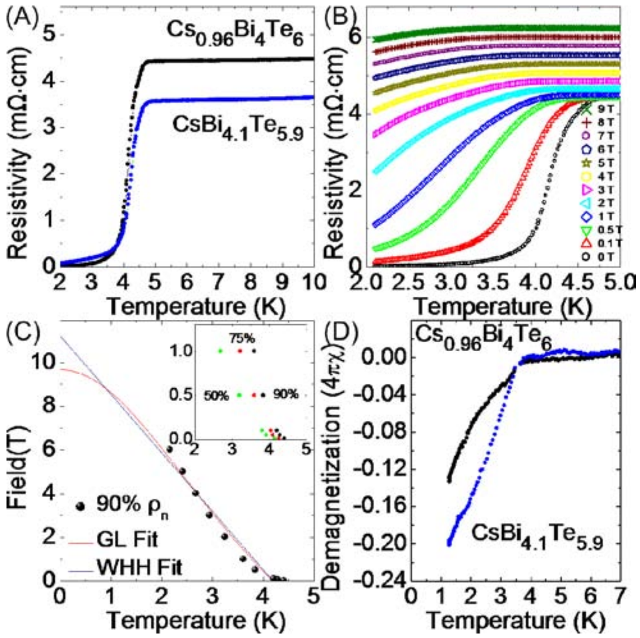

Figure 3. (A) Temperature-dependent resistivity for $Cs_{0.96}Bi_4Te_6$ and $CsBi_{4.1}Te_{5.9}$, showing a sharp superconducting transition at ~4.4 K at zero field. (B) Temperature-dependent resistivity for $Cs_{0.96}Bi_4Te_6$ at various magnetic fields, showing a superconducting transition even up to 9 T. (C) Upper critical fields as a function of temperature for $Cs_{0.96}Bi_4Te_6$. The red solid line indicates the fitting based on the Ginzburg–Landau (GL) theory and the blue solid line the fitting based on the Werthamer–Helfand–Hohenberg (WHH) theory. Both models yield an upper critical field close to 10 T. Inset shows the upper critical field as a function of temperature obtained for 50%, 75%, and 90% criteria of the normal state value.[23] (D) Magnetic susceptibility as a function of temperature for $Cs_{0.96}Bi_4Te_6$ and $CsBi_{4.1}Te_{5.9}$ at 1 G. The lower limit of the superconducting volume fraction is around 14% for $Cs_{0.96}Bi_4Te_6$ and 20% for $CsBi_{4.1}Te_{5.9}$ at 1.2 K.

The origin of superconductivity in $CsBi_4Te_6$ is not known; however, it is worth pointing out that both electronic structure calculations[25] and X-ray photoemission spectroscopy[26] on $CsBi_4Te_6$ indicate a very high DOS in the valence band (VB) of this material. The p-type doping lowers the Fermi level to the region of high DOS in the VB. This is reminiscent of the p-type Tl-doped PbTe system, which also exhibits superconductivity at 2 K.[27] Based on previous band calculations and photoemission work, the metallic conductivity in p-doped $CsBi_4Te_6$ arises from a small Fermi surface at the Γ point in the Brillouin zone surface produced by direct hole doping into the VB. The Fermi surface is highly anisotropic, and the holes have vastly different effective masses in different crystallographic directions. The lowest effective mass of holes is along the monoclinic *b*-axis (the so-called needle axis), while along the direction (*c*-axis) perpendicular to the Cs layers the hole effective mass is 4.5 times larger. The heaviest VB mass direction is parallel to the Bi−Bi bonds (*a*-axis) and is by a factor of 50 larger than the lightest VB mass. According to Bardeen−Cooper−Schrieffer theory, strong bonding with an ionic component and a considerable electronic DOS near the Fermi level can produce strong electron−phonon coupling and presumably also superconductivity.

