Evidence of topological nodal lines and surface states in the centrosymmetric superconductor SnTaS₂

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The discovery of signatures of topological superconductivity in superconducting bulk materials with topological surface states has attracted intensive research interests recently. Utilizing angle-resolved photoemission spectroscopy and first-principles calculations, here, we demonstrate the existence of topological nodal-line states and drumheadlike surface states in centrosymmetric superconductor SnTaS₂, which is a type-II superconductor with a critical transition temperature of about 3 K. The valence bands from Ta 5d orbitals and the conduction bands from Sn 5p orbitals cross each other, forming two nodal lines in the vicinity of the Fermi energy without the inclusion of spin-orbit coupling (SOC), protected by the spatial-inversion symmetry and time-reversal symmetry. The nodal lines are gapped out by SOC. The drumheadlike surface states, the typical characteristics in nodal-line semimetals, are quite visible near the Fermi level. Our findings indicate that SnTaS₂ offers a promising platform for exploring the exotic properties of the topological nodal-line fermions and gives a help to study topological superconductivity.

I. INTRODUCTION

The long-sought topological superconductor (TSC) with Majorana fermions extends scientific territory and plays an important role in strategies for topological quantum computing, though it still remains elusive in real materials. A typical TSC can be found in a $p+ip$ system, where the core of the superconducting vortex contains a localized quasiparticle with exactly zero energy [1]. However, the properties of several experimental candidates for $p$-wave superconductivity remain unclear [2]. Besides the $p$-wave pairing, the TSC could also be realized in the system with an $s$-wave pairing plus the spin-orbit coupling (SOC) and spin polarization, which is equivalent to the $p+ip$ system with broken spin-rotation symmetry [3,4]. Due to the proximity effect [3,5], an effective $p$-wave pairing can be realized on the interface of a heterostructure between a strong topological insulator (TI) and an $s$-wave superconductor (e.g., Bi$_2$Se$_3$/NbSe$_2$, Bi$_2$Te$_3$/NbSe$_2$, and Bi$_2$Se$_3$/Pb) [6–10], or a full-gapped bulk superconductor with topologically protected gapless surface (or edge) states (e.g., $\beta$-PdBi, FeTe$_{1-x}$Se$_x$, Cu$_3$Bi$_2$Se$_3$, Li$_{0.54}$Fe$_{0.16}$OHFeSe, and 2M-WS$_2$) [11–20]. Based on the latter scenario, the type-II superconductors with nontrivial surface states are promising candidates for TSCs. The surface states and superconducting gaps can be experimentally determined by angle-resolved photoemission spectroscopy (ARPES), and quasi-particle scattering interference imaging combined with scanning tunneling spectra. The scanning tunneling spectra can further be used to search for Majorana zero modes in the vortex core of these materials.

Besides, noncentrosymmetric superconductors with strong SOC have been proposed as a kind of TSCs, because of the breaking of spin degeneracy by asymmetric SOC [21]. It has been reported that noncentrosymmetric PbTaSe$_2$ hosting topological nodal lines and nontrivial surfaces states around the Fermi level ($E_F$) is a candidate for TSC without the aid of doping or artificial heterostructures [22–28]. The superconductivity on its surface states induced by the proximity effect can be stronger than that in TI/$s$-wave superconductor heterostructures [23]. Combining its helical spin-polarized surface state [23] with superconductivity, PbTaSe$_2$ therefore could be TSC even without asymmetric SOC. Here, we find a centrosymmetric superconductor SnTaS$_2$, which is isoelectronic to PbTaSe$_2$ and also has a crystal structure similar to that of layered PbTaSe$_2$. This centrosymmetric crystal structure is protected by the spatial-inversion symmetry and the time-reversal symmetry ($T$-$P$ symmetