Observation of Surface Superconductivity in a 3D Dirac Material

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Superconductivity becomes more interesting when it encounters dimensional constraint or topology because it is of importance for exploring exotic quantum phenomena or developing superconducting electronics. Here, the coexistence of naturally formed surface superconducting state and 3D topological Dirac state in single crystals of BaMg2Bi2 is reported. The electronic structure obtained from the first-principles calculations demonstrates that BaMg2Bi2 is an ideal Dirac material, in which the Dirac point is very close to the Fermi level and no other energy band crosses the Fermi level. Superconductivity up to 4.77–5.17 K can be observed under ambient pressure in the measurements of resistivity. The anisotropic upper critical field and angle dependent magnetoresistance reveals the 2D characteristic of superconductivity, indicating that superconductivity occurs on the surface of the sample and is absent in the bulk state. The study not only provides BaMg2Bi2 as a suitable platform to study the interplay between superconductivity and topological Dirac state but also indicates that MgBi-based materials may be a promising system for exploring new superconductors.

1. Introduction

The study of 2D superconductivity provides insight into a variety of quantum phenomena in condensed matter physics and material science.[1] The 2D superconductivity can be realized in systems such as heterogeneous interfaces or atomically ultrathin materials.[3] The 2D interfacial superconductivity has been observed in LaAlO3/SrTiO3,[2] FeSe/SrTiO3,[3,4] EuO/KTaO3(111),[5] etc. Few-layer stanene and 1T-T2-MoTe2 also exhibit superconductivity at low temperature.[6–8] In addition, superconductivity up to 14.9 K was discovered in thin film of infinite-layer nickelate NdxSr1–xNiO2, indicating the possibility of a family of nickelate superconductors. Recently, surface superconductivity can also be found in some topological materials,[10,11] such as topological insulator Sb2Te3,[12] Dirac semimetal KZnBi,[13] Cd3As2 nanoplate (proximity-induced)[14] and type II Weyl semimetal TaIrTe4,[15] which provide more platforms for studying 2D superconductivity.

Searching for superconductivity in topological materials has attracted a lot of interest for the possibility of obtaining novel topological phases, for example, the topological superconductivity (TSC).[16,17] Topological superconductors host superconducting bulk state and gapless Majorana surface states.[18,19] The Majorana fermions exist in the superconducting gap and have the potential to be applied to topological quantum computation. Recently, Zhang et al. reported the observation of TSC on the surface states of FeTe0.55Se0.45.[20]
Liu et al. demonstrated the Majorana zero mode arising from the chiral topological surface state of (Li_{0.84}Fe_{0.16})OHFeSe.[21] The TSC can also be induced by the proximity effect between an s-wave superconductor and surface Dirac fermions of topological insulator.[22] Experimentally, many attempts have been made to induce superconductivity on the surface of topological materials, including the fabrication of heterostructure,[23–27] tip/proximity-induced superconductivity[14,28–30] etc.

In this work, we grow the single crystals of BaMg_{2}Bi_{2} and study the transport properties and electronic structure. The first-principles calculations show that BaMg_{2}Bi_{2} is a 3D Dirac material, in which the Dirac point exists in the direction of Γ-A and is protected by the symmetry. The Dirac point is very close to the Fermi level. In addition, only a small hole-type Fermi surface carrying the Dirac fermions crosses the Fermi level in the band structure, indicating that BaMg_{2}Bi_{2} is an ideal material to explore extraordinary properties associated with Dirac fermions. Interestingly, superconductivity emerges at low temperature in the measurements of resistivity. The upper critical field shows an anisotropy between in-plane and out of plane, which supports the occurrence of surface superconductivity in the sample. The polar plots of the angle dependent magnetoresistance (MR) show a twofold symmetry in the superconducting state, further indicating the 2D characteristic of the observed superconductivity. Our findings demonstrate the coexistence of surface superconductivity and 3D topological Dirac state in BaMg_{2}Bi_{2}.

2. Results and Discussion

Figure 1a illustrates the crystal structure of BaMg_{2}Bi_{2}, which consists of alternating Ba atoms and MgBi layers. BaMg_{2}Bi_{2} crystallizes in the hexagonal CaAl_{2}Si_{2}-type structure with the space group of P3m1 (No. 164). The crystal structure has C_{3} rotational symmetry, as shown in the view from c-axis direction (Figure 1b). Figure 1c shows a typical image of the grown BaMg_{2}Bi_{2} single crystal, from which the hexagonal feature can be clearly seen. The first-principles calculations have been employed to study the electronic structure of BaMg_{2}Bi_{2}. When the spin-orbital coupling (SOC) effect is ignored, the band structure exhibits a gap around the Γ point (Figure S2, Supporting Information). As shown in Figure 1e,f, when the SOC effect is included, a Dirac point appears in the Γ-A direction, which is protected by the C_{3} symmetry. The band inversion is mainly contributed by the Mg s orbital and the Bi p orbital. It should be noted that the Dirac point is very close to the Fermi level and locates only ~8.5 meV above the Fermi level. Except for the Dirac fermion, there is no other energy band near the Fermi level. From the band structure, Dirac fermion will dominate the transport properties of BaMg_{2}Bi_{2}. The absence of quantum oscillations indicates that the Dirac fermion may occupy the zeroth Landau level and be in the quantum limit (Supporting Information).[31,32] The calculated band structure is consistent with the previous report on angle-resolved photoemission spectroscopy (ARPES) experiments,[33] revealing the 3D topological Dirac state in BaMg_{2}Bi_{2}.

Figure 2a presents the temperature dependent resistivity ρ(T) of BaMg_{2}Bi_{2} measured on Sample 2. The applied current is 100 µA. At first, the resistivity decreases with the decrease of temperature, exhibiting the metallic behavior. After the minimum at 160 K, an upturn appears in the resistivity curve with decreasing temperature, similar to a metal-insulator transition. Surprisingly, a sharp resistivity drop shows up at low temperature, indicating the transition to superconducting state. The superconducting transition temperature determined by linear epitaxy of normal curve and falling curve is T_c ~4.77 K (inset in Figure 2a). The observed superconducting state has been further characterized by changing magnetic field and current intensity. Figure 2b shows the temperature dependent
resistivity of BaMg$_2$Bi$_2$ under various magnetic fields. The applied field is perpendicular to the current direction. Superconductivity is gradually suppressed with increasing the field. At 8 T and 9 T, there is only a small drop in resistivity. The temperature dependence of critical field $H_c_2$ can be well described by the empirical formula $H_c_2 = H_c_2(0)[1 – (T/T_c)^2]$ (Figure S3, Supporting Information). The obtained upper critical field at 0 K is 8.7 T. The temperature dependent resistivity with different currents is shown in Figure 2c. The superconducting transition temperature shifts toward lower temperatures with increasing current. When the current reaches 4 mA, the superconductivity is almost completely suppressed. The variation of critical current $I_c$ with temperature (Figure S3, Supporting Information) is similar to the interfacial superconductivity in TaAs/Ag heterostructure and LaAlO$_3$/SrTiO$_3$ system.

Since BaMg$_2$Bi$_2$ exhibits a superconducting transition in the measurement of resistivity, the Meissner effect and specific heat jump are expected. However, after testing on several samples, it turns out that although superconducting transition can be observed in resistivity, the Meissner effect and a jump in heat capacity are absent (Figures S4 and S5, Supporting Information). This implies the possibility of surface superconductivity in the samples of BaMg$_2$Bi$_2$. Superconductivity only occurs on the surface of the sample, but the bulk state accounts for a large proportion in the measurements of magnetic susceptibility and specific heat. Thickness control experiments support the surface superconductivity in BaMg$_2$Bi$_2$ (Figure S6, Supporting Information). For a bulk superconductor, the critical current $I_c$ will decrease as the thickness decreases. However, the $I_c$ of samples with different thicknesses in BaMg$_2$Bi$_2$ almost remains the same magnitude. Surface superconductivity usually holds an anisotropic upper critical field. The anisotropy of the upper critical field in BaMg$_2$Bi$_2$ has been examined. The measurements were performed on Sample 10. Figure 3a shows the temperature dependent resistivity under different magnetic fields. The field is along the $c$-axis of the crystal and perpendicular to the current. The superconducting transition temperature under zero field is $T_c = 5.17 \text{ K}$, which is slightly higher than that of Sample 2. Since Sample 10 and Sample 2 come from different batches, it indicates that superconductivity may be related to the chemical potential in the samples. Figure 3b presents the $\rho(T)$ curves with the magnetic field deviates $45°$ and $90°$ from $z$-axis in the $yz$ plane, respectively. Figure 3c presents the similar measurements in the $xz$-plane. The configurations of the measurements can be seen from the insets. For $0°$ and $45°$, a magnetic field of 8 T can almost completely suppress the superconductivity. However, when the magnetic field rotates into the plane ($90°$), a magnetic field of 10 T is required to suppress the superconductivity. Figure 3f shows the plots of critical field $H_c_2$ as a function of $T/T_c$. The data points are extracted from Figure 3a–e and can be well fitted by the empirical formula. In both cases, the data of $0°$ and $45°$ almost coincide, while the data of $90°$ deviate significantly from them and have a higher upper critical field. When the magnetic field rotates in the $yz$-plane, the upper critical field shows an anisotropy of $H_{c2}(90°)/H_{c2}(0°) \approx 1.26$ (Figure 3f). This value is 1.19 for the case that the magnetic field rotates in the $xz$-plane (Figure 3g). The anisotropic parameter in BaMg$_2$Bi$_2$ is smaller than that in typical 2D superconductors but can be compared with that in Sb$_2$Te$_3$ and KZnBi.[13] The observation of anisotropic upper critical field provides evidence for surface superconductivity in BaMg$_2$Bi$_2$.

In order to further understand the unusual superconductivity in BaMg$_2$Bi$_2$, the measurements of angle dependent resistivity under magnetic field are performed. The schematic diagram of the measurements are plotted in Figure 4a. The current is along the hexagonal edge of crystal and the magnetic field rotates in the $yz$-plane and $xz$-plane, respectively. In the former configuration, as shown in Figure 4b, the polar plots of the angle dependent MR exhibit twofold symmetry with a period of $\pi$. The maximum and minimum values of resistivity appear at $0°$, $180°$ ($B//ab$ plane), and $90°$, $270°$ ($B//ab$ plane), respectively.
In the latter configuration, the patterns in Figure 4e,f shows a slight distortion, but the twofold symmetry remains. It should be noted that the twofold symmetry only exists in the superconducting state. Once the superconducting state is gradually suppressed with the increase of magnetic field or temperature, the twofold symmetry will be weakened and disappear. In the nonsuperconducting state, the angle dependent MR shows isotropic characteristic, which comes from the 3D Fermi surface of the bulk state. In general, the twofold symmetry means that the conductive layer is 2D. In materials, the Lorentz force affects the carrier momentum component in the plane perpendicular to the magnetic field. For a 2D conductive layer, the carrier only responds to the magnetic field component $B\cos\theta$, resulting in the twofold symmetry of the polar plots. In addition, the observed twofold symmetry cannot be derived from the bulk state because the bulk state is a small 3D Fermi surface, as demonstrated by the first-principles calculations and previous ARPES experiment. Thus, the superconductivity in BaMg$_2$Bi$_2$ is considered to be a 2D superconductivity that occurs on the surface of the sample.