$CsBi_4Te_6$ appears to be an unconventional superconductor. For example, the carrier concentration ($\sim 10^{19}$ cm^{-3}) is 3 orders of magnitude lower than that of normal metals ($\sim 10^{22}$ cm^{-3}) with a similar T_c. Interestingly, among the known non-oxidic superconductors that derive from semiconductors, $CsBi_4Te_6$ has the lowest crystal symmetry, yet it features the highest T_c. In order to understand the origin of superconductivity of this class of semiconducting compounds, our immediate plans for further characterization include magnetization under pressure, neutron diffraction for the phonon density of states, and angle-resolved photoemission spectroscopy measurements of superconducting and non-superconducting samples. Narrow-gap semiconductors can be a promising platform for the discovery of superconductors where proper doping may uncover a superconducting ground state. The discovery of superconductivity in the low-symmetry $CsBi_4Te_6$ system opens the path for further investigation of different homologous series, like $Cs_4[Bi_{2n+4}Te_{3n+6}]$,[16] where a larger class of Bi-containing superconducting compounds may exist and may be structurally designed or predicted based on the concept of homologous series.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Magnetic susceptibility and field-dependent resistivity data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(17) Stoichiometric $CsBi_4Te_6$ sample was synthesized by using a small excess (~1%) of Cs metal in a stoichiometric mixture of Cs and Bi_2Te_3. Doped samples were synthesized by reacting Cs, Bi_2Te_3, Bi, and Te at the nominal stoichiometry $CsBi_{4.1}Te_{5.9}$. Starting materials were pre-reacted in a N_2-filled glovebox by adding initially a very small amount of Bi_2Te_3 powder in molten Cs metal in fused silica tubes. Once the reaction was completed, the rest of the Bi_2Te_3 powder (plus Bi and Te for the doped samples) was added into the tubes, which were evacuated to $<10^{-4}$ mbar and flame sealed. The tubes were heated to 700 °C at a rate of 1 °C/min in a box furnace, kept at 700 °C for 2 h, rocked in order to facilitate the formation of a homogeneous melt, and then air-quenched to room temperature. Tubes were opened in the glovebox, and metallic-looking ingots of pure phase (Figure 1A) were obtained.

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(20) Resistivity measurements were performed in a quantum design physical property measurement system (PPMS). The standard four-probe technique, employing silver paste contacts cured at room temperature, was used for resistivity measurements, with the electric current applied in an arbitrary direction. Since the surface of the $CsBi_4Te_6$ system was found to be sensitive upon exposure to ambient conditions, all handling of the materials, including mounting of electrical contacts, was performed in an Ar-filled glovebox. A small piece was cut from each as-grown polycrystalline ingot, and the specimen was polished to a rectangular shape using sandpaper. Bundles of the needle-like crystallites were oriented approximately along the growth direction (*b*-axis) in each specimen. Additionally, samples used for transport measurements were protected by coating them with epoxy glue before they were taken outside the glovebox. The criterion of $90\%\rho_n$ of resistivity was used in order to estimate the upper critical field $H_{c2}(T)$ based on the GL theory using $H_{c2}(T) = H_{c2}(0)(1 - t^2)/(1 + t^2)$, where $t = T/T_c$ is the reduced temperature and $H_{c2}(0)$ is the upper critical field at zero temperature. The WHH model was also tested since the spin−orbit coupling is strong in $CsBi_4Te_6$ using $H_{c2}(0) = -0.693T_c(dH_{c2}/dT)T = T_c$. Room-temperature Hall effect measurements were performed up to 9 T in a PPMS. The magnetic-field dependence of Hall resistivity ρ_{xy} was taken as $\rho_{xy} = [\rho(+H) - \rho(-H)]/2$ at each field point to eliminate the effect of any misalignment of the Hall electrodes. A home-built low-field quantum interference device (SQUID) magnetometer was used to measure the direct current magnetization at an applied field of 1 G. (Vandervoort, K. G.; Griffith, G.; Claus, H.; Crabtree, G. W. *Rev. Sci. Instrum.* **1991**, *62*, 2271). Superconducting volume fraction was estimated by converting the magnetic susceptibility data to $4\pi(1 - DF)dM/Hm$, where DF is the demagnetization factor, *d* the density (g

cm^{-3}), M the magnetic susceptibilty (emu), H the applied field (G), and m the mass of the sample (g). High-resolution powder XRD measurements (λ = 0.413894 Å) were performed at beamline BM-11-B at the Advanced Photon Source (APS) at Argonne National Laboratory. The samples were placed in Kapton capillaries and spun at ~600 rpm during collection.

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