Experimental studies of the topological superconductor \( \text{Cu}_x\text{Bi}_2\text{Se}_3 \)

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Abstract. \( \text{Cu}_x\text{Bi}_2\text{Se}_3 \) was recently elucidated to be the first example of a time-reversal-invariant topological superconductor characterized by the gapless surface quasiparticle states consisting of helical Majorana fermions. The evidence for topological superconductivity in \( \text{Cu}_x\text{Bi}_2\text{Se}_3 \) was obtained by the point-contact spectroscopy that indirectly detected the itinerant massless Majorana state on the surface. In this paper, we show new point-contact spectroscopy data which supplement the previous conclusion. We also present the anisotropic normal-state resistivity data for superconducting samples of \( \text{Cu}_x\text{Bi}_2\text{Se}_3 \) which strongly suggest that not only the effective mass but also the scattering rate is anisotropic in this material by a factor of \( \sim 3 \).

1. Introduction
Topological superconductors (TSCs) are characterized by a nontrivial topological structure of the Hilbert space spanned by the bulk wave functions [1, 2, 3]. Due to the bulk-edge correspondence [4], a topologically nontrivial bulk state of a superconductor dictates the appearance of a surface quasiparticle state consisting of Majorana fermions [1, 2, 3], which are their own antiparticles and are of significant current interest [5, 6]. The Majorana nature of the quasiparticles in the surface states stems essentially from the particle-hole symmetry that is an inherent property of the low-energy physics of a superconductor described by the Bogoliubov-de Gennes equation [6].

Among the various kinds of TSCs classified by their symmetries [1], of particular interest is the new topological state preserving time-reversal symmetry [7], which dictates the Majorana fermions to have helical spin structure [2]. Recently, it was theoretically predicted [8] that the superconducting doped topological-insulator material \( \text{Cu}_x\text{Bi}_2\text{Se}_3 \) [9] may be such a time-reversal-invariant TSC because of its peculiar band structure. This prediction motivated us to perform point-contact spectroscopy experiments on this material, and we found a pronounced zero-bias conductance peak (ZBCP) [10]; careful examinations of its magnetic-field dependence as well as the contact dependence allowed us to conclude [10] that the observed ZBCP is a signature of surface Andreev bound states, which gives direct evidence for unconventional superconductivity [11]. Knowing that only four types of superconducting gap functions [8] are allowed by the symmetry of this material [12] and that all possible unconventional states are topological [10], it was possible to further conclude that \( \text{Cu}_x\text{Bi}_2\text{Se}_3 \) is a TSC [10].

Although \( \text{Cu}_x\text{Bi}_2\text{Se}_3 \) has been identified to be the first concrete example of a time-reversal-invariant TSC, there are many remaining issues that need to be experimentally clarified. For example, the exact pairing symmetry should be determined, possibly by \( \pi \)-junction type...
experiments; also, existence of a Majorana bound state in the vortex core should be elucidated, possibly by STM experiments. However, before conducting such advanced experiments, one should understand this material better, because \( \text{Cu}_x\text{Bi}_2\text{Se}_3 \) samples have a problem of intrinsic inhomogeneity and strong disorder [13, 14, 15].

One issue that remained unresolved in our previous point-contact experiment [10] was the onset temperature of the ZBCP; namely, the ZBCP was found to grow below 1.2 K, while the \( T_c \) of the measured sample was 3.2 K. One possibility for this difference was that the ZBCP is prone to thermal smearing and needs a low temperature to become observable. Another possibility was that the \( T_c \) was locally 1.2 K at the position beneath the point contact, since the temperature dependence of the diamagnetic signal suggested a broad distribution of local \( T_c \). In this paper, we show new point-contact spectroscopy data in which the ZBCP starts to grow below 3.2 K, suggesting that the second possibility mentioned above was actually the case.