In fact, the properties of BaMg$_2$Bi$_2$ are similar to KZnBi, which also hosts the surface superconductivity (0.85 K) and Dirac state. In both samples, the superconductivity naturally forms on the surface without external stimuli while the bulk state remains nonsuperconducting. The $T_c$ of BaMg$_2$Bi$_2$ is much higher than that of KZnBi, which may be related to the position of Dirac point. Taking Sb$_2$Te$_3$ as an example, it is a nonsuperconducting topological insulator, but the surface superconductivity can be induced by a minor tuning of growth chemistry. The tuning depletes bulk conduction channels and shifts Fermi energy toward the Dirac point, leading to the emergence of superconductivity. The relative position of Dirac point and Fermi level seems to play an important role in this process. In the case of BaMg$_2$Bi$_2$, the Dirac point is suggested to be closer to the Fermi level than that in KZnBi. The higher contribution of Dirac fermions to transport properties may lead to higher $T_c$.

Tremendous efforts have been made to explore superconductivity in topological materials for possible unconventional superconductivity. Since Dirac fermions exist in the bulk state of BaMg$_2$Bi$_2$, it is worth exploring the relationship or interplay between the superconductivity and topological state. The ARPES experiment at lower temperature is needed to reveal the detailed electronic structure in superconducting state, which may provide more information to the origin of this unusual surface superconductivity. In addition, it remains unclear whether and how the Dirac fermions fall into Cooper pairing, which is important for understanding the role of the Dirac fermions in surface superconductivity and it needs further investigation and theoretical studies. On the material side, BaMg$_2$Bi$_2$ possesses the MgBi layers that are important for transport properties and the formation of Dirac state. The MgBi-based materials may provide more opportunities for exploring new superconductors.

3. Conclusions

In summary, we report the observation of surface superconductivity up to 4.77—5.17 K under ambient pressure in the single crystals of BaMg$_2$Bi$_2$, which hosts the 3D topological Dirac state. The Dirac state has been described by the band structure from
first-principles calculations. The superconductivity was characterized by the measurements of resistivity. The 2D nature of superconductivity was verified by the anisotropic upper critical field and angle dependent MR, supporting that the superconductivity in BaMg$_2$Bi$_2$ occurs on the surface rather than in the bulk.

4. Experimental Section

Crystal growth and transport measurements: Large single crystals of BaMg$_2$Bi$_2$ were grown by flux method. The starting elements, Ba, Mg, and Bi, were mixed and put into the alumina crucible with a molar ratio of Ba : Mg : Bi = 1 : 5 : 9. The crucible was then sealed into an evacuated quartz tube and heated to 900 °C. After cooling to 650 °C in 300 h, the excess flux was removed with a centrifuge. The atomic composition of BaMg$_2$Bi$_2$ has been checked by energy dispersive X-ray spectroscopy. The measurements of transport properties were performed on a Quantum Design physical property measurement system (PPMS). The obtained crystals are sensitive to both air and GE varnish. The samples can survive in air for only several minutes. The electrodes used in the measurements were made in a glove box and then covered with a layer of N-grease.

Electronic structure calculations: The first-principles electronic structure calculations were performed with the projector augmented wave (PAW) method\cite{37,38} as implemented in the Vienna ab initio simulation package (VASP)\cite{39,40,41}. The generalized gradient approximation (GGA) of Perdew–Burke–Ernzerh (PBE) type\cite{42} was adopted for the exchange-correlation potential. The kinetic energy cutoff of the plane wave basis was set to be 400 eV. For the Brillouin zone sampling, a 15x 15 x9 k-point mesh was employed. The Gaussian smearing with a width of 0.02 eV was used around the Fermi surface. In structural optimization, both cell parameters and internal atomic positions were allowed to relax until all forces on atoms were smaller than 0.01 eV Å$^{-1}$. The relaxed structure parameters are well agreed with experimental results. The SOC effect was included in the calculations of the electronic properties.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.
