Superconductivity with two-fold symmetry in topological superconductor Sr$_x$Bi$_2$Se$_3$

Guan Du$^1$, YuFeng Li$^1$, J. Schneeloch$^2$, R. D. Zhong$^2$, GenDa Gu$^2$, Huan Yang$^{1,3}$, Hai Lin$^1$, and Hai-Hu Wen$^{1,3*}$

$^1$National Laboratory of Solid State Microstructures and Department of Physics, Nanjing University, Nanjing 210093, China; $^2$Condensed Matter Physics and Materials Science Department, Brookhaven National Laboratory, Upton, New York 11973, USA; $^3$Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210093, China

Received December 22, 2016; accepted December 30, 2016; published online January 11, 2017

Topological superconductivity is the quantum condensate of paired electrons with an odd parity of the pairing function. By using a Corbino-shape like electrode configuration, we measure the $c$-axis resistivity of the recently discovered superconductor Sr$_x$Bi$_2$Se$_3$ with the magnetic field rotating within the basal planes, and find clear evidence of two-fold superconductivity. The Laue diffraction measurements on these samples show that the maximum gap direction is either parallel or perpendicular to the main crystallographic axis. This observation is consistent with the theoretical prediction and strongly suggests that Sr$_x$Bi$_2$Se$_3$ is a topological superconductor.

1 Introduction

Topological superconductors (TSCs) are novel quantum phases characterized by topologically nontrivial Cooper pairing orders [1]. The unconventional superconductivity in TSCs cannot be connected to a topological trivial phase adiabatically without closing the superconducting gap. As a consequence, a TSC is supposed to possess robust gapless excitations on the boundary or surface. Because of the particle-hole symmetry of superconducting states, the excitation at zero energy is composed of same weight of electrons and holes. Such a zero energy excitation satisfies the requirement of Majorana fermions whose antiparticle is identical to itself [1-3]. The Majorana fermions in TSCs have various exotic phenomena and can help to realize topological quantum computation [1-3]. Tremendous efforts have been devoted to study the one-dimensional [4, 5], two-dimensional [6-8] and three-dimensional [9-20] topological systems, however, the experimental realization and detection of TSCs and Majorana fermions are still open issues.

Among the three dimensional systems, superconductors derived from Bi$_2$Se$_3$ by chemical doping are predicted to be candidates of TSCs [11, 12] and have been intensively studied. Point contact tunneling measurements indicate the zero-bias conductance peaks (ZBCPs) on the surface of Cu$_x$Bi$_2$Se$_3$, which is interpreted as signatures of Majorana fermions [9, 10]. In contrast, the ZBCPs are absent in scanning tunneling spectroscopy (STS) on the same material [14]. Recently, superconductivity has been discovered in Sr$_x$Bi$_2$Se$_3$ which is supposed to be a promising candidate...
of TSC [17-19]. However, the STS studies revealed a full superconducting gap without any abnormal in-gap states [20]. The absence of ZBCPs in the STS studies of Cu$_x$Bi$_2$Se$_3$ and Sr$_x$Bi$_2$Se$_3$ questions whether these materials are TSCs, or the theoretical understanding on the tunneling spectrum needs to be modified, this makes the issue under intensive debates. Recently the NMR studies are conducted on Cu$_x$Bi$_2$Se$_3$, and the unusual two-fold symmetry of the Knight shift in the hexagonal plane is observed [21]. The angle-dependent specific heat measurements on Cu$_x$Bi$_2$Se$_3$ also shows similar two-fold symmetry [22]. Both results support the nematic superconductivity, which may indicate a two-fold nodeless superconducting gap [23] in the material with a trigonal $D_{3h}$ crystallographic point group.

In this paper, we report the $c$-axis resistivity measured on high-quality Sr$_x$Bi$_2$Se$_3$ single crystals with the magnetic field rotating in the basal planes. With this configuration, the vortex contribution to resistivity is supposed to be the same for any angles. However, we find that all the angle-dependent resistivity obtained in the superconducting transition region has two-fold symmetry in low temperature and magnetic field regions. Our data suggest that the superconducting gap has a two-fold symmetry with gap maximum direction parallel or perpendicular to the main crystallographic axis, which is consistent with the expectation for TSCs.