Another issue is the robustness of the odd-parity paring state in \( \text{Cu}_x\text{Bi}_2\text{Se}_3 \) against disorder. According to the common wisdom [16, 17], the odd-parity pairing state should be strongly suppressed by impurity scattering [18]. Given the strong disorder in \( \text{Cu}_x\text{Bi}_2\text{Se}_3 \) [14, 15], one might expect that the odd-parity pairing state cannot survive in real samples. In this context, a recent theory by Michaeli and Fu [19] showed that odd-parity superconductivity in strongly spin-orbit coupled semiconductors like \( \text{Cu}_x\text{Bi}_2\text{Se}_3 \) are much more robust against the pair-breaking effect induced by impurity scattering than in more ordinary odd-parity superconductors. Nevertheless, this theory assumed a scalar impurity potential, so the information of the scattering anisotropy in \( \text{Cu}_x\text{Bi}_2\text{Se}_3 \) is important for better understanding the protection of the odd-parity state from impurity scattering. In this paper, we show the anisotropic normal-state resistivity data which strongly suggest that not only the effective mass but also the scattering rate is anisotropic, but the scattering rate anisotropy is only a factor of \( \sim 3 \).

2. \( \text{Cu}_x\text{Bi}_2\text{Se}_3 \) superconductor
The prototypical topological insulator \( \text{Bi}_2\text{Se}_3 \) consists of basic crystallographic units of Se–Bi–Se–Bi–Se quintuple layers, which are weakly bonded by the van der Waals force. When Cu is intercalated into the van der Waals gap, superconductivity appears below the critical temperature \( T_c \) of up to \( \sim 3.8 \) K [9]. However, \( \text{Cu}_x\text{Bi}_2\text{Se}_3 \) is difficult to synthesize and samples with a large superconducting volume fraction are rarely obtained with the usual melt-growth method [9, 20]. This problem was recently ameliorated by the development of electrochemical synthesis technique [14] which allowed the synthesis of superconducting samples with the shielding fraction exceeding 50% [13]. In this work, we used \( \text{Cu}_x\text{Bi}_2\text{Se}_3 \) single crystals of slab-like geometry prepared by the electrochemical technique described in detail in Ref. [14].

3. Measurements
The point contacts were prepared on a freshly cleaved surface with the so-called “soft point-contact” technique described in Refs. [10] and [21]. The \( dI/dV \) spectra were measured with a lock-in technique by sweeping a dc current that is superimposed with a small-amplitude ac current. The anisotropic resistivity was measured with the Montgomery method [22] by putting four line-shaped contacts along the four parallel edges of a parallelepiped: for this measurement, we employed the dc four-probe technique with a scanner switching the combinations of the current and voltage contacts. All the samples were characterized by a commercial SQUID magnetometer to check for the \( T_c \) and the shielding fraction.

4. Zero-bias conductance peak
Figure 1 shows the \( dI/dV \) spectra measured at various temperatures on a new \( \text{Cu}_x\text{Bi}_2\text{Se}_3 \) sample with \( x = 0.31 \). One can see that the conductance near zero bias is slightly enhanced at 3.2 K compared to that at 4.0 K, and a clear peak is formed at 2.4 K and below. The inset of Fig.
Figure 1. $dI/dV$ spectra at various temperatures measured on a cleaved surface of a Cu$_x$Bi$_2$Se$_3$ single crystal ($x = 0.31$) using the soft point-contact technique. Inset shows the temperature dependence of the conductance at $V = 0$.

1 shows the temperature dependence of the conductance at zero bias, $G_{PC}$, which presents a weak enhancement below $\sim 3.8$ K and a stronger enhancement below $\sim 2.7$ K. Since the $T_c$ of this sample measured by the magnetization was 3.3 K, which is typical for $x = 0.31$, the present result strongly suggest that the zero-bias conductance can start to grow immediately below $T_c$ if the point contact hits a good spot. (The shielding fraction of this sample at 1.8 K was 38%.) Therefore, one may conclude that thermal smearing plays little role in determining the observability of the ZBCO in Cu$_x$Bi$_2$Se$_3$.

