Bulk superconducting phase with a full energy gap in the doped topological insulator

Cu$_2$Bi$_2$Se$_3$

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The superconductivity recently found in the doped topological insulator Cu$_2$Bi$_2$Se$_3$ offers a great opportunity to search for a topological superconductor. We have successfully prepared a single-crystal sample with a large shielding fraction and measured the specific-heat anomaly associated with the superconductivity. The temperature dependence of the specific heat suggests a fully-gapped, strong-coupling superconducting state, but the BCS theory is not in full agreement with the data, which hints at a possible unconventional pairing in Cu$_2$Bi$_2$Se$_3$. Also, the evaluated effective mass of 2.6$m_e$ ($m_e$ is the free electron mass) points to a large mass enhancement in this material.

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In the past two years, the three-dimensional (3D) topological insulator (TI) is attracting a lot of interest as a new state of matter [1,3]. It is characterized by the existence of a gapless surface state that emerges because of the non-trivial $Z_2$ topology of the insulating bulk state and is protected against backscattering by time-reversal symmetry. The discovery of the 3D TI stimulated the search for a superconducting (SC) analogue, a time-reversal-invariant topological superconductor [3–9], which is characterized by a fully-gapped, odd-parity pairing state that leads to the emergence of gapless Majorana surface states. Such a SC phase has implications on topological quantum computing [4,10–12] because (i) it is a potential candidate [18] to realize a 3D topological superconductor, and (ii) if its bulk turns out to be an ordinary $s$-wave superconductor, the topological surface state may turn into a 2D topological superconductor as a result of a SC proximity effect [4]. Therefore, it is important to confirm whether the superconductivity is really occurring in the bulk of Cu$_2$Bi$_2$Se$_3$ and, if so, to elucidate the fundamental nature of its SC state.

Bi$_2$Se$_3$ has a layered crystal structure (R₃m, space group 166) consisting of stacked Se-Bi-Se-Bi-Se quintuples that are only weakly van-der-Waals bonded to each other. We call the rhombohedral [111] direction the $c$ axis and the (111) plane the $ab$ plane. When Cu is introduced into Bi$_2$Se$_3$, it may either intercalate as Cu$^{1+}$ into the van-der-Waals gaps and act as a donor, or replace Bi as a substitutional impurity and act as an acceptor [19]: hence, Cu is an ambipolar dopant [20,21]. The nominal formula of Cu$_x$Bi$_2$Se$_3$ suggests that most Cu atoms in this SC material occupy the intercalation sites; however, the reported carrier density of $\sim$10$^{20}$ cm$^{-3}$ [15] corresponds to only $\sim$1% of electron doping, which is much smaller than that expected from the $x$ value. This discrepancy suggests either that most of the intercalated Cu ions remain inactive as donors, or that substitution of Bi with Cu also occurs in this material and it almost compensates the electrons doped by the intercalated Cu. Partly related to such an uncontrollability of the Cu atoms in Cu$_x$Bi$_2$Se$_3$, the quality of the SC samples has been poor as mentioned above, and improvements in the sample quality are indispensable for a solid understanding of the SC state in this material.

In this Letter, we report a comprehensive study of the basic SC properties of a Cu-intercalated Bi$_2$Se$_3$ single crystal by means of resistivity, magnetization, and specific heat measurements. For the first time in this material, we observed zero-resistivity and a specific-heat jump at the SC transition. The apparent shielding fraction of our sample exceeds 40%, and the specific-heat data confirms the bulk nature of the superconductivity. Most importantly, the temperature dependence of the specific heat suggests a fully-gapped, strong-coupling SC state, but the data do not fully agree with the strong-coupling BCS calculation. This suggests that the pairing symmetry may not be simple isotropic $s$-wave. Furthermore, the effective mass is found to be 2.6$m_e$ ($m_e$ is the free electron mass)
Single crystals of Bi$_2$Se$_3$ were grown by melting stoichiometric amounts of elemental shots of Bi (99.9999%) and Se (99.999%) in sealed evacuated quartz glass tubes at 800°C for 48 h, followed by a slow cooling to 550°C over 48 h and keeping at that temperature for 24 h. The crystals were cleaved and cut into rectangular pieces, and then the Cu intercalation was done by an electrochemical technique under inert atmosphere inside a glove box, using CuI reagent in CH$_3$CN solvent. The sample was wound with a Cu wire, and a Cu stick was used as counter and reference electrode. The current was fixed at typically 10 μA. The concentration of intercalated Cu was determined from the weight change before and after the intercalation process, and the sample was briefly annealed afterward. The particular sample used in the present study was 3.9×1.6 mm$^2$ in the $ab$ plane with a thickness of 0.40 mm, and its Cu concentration was $x = 0.29$. In fact, by employing electrochemical intercalation, we found that samples with $x$ of up to ~0.5 become superconducting; the precise phase diagram is currently under investigation.