### 2 Experimental details

We used the melt-growth method to grow the crystals. The stoichiometric amounts of Sr, Bi, and Se were sealed in an ampoule that was sealed within another ampoule (double-sealed) under 0.2 bar Ar, then the ampoule was placed horizontally in a small box furnace, heated up to 900°C, rocked to mix the liquid for 10 h, cooled to 640°C at 0.5°C/h, and then quenched in liquid nitrogen. The inner ampoules were 2 mm thick, had 10 mm inner diameter, and were 15 cm long; the outer ampoules had similar dimensions and were 1 mm thick. Typically, Sr$_x$Bi$_2$Se$_3$ was made this way in 30 g batches.

The dc magnetic susceptibility was measured using a commercial superconducting quantum interference device with the vibrating sample magnetometer facility (SQUID-VSM, Quantum Design). The Laue X-ray crystal alignment system (Photonic Science Ltd.) was used to investigate the crystal orientation of the cleaved surface. The angle-dependent measurements are carried out on a physical property measurement system (PPMS, Quantum Design). The sample was cleaved along the Van der Waals layers and cut into square. The four-electrode method is performed and the electrodes are made on the cleaved surfaces of the sample with the Corbino-shape like configuration. To eliminate the influence of the slight Hall signals on the raw data of angular dependence of resistivity, the resistivity taken at every angle has been averaged with positive and negative magnetic fields.

### 3 Results and discussion

The measurements were performed on 4 different Sr$_x$Bi$_2$Se$_3$ single crystals. All samples show rather sharp superconducting transitions. For brevity, we name samples No.1 to No.4 as S1 to S4, respectively. Taking S1 for example, the temperature dependent magnetization curves obtained with zero-field-cooled (ZFC) and field-cooled (FC) processes are displayed in Figure 1(a). The superconducting transition temperature is about 2.8 K. The calculated magnetic screening volume is about 92.4% from the ZFC data at 1.8 K by considering the demagnetization factor $N_m = 0.713$ determined from the geometric dimensions of the cuboid specimen, indicating good quality of the sample. The resistance measurements were carried out with the electrode configuration presented as the cartoon picture shown in the right bottom inset of Figure 1(b). The four-electrode method is performed and electrodes are made on the cleaved opposite surfaces with the Corbino-shape like configuration to allow the current flow mainly along the $c$-axis. The magnetic field is rotated in the basal plane, and the current is always perpendicular to the magnetic field. The main panel of Figure 1(b) displays the resistivity versus temperature of S1 measured under zero magnetic field. The superconductivity transition occurs at about 2.78 K which is obtained with the criterion of half normal state value $\rho_n$. Figure 1(c) shows the Laue diffraction patterns of the cleaved surface of S1. By comparing with the simulated pattern of Sr$_x$Bi$_2$Se$_3$ shown in the right hand side of Figure 1(c), the corresponding lattice structure of the Se terminated surface is deduced and shown in the top part of Figure 1(c). To show the relationship between the experimental data of different samples more clearly, we define a Se-Se direction as the zero-degree direction, and $\theta$ is the angle enclosed between the magnetic field and the selected Se-Se direction as indicated in the figure. Figure 1(d) shows the angle-dependent resistivity of S1 at 1.9 K and 0.5 T. The clear two-fold symmetry feature is viewed with two obvious peaks. Such a two-fold symmetry feature is more dramatically demonstrated in the polar coordinate representation as shown in the inset of Figure 1(d).

Figure 2 shows the angle-dependent resistivity measured at various magnetic fields and temperatures for S1, S2, and S3. To avoid the possible asymmetric problem, the data shown here have been taken by averaging the raw data with positive and negative magnetic fields. All the data taken on different samples show the two-fold symmetry in general. The data measured at 1.9 K and different fields shown in Figure 2(a), (c), and (e) are simply dumbbell-shaped below 1 T. When the
Figure 1 (Color online) Superconducting properties of S1. (a) Temperature dependence of magnetic susceptibility of S1 measured with ZFC and FC processes at 3 Oe. (b) Temperature dependence of resistivity of S1 at zero field. The insets show the photograph of S1 with the electrodes (above) and the Corbino-shape like electrode configuration (below). The field is applied within the basal plane of the sample. (c) The experimental Laue diffraction patterns of the cleaved top surface of S1 (left), theoretically simulated Laue diffraction patterns (right), and the derived lattice structure of the terminated Se surface (above). (d) Angular dependence of c-axis resistivity of S1 measured at 0.5 T and 1.9 K. The inset shows the representation of the same data by polar coordinates.