5. Resistivity anisotropy

Since the Montgomery method can sometimes be inaccurate depending on the aspect ratio and the inhomogeneity of the sample, we measured two samples with different aspect ratios to confirm the reproducibility of the result. Figures 2(a) and 2(b) show the temperature dependences of the in-plane resistivity $\rho_{ab}$ and the c-axis resistivity $\rho_c$ measured on two different samples cut from the same single crystal ($x = 0.35$), which showed the $T_c$ of 3.2 K and the shielding fraction of 48% at 1.8 K. Figure 2(c) shows the resistivity anisotropy ratio $\rho_c/\rho_{ab}$ for the two samples. One can see that $\rho_c/\rho_{ab}$ is around 10, and the possible uncertainty (inferred from the difference

Figure 2. (a),(b) Temperature dependences of $\rho_{ab}$ and $\rho_c$ measured on two samples with different aspect ratios using the Montgomery method. Sample #1 had the thickness $d = 0.334$ mm, the width $w = 0.649$ mm, and the length $L = 1.33$ mm, while the dimensions of sample #2 were $d = 0.340$ mm, $w = 1.64$ mm, and $L = 2.14$ mm. (c) Resistivity anisotropy ratio calculated from the data shown in panels (a) and (b).
between the two data sets) is about 20%.

6. Scattering-rate anisotropy

One should remember that the source of the resistivity anisotropy is usually an effective-mass anisotropy, $m_c/m_{ab}$. In anisotropic superconductors [23], the anisotropy ratio $\gamma$ is defined as $\gamma = \xi_{ab}/\xi_c$, where $\xi_{ab}$ and $\xi_c$ are the coherence lengths in the in-plane and the $c$-axis directions, respectively. By using the anisotropic Ginzburg-Landau theory, one obtains $\gamma = \sqrt{m_c/m_{ab}}$ [23].

Since the mass anisotropy also determines the resistivity anisotropy via $\rho_c/\rho_{ab} = m_c/m_{ab}$ when the scattering rate is isotropic, the resistivity anisotropy in the normal-state resistivity and the anisotropy ratio in the superconducting properties are often related by $\rho_c/\rho_{ab} = \gamma^2$. In fact, in a high-$T_c$ cuprate $\text{YBa}_2\text{Cu}_3\text{O}_y$ near optimum doping, $\gamma \approx 5$ and $\rho_c/\rho_{ab} \approx 25$ [23].

In the present case of $\text{Cu}_x\text{Bi}_2\text{Se}_3$, we observed that $\gamma \approx 1.8$ and it is essentially independent of $x$ [15]. This implies that the effective-mass anisotropy in $\text{Cu}_x\text{Bi}_2\text{Se}_3$ is $m_c/m_{ab} = \gamma^2 \approx 3.2$, which is smaller than the observed $\rho_c/\rho_{ab}$. Therefore, it is most likely that the scattering rate is not isotropic in $\text{Cu}_x\text{Bi}_2\text{Se}_3$ and it adds additional anisotropy in the normal-state transport properties. One can estimate the scattering-rate anisotropy from $(\rho_c/\rho_{ab})/(m_c/m_{ab})$ to be $\sim 3$.

7. Summary

We presented new point-contact spectroscopy data as well as the anisotropic normal-state resistivity data to better understand the topological superconductor $\text{Cu}_x\text{Bi}_2\text{Se}_3$. The new point-contact spectra showed that the zero-bias conductance peak starts to grow immediately below $T_c$, removing the ambiguity about the possible role of thermal smearing. The resistivity anisotropy was found to be $\sim 10$, which, in combination with the effective-mass anisotropy of 3.2 determined from the anisotropic superconducting properties [15], suggests that the scattering rate is anisotropic by a factor of $\sim 3$. Hence, the scattering potential in $\text{Cu}_x\text{Bi}_2\text{Se}_3$ is not strongly anisotropic, which is important for theoretically elucidating the robustness of the odd-parity pairing against impurity scattering.

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