FIG. 1. (color online) (a) $\rho_{xx}(T)$ data of the Cu$_{0.29}$Bi$_2$Se$_3$ sample. (b) Temperature dependence of $R_H$; inset shows the $\rho_{xx}(B)$ data at 5 K. (c,d) $\rho_{xx}(B)$ data for $B \parallel ab$ and $B \perp ab$, respectively. (e) $B_{c_2}$ vs. $T$ phase diagram determined from the midpoint in $\rho_{xx}(B)$ at various temperatures; dashed lines show the WHH behavior. The midpoint definition for $B_{c_2}$ gives $T_c = 3.2$ K consistent with the $M(T)$ data.

FIG. 2. (color online) (a) Temperature dependence of the apparent shielding fraction of Cu$_{0.29}$Bi$_2$Se$_3$ measured in $B = 0.2$ mT || $ab$. (b) $M(B)$ curves at 1.8 and 2.4 K after subtracting the diamagnetic background. (c) Initial $M(B)$ behavior after ZFC to various temperatures. Arrows mark the position of $B_{c1}$, Note the very small magnetic-field scale. (d) Plots of $\Delta M \equiv M - aB$, where $a$ is the initial slope, and the determination of $B_{c1,\perp}$ shown by arrows. (e) $B_{c1,\parallel}$ vs. $T$ phase diagram; the solid line is a fit within the local dirty limit.
c) obtained after subtracting the phonon term determined in
demagnetization effect, though it is small for
discussed later, this apparent value was corrected for the
[25] to fit the extracted data points (T

by strong-coupling BCS theory with
the standard Debye formula. (b) Electronic term
c3(a) as
Determined c3/T curve given
by strong-coupling BCS theory with \( \alpha = 1.9 \); the dashed line is the BCS curve for \( \alpha = 2.3 \), which is obtained from \( B_c, N_0 \), and \( T_c \). The horizontal dash-dotted line denotes the value of
\( \gamma_n \), and its breakdown to \( \gamma_0 \) and \( \gamma_{res} \) is indicated.

cooling (ZFC) and field-cooled (FC) measurements are shown in Fig. 2(a), where the onset of the Meissner signal
occurs at \( T_c = 3.2 \) K and the apparent shielding fraction reaches 43\% at 1.8 K [23]. Note that this Meissner
\( T_c \) corresponds to the midpoint of the resistivity transition. Neither ZFC nor FC data saturate at 1.8 K.

Magnetization \( M(B) \) curves are shown in Figs. 2(b) and (c): each data set was obtained after cooling to its
respective temperature from above \( T_c \) in zero field, and the background diamagnetism, which can be easily
determined at \( B > B_{c2,ab} \), is subtracted from the data. As already noted by Hor et al. [13], the lower critical field
\( B_{c1} \) is very small: Using the deviation of the \( M(B) \) curve from its initial linear behavior as a measure of \( B_{c1,ab} \) [Fig.
2(d)], we obtained the \( B_{c1,ab}(T) \) data shown in Fig. 2(e). To determine the 0-K limit, we used
\( B_{c1} \propto 1/\lambda_{eff} \propto \sqrt{\Delta(T)/\Delta(0)\tanh(\Delta(T)/2k_B T)} \) for the local dirty limit
[23] to fit the extracted data points (\( \lambda_{eff} \) is the effective
penetration depth and \( \Delta \) is the SC gap [24]). We then obtain \( B_{c1,ab}(0) = 0.43 \) mT. For the quantitative analysis
discussed later, this apparent value was corrected for the
demagnetization effect, though it is small for \( B \parallel ab \): Using
the approximation given for the slab geometry [24], we obtain
\( B_{c1,ab}(0) = B_{c1,ab}^{ns}(0)/\sqrt{0.36b/a} = 0.45 \) mT, where
\( b/a = 3.9/0.40 \) in our case. Note that the flux pinning
in the present system is weak as evidenced by the
low irreversibility field of \( \sim 0.1 \) T at 1.8 K [Fig. 2(b)].

The temperature dependence of \( c_p \) is shown in Fig.
3(a) as \( c_p/T \) vs. \( T \) for the SC state \( (B = 0 \) T \) and
the normal state achieved by applying \( B \perp ab \) of 2 T
\( (B_{c2,ab}) \). As shown by the dotted line in Fig. 3(a), a
conventional Debye fit to the normal-state data below
4 K using \( c_p = c_{el} + c_{ph} = \gamma_n T + A_3 T^3 + A_5 T^5 \), with
the normal-state specific-heat coefficient \( \gamma_n \) and the coefficient of the phononic contribution \( A_3 \) and \( A_5 \), yields a good description of the data. The obtained parameters are \( \gamma_n = 1.95 \) mJ/molK\(^2\), \( A_3 = 2.22 \) mJ/molK\(^4\) [27], and \( A_5 = 0.05 \) mJ/molK\(^6\). Subtracting the phononic contribution from the zero-field data gives the electronic
specific heat \( c_{el} \) in the SC state plotted in Fig. 3(b),
revealing a clear jump around \( T_c \). This provides compelling evidence for bulk superconductivity in Cu\(_2\)BiSe\(_3\). In
passing, we note that our \( c_p \) data in 2 T do not exhibit
any Schottky anomaly related to electron spins, suggesting
that there is no local moment possibly associated with
Cu\(^{2+}\) ions.

From the above results, one can estimate various basic
parameters. Assuming a single spherical Fermi surface,
one obtains the Fermi wave number \( k_F = (3\pi^2 n_0)^{1/3} \)
1.6 nm\(^{-1}\). The effective mass \( m^* \) is evaluated as \( m^* = (3\hbar^2/\pi n_0)(V_{mol} k_F^2/k_F) = 2.6m_e \), with the molar volume of
Bi\(_2\)Se\(_3\) \( V_{mol} \approx 85\) cm\(^3\)/mol. Note that the effective mass of pristine Bi\(_2\)Se\(_3\) is \( \sim 0.2m_e \) [28], so there is an order-of-magnitude mass enhancement in Cu\(_2\)BiSe\(_3\) [29]. Since electron correlations are weak in Bi\(_2\)Se\(_3\), the origin of this enhancement is most likely a change in the band
curvature near the Fermi level. From \( B_{c2,ab} \) = 1.71 T,
the coherence length \( \xi_{ab} = \sqrt{\Phi_0/(2\pi B_{c2,ab})} = 13.9 \) nm is obtained, while from \( B_{c1,ab} \) we use \( c_{el}\xi_{ab} = \Phi_0/(2\pi B_{c1,ab}) \) and obtain \( \xi_{ab} = 7.9 \) nm. Since we have the \( B_{c1} \) value only for \( B \parallel ab \), we define the effective GL parameter
\( \kappa_{ab} = \sqrt{\lambda_{ab}\lambda_{bc}\xi_{ab}\xi_{bc}} \) and use \( B_{c1,ab} = \Phi_0\ln\kappa_{ab}/(4\pi\lambda_{ab}\lambda_{bc}) \)
and the theoretical term \( 1B_{c2,ab}/B_{c1,ab} = 2\gamma_{c1,ab}/\ln\kappa_{ab} \) [31] to obtain
\( \kappa_{ab} \approx 128 \). We then obtain the thermodynamic critical field
\( B_c = \sqrt{B_{c1,ab}B_{c2,ab}}/\ln\kappa_{ab} = 16.7 \) mT.

To analyze \( c_{el}/T \) in the SC state shown in Fig. 3(b), we tried to fit the BCS-type temperature dependence
to the data. Since the simple weak-coupling BCS model does not describe the \( c_{el}/T \) data (not shown), we use
the modified BCS model applicable to strong-coupling superconductors as proposed in Ref. [31], where it is called
“\( \alpha \) model” with \( \alpha = \Delta_0/T_c \) and \( \Delta_0 \) is the SC gap
size at 0 K. We note that strong coupling means \( \alpha > \alpha_{BCS} = 1.764 \), and that this model still assumes a fully-gapped isotropic s-wave pairing. Using the theoretical curve \( c_{BCS}^{\alpha1} \) of the \( \alpha \) model [31], we tried to reproduce the experimental data with \( c_{el}(T)/T = \gamma_{res} + c_{el}^{\alpha1}(T)/T \). Note that the parameter \( \gamma_{res} \) is necessary for describing the contribution of the non-SC part of the sample [32]; also, the theoretical term \( c_{BCS}^{\alpha1}/T \) is set to yield \( \gamma_s \) \( = \gamma_n - \gamma_{res} \) at \( T > T_c \).

It turned out that with \( \alpha = 1.9, \gamma_{res} = 0.6 \) mJ/molK\(^2\), and \( \gamma_s = 1.185 \) mJ/molK\(^2\), the experimental data is reasonably
well reproduced and the entropy balance is satisfied, as shown in Fig. 3(b) by the dotted line and the
dash-dotted line [33]. This result strongly suggests that the SC state of Cu\(_2\)BiSe\(_3\) is fully gapped. The resulting
\( \gamma_n \) \( = \gamma_{res} + \gamma_s \) value of 1.785 mJ/molK\(^2\) slightly devi-
ates from the $\gamma_n$ value estimated from the Debye fit to the normal-state data in 2 T, 1.95 mJ/molK$^2$. This slight difference ($\sim$9\%) might be the result of a possible field dependence of the normal-state Sommerfeld parameter, which has to be clarified in future studies.

To gain further insight into the nature of the SC state in Cu$_2$Bi$_2$Se$_3$, we examine the implication of the obtained $\gamma_s$ value: The density of states (DOS) $N_0$ is calculated from $\gamma_s$ via $N_0 = \gamma_s/(2\pi^2k_B^2/3) = 1.51$ states/eV per unit cell, which is large for a low-carrier-density system and is in accord with the “high” $T_c$. This value allows us to calculate $\Delta_0$ through the expression for the SC condensation energy $\frac{1}{2}N_0\Delta_0^2 = (1/2\mu_0)B_c^2$. With $B_c \approx 16.7$ mT already calculated, we obtain $\Delta_0 = 7.3$ K which gives the coupling strength $\alpha = \Delta_0/T_c = 2.3$. This exceeds the BCS value of 1.764 and hence Cu$_2$Bi$_2$Se$_3$ is a strong-coupling superconductor, as was already inferred in our analysis of the $c_{el}/T$ data. More importantly, the $\alpha$ value of 2.3 obtained from $\gamma_s$ is too large to explain the $c_{el}(T)$ data within the strong-coupling BCS theory: As shown in Fig. 3(b) with the dashed line, the expected BCS curve for $\alpha = 2.3$ does not agree with the data at all. This probably means that the actual temperature dependence of $\Delta$ in Cu$_2$Bi$_2$Se$_3$ is different from that of the BCS theory, which suggests that the pairing symmetry may not be the simple isotropic $s$-wave. Obviously, a direct measurement of $\Delta_0$ and $\Delta(T)$ is strongly called for. On the other hand, the low-temperature behavior of $c_{el}(T)$ robustly indicates the absence of nodes and points to a fully-gapped state. It will be interesting to see if the fully-gapped, time-reversal-invariant $p$-wave state proposed for Cu$_2$Bi$_2$Se$_3$ would provide a satisfactory explanation of our data.

In summary, we report a comprehensive study of the superconductivity in Cu$_2$Bi$_2$Se$_3$ by means of resistivity, magnetization, and specific-heat measurements on a single crystal with $x = 0.29$ that shows, for the first time in this material, zero-resistivity and a shielding fraction of more than 40\%. An analysis in the framework of a generalized BCS theory leads to the conclusion that the superconductivity in this system is fully gapped with a possibly non-BCS character. The fully-gapped state qualifies this system as a candidate for a topological superconductor: Since this system hosts a topological surface state above $T_c$, depending on whether the parity of the bulk SC state is even or odd, either the surface or the bulk should realize the topological SC state associated with intriguing Majorana edge states.

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[1] M.Z. Hasan and C.L. Kane, Rev. Mod. Phys. 82, 3045 (2010).
[2] J.E. Moore, Nature (London) 464, 194 (2010).
[3] X.L. Qi and S.C. Zhang, arXiv:1008.2026v1.
[4] L. Fu and C.L. Kane, Phys. Rev. Lett. 100, 096407 (2008).
[5] A.P. Schnyder et al., Phys. Rev. B 78, 195125 (2008).
[6] X.-L. Qi et al., Phys. Rev. Lett. 102, 187001 (2009).
[7] X.-L. Qi, T.L. Hughes, and S.-C. Zhang, Phys. Rev. B 81, 134508 (2010).
[8] J. Linder et al., Phys. Rev. Lett. 104, 067001 (2010).
[9] M. Sato, Phys. Rev. B 81, 220504(R) (2010).
[10] L. Fu and C.L. Kane, Phys. Rev. Lett. 102, 216403 (2009).
[11] A.R. Akhmerov, J. Nilsson, and C.W.J. Beenakker, Phys. Rev. Lett. 102, 216404 (2009).
[12] Y. Tanaka et al., Phys. Rev. B 79, 060505(R) (2009).
[13] H. Zhang et al., Nat. Phys. 5, 438 (2009).
[14] X. Nin et al., Nat. Phys. 5, 398 (2009).
[15] Y.S. Hor et al., Phys. Rev. Lett. 104, 057001 (2010).
[16] M.L. Cohen, in Superconductivity, ed. by R.D. Parks, Vol. 1 (Marcel Dekker, 1969), Chap. 12.
[17] L.A. Wray et al., Nat. Phys. 6, 855 (2010).
[18] L. Fu and E. Berg, Phys. Rev. Lett. 105, 097001 (2010).
[19] When Cu substitutes Bi, one $4s$ electron of Cu replaces three $6p$ electrons of Bi to form a $\sigma$ bond, creating two holes (see Ref. [21]).
[20] L.P. Caywood and G.R. Miller, Phys. Rev. B 2, 3209 (1970).
[21] A. Vaško et al., Appl. Phys. 5, 217 (1974).
[22] This midpoint definition for $B_{c2}$ yields a $T_c$ value consistent with the magnetization and specific heat data.
[23] This shielding fraction becomes 41\% if the demagnetization effect is considered.
[24] E.H. Brandt, Phys. Rev. B 60, 11939 (1999).
[25] The present situation is actually in-between the dirty and clean limits, because we estimate $\Theta_d = k_B\pi/\lambda\Delta_0 = 24$ nm and $\lambda = h c p/(k_B n_e^2) = 25$ nm. However, the difference in $1/\lambda^2(T)$ between the two limits is small in the local case; see M. Tinkham, Introduction to Superconductivity (McGraw-Hill, 1975), p. 81.
[26] For the calculation of $\lambda_{sr}$, we used the strong-coupling $\Delta(T)$ with $\alpha = 1.9$ consistent with the $c_{el}$ analysis.
[27] This $A_3$ gives the Debye temperature $\Theta_D = 120$ K via $A_3 = (12/5\pi^4)N\hbar k_B/\Theta^3_D$ with the number of atoms per formula unit $N = 5$ and the Avogadro number $N_A$.
[28] H. Köhler and H. Fisher, Phys. Status Solidi (b) 69, 349 (1975).
[29] The contribution of the second conduction band minima (Ref. [25]), whose effective mass is only $\sim 0.1m_\infty$, does not significantly alter this conclusion.
[30] J.R. Clem, Physica C 162-164, 1137 (1989).
[31] H. Padamsee, J.E. Neighbors, and C.A. Shiffman, J. Low Temp. Phys. 12, 387 (1973).
[32] In a homogeneous nodal superconductor with 100\% volume fraction, impurity scattering leads to a finite DOS even at $T = 0$. However, the sample used here consists of superconducting and non-superconducting (metallic) parts, and the volume fraction of the latter ($\sim 60\%$) entirely accounts for the observed residual DOS, which is 33\% of the total DOS.
[33] We allowed $\gamma_{res}$ and $\gamma_s$ to be tuned independently.