Figure 2 (Color online) The angular dependence of resistivity of S1-S3 measured at various fields and temperatures. (a), (c), (e) The angular dependence of c-axis resistivity measured at 1.9 K and different magnetic fields for S1 (a), S2 (c), and S3 (e). (b), (d), (f) The angular dependence of resistivity measured at 0.5 T and different temperatures for S1 (b), S2 (d), and S3 (f).
further analyzed the data at 1.5 T with Fourier transformation, and six-fold as well as four-fold symmetric components are found, as detailed in the Supporting Information section. We argue that the six-fold symmetric component may contain the information contributed by the six-fold crystal structure, and the tiny four-fold structure may result from the frequency doubling effect of the two-fold component.

We further measured the temperature dependent resistivity at angles $\theta^{\text{max}}$ and $\theta^{\text{min}}$. The data have been averaged with positive and negative fields to remove the possible Hall components. As shown in Figure 3, superconductivity can be more easily suppressed by field applied at $\theta^{\text{max}}$ than that at $\theta^{\text{min}}$. In order to obtain the upper critical field $H_c2$ anisotropy between $\theta^{\text{max}}$ and $\theta^{\text{min}}$ directions, we record $H_c2$ by taking the half of the $\rho_{\alpha}$ as the criterion for different samples, and the data are shown in Figure 3(c), (f), and (i). We then fitted the data by the equation

$$ H_{c2}(T) = H_{c2}(0) \frac{1 - (\frac{T}{T_c})^2}{1 + (\frac{T}{T_c})^2}. $$

In above equation we choose the two components $(1-r^2)$ and $(1+r^2)$ since they are the basic ingredients for constructing the temperature dependence of the thermodynamic critical field, or the coherence length $\xi$, or the magnetic penetration depth $\lambda$. In the case of Ginzburg-Landau (GL) theory, $\alpha = 1$. The fitting parameters for the three samples are illustrated in Table S1 of the Supporting Information section, and the fitting curves are plotted in Figure 3(c), (f), and (i) as solid lines. The resultant anisotropy of the in-plane $H_{c2}(0)$ is from 1.96 to 2.84 (See the Supporting Information section for details). We also notice that the resistivity curves measured on S1 and S2 have “peak” structures near $T_c$. This “peak effect” is not a common phenomenon and may have the same reason as the complex angular dependent behavior at high fields and temperatures.

Figure 4 shows the angle-dependent resistivity measured at 1.9 K and 0.5 T on three samples. As determined above, $\theta^{\text{min}}$ for S1, S2, and S3 are 176°, 176°, and 93° and are indicated by the red lines in Figure 4. The corresponding crystal structures on the Se-Se plane is also shown to indicate the angular relationship between resistivity anisotropy and the crystal axis direction of the Se-Se plane.

To prove that the two-fold symmetry appeared in Sr$_2$B$_2$Se$_3$ is not induced by accident or by experimental error, we did the same measurement on an optimally doped iron-based superconductor Ba$_{6.5}$K$_{0.35}$Fe$_2$As$_2$ which has the in-plane isotropic property. All the data shown in Figure 5 are measured by the Corbino-shape like electrode as displayed in the inset of Figure 1(b). With the applied field of 15 T, the superconducting transition is still very sharp that the resistivity is zero below 35 K and quickly increase to the value of the
normal state above 36 K as presented in Figure 5(b). And further, one finds no trace of the clear dumbbell-shaped feature that appears in Sr$_2$Bi$_2$Se$_3$ demonstrating the in-plane isotropy of the Bi$_{0.65}$K$_{0.35}$Fe$_2$As$_2$ single crystal. The slight ellipse profile in Figure 5(b) may be caused by the asymmetry of the electrodes on either side of the sample.

With the six-fold crystallographic structure, it is a surprise to observe a two-fold symmetry of resistivity in the superconducting transition region. One may argue that the two-fold symmetric feature is caused by the possible ordering of the intercalated Sr atoms in a two-fold symmetry, like the strip structures. However, we have already studied the cleaved surfaces of Sr$_2$Bi$_2$Se$_3$ single crystals by scanning tunneling microscope and no any regular patterns of intercalated Sr have been observed [20]. Further, the dumbbell-shaped feature is absent in the data of the in-plane isotropic superconductor Bi$_{0.65}$K$_{0.35}$Fe$_2$As$_2$, demonstrating that the two-fold symmetric feature results from the intrinsic property of Sr$_2$Bi$_2$Se$_3$ instead of accident or experimental error. Since the two-fold symmetry only emerges in the superconducting transition range, it is obvious that such feature is strongly correlated with the symmetry of the superconducting gap.

Intuitively, the two-fold symmetric resistivity curves imply that the superconducting gap may have a two-fold symmetric feature by considering the relation of the $H_{c2}$ and the gap value. According to the Pippard equation, we have

$$\xi_0 = \frac{\hbar v_F}{\pi \Delta(0)},$$

(2)

here $v_F$ is the Fermi velocity, and $\Delta(0)$ is the superconducting gap at zero temperature. For a type-II superconductor, the GL theory gives that $H_{c2}(0) = \Phi_0/(2\pi\xi_0^2)$, where $\Phi_0$ is the magnetic flux quantum. Thus we get

$$H_{c2}(0) = \frac{\Phi_0 \pi}{\hbar^2 v_F^2} \Delta(0)^2.$$  

(3)

Now it becomes clear that the upper critical field will correlate with the gap, and the angle dependence of the $c$-axis resistivity with a two-fold symmetry can get a good explanation. Along $\theta_{\text{min}}$ directions, $H_{c2}$ reaches its maximum as shown in Figure 3. Consequently, in the same direction, the superconducting gap also has the maximum value. Therefore, the red lines in Figure 4 also indicate the directions of...
the maximum superconducting gaps. Our STS studies suggest that the superconducting gap of Sr$_x$Bi$_2$Se$_3$ is nodeless but has an anisotropic component [20], which is qualitatively consistent with the existence of superconducting gap with a two-fold symmetry. For S1 and S2, the direction of the maximum gap is most likely to be pinned along the Se-Se crystallographic axis as indicated by the lattice structure illustration in Figure 4(a) and (b). However, for S3 shown in Figure 4(c), the gap maximum direction is approximately vertical to the Se-Se crystallographic axis, with the uncertainty less than 4°. Above all, we can conclude that the superconductivity in Sr$_x$Bi$_2$Se$_3$ is nodeless and two-fold symmetric, and the gap maximum direction prefers to be parallel or perpendicular to the crystallographic axis. This is consistent with the earlier experiments by NMR [21] and angle resolved magnetocaloric [22] measurements.

According to the theoretical studies [23], for the crystal structure of Cu$_x$Bi$_2$Se$_3$ and Sr$_x$Bi$_2$Se$_3$, there are six irreducible representations characterizing the superconducting pairing symmetry, i.e., $A_{1g}$, $A_{1u}$, $A_{2u}$, $A_{2g}$, $E_u$, and $E_g$. Among them, only the $E_u$ representation is satisfied with our results. Since the $E_u$ represents the odd parity of Cooper pairing, our results here suggest that Sr$_x$Bi$_2$Se$_3$ is a topological superconductor.

4 Conclusions

In summary, we performed the $c$-axis resistivity measurements with an angle-dependent in-plane magnetic field on four Sr$_x$Bi$_2$Se$_3$ samples with the Corbino-shape like electrode configuration. Dramatic two-fold symmetry features are observed in all the experiments at low magnetic fields and temperatures. This along with the $H_{c2}$ measurements and the previous STS experiment provide the evidence of nodeless but two-fold symmetric superconducting gaps. We also find that the gap maximum direction prefers to be pinned parallel or perpendicular to the crystallographic axis. This is consistent with the prediction of topologically non trivial superconductivity in Sr$_x$Bi$_2$Se$_3$.

Note added: When preparing the manuscript, we became aware of another investigation which also achieves the conclusion about the two-fold anisotropy of the in-plane resistivity measured on Sr$_x$Bi$_2$Se$_3$. In that measurement the resistivity induced by the flux motion driven by Lorentz force will naturally show a two-fold oscillation. Resistivity along $c$-axis was later added in their supplementary [24].

We thank Profs. GuoQing Zheng and Liang Fu for helpful discussions. This work was supported by the National Natural Science Foundation of China (Grant Nos. 0402/11534005, and 11190023), the Ministry of Science and Technology of China (Grant No. 2016YFA0300401). The work in Brookhaven was supported by the Office of Science, U.S. Department of Energy (Grant No. DE-SC0012704). J. Schneeloch and R. D. Zhong are supported by the Center for Emergent Superconductivity, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science.

Supporting Information

The supporting information is available online at phys.scichina.com and http://link.springer.com/journal/11433. The supporting materials are published as submitted, without typesetting or editing. The responsibility for scientific accuracy and content remains entirely with the authors.

1. X. L. Qi and S. C. Zhang, Rev. Mod. Phys. 83, 1057 (2011).
2. M. Leijnse, and K. Flensberg, Semicond. Sci. Technol. 27, 124003 (2012).
3. C. W. J. Beenakker, Annu. Rev. Condens. Matter Phys. 4, 113 (2013).
4. V. Mourik, K. Zuo, S. M. Frolov, S. R. Plissard, E. P. A. M. Bakkers, and L. P. Kouwenhoven, Science 336, 1003 (2012).
5. S. Nadj-Perge, I. K. Drozdov, J. Li, H. Chen, S. Jeon, J. Seo, A. H. MacDonald, B. A. Bernevig, and A. Yazdani, Science 346, 602 (2014).
6. M. X. Wang, C. Liu, J. P. Xu, F. Yang, L. Miao, M. Y. Yao, C. L. Gao, C. Shen, X. Ma, X. Chen, Z. A. Xu, Y. Liu, S. C. Zhang, D. Qian, J. F. Jia, and Q. K. Xue, Science 336, 52 (2012).
7. J. P. Xu, M. X. Wang, Z. L. Liu, J. F. Ge, X. Yang, C. Liu, Z. A. Xu, D. Guan, C. L. Gao, D. Qian, Y. Liu, Q. H. Wang, F. C. Zhang, Q. K. Xue, and J. F. Jia, Phys. Rev. Lett. 114, 017001 (2015).
8. H. H. Sun, K. W. Zhang, L. H. Hu, C. Li, G. Y. Wang, H. Y. Ma, Z. A. Xu, C. L. Gao, D. Duan, Y. Y. Li, C. Liu, D. Qian, Y. Zhou, L. Fu, S. C. Li, F. C. Zhang, and J. F. Jia, Phys. Rev. Lett. 116, 257003 (2016).
9. S. Sasaki, M. Kriener, K. Segawa, K. Yada, Y. Tanaka, M. Sato, and Y. Ando, Phys. Rev. Lett. 107, 217001 (2011).
10. T. Kirzhner, E. Lahoud, K. B. Chaska, Z. Salman, and A. Kanigel, Phys. Rev. B 86, 064517 (2012).
11. L. Fu, and E. Berg, Phys. Rev. Lett. 105, 097001 (2010).
12. T. H. Hsieh, and L. Fu, Phys. Rev. Lett. 108, 170507 (2012).
13. A. Yamakage, K. Yada, M. Sato, and Y. Tanaka, Phys. Rev. B 85, 180509 (2012).
14. N. Levy, T. Zhang, J. Ha, F. Shariﬁt, A. A. Talin, Y. Kuk, and J. A. Stroscio, Phys. Rev. Lett. 110, 117001 (2013).
15. S. Sasaki, Z. Ren, A. A. Taskin, K. Segawa, L. Fu, and Y. Ando, Phys. Rev. Lett. 109, 217004 (2012).
16. G. Du, Z. Du, D. Fang, H. Yang, R. D. Zhong, J. Schneeloch, G. D. Gu, and H. H. Wen, Phys. Rev. B 92, 020512 (2015).
17. Z. Liu, X. Yao, J. Shao, M. Zuo, L. Pi, S. Tan, C. Zhang, and Y. Zhang, J. Am. Chem. Soc. 137, 150814061030009 (2015).
18. Shruti, V. K. Maurya, P. Neha, P. Srivastava, and S. Patnaik, Phys. Rev. B 92, 020506 (2015).
19. C. Q. Han, H. Li, W. J. Chen, F. Zhu, M. Y. Yao, Z. J. Li, M. Wang, B. F. Gao, D. D. Guan, C. Liu, C. L. Gao, D. Qian, and J. F. Jia, Appl. Phys. Lett. 107, 171602 (2015).
20. G. Du, J. Shao, X. Yang, Z. Du, D. Fang, C. Zhang, J. Wang, K. Ran, J. Wen, H. Yang, Y. Zhang, and H. H. Wen, arXiv: 1604.08198.
21. K. Matano, M. Kriener, K. Segawa, Y. Ando, and G. Zheng, Nat. Phys. 12, 852 (2016).
22. S. Yonezawa, K. Tajiri, S. Nakata, Y. Nagai, Z. Wang, K. Segawa, Y. Ando, and Y. Maeno, Nat. Phys., doi:10.1038/nphys3907 (2016).
23. L. Fu, Phys. Rev. B 90, 100509 (2014).
24. Y. Pan, A. M. Nikitin, G. K. Araizi, Y. K. Huang, Y. Matsushita, T. Naka, and A. de Visser, Sci. Rep. 6, 28632 (2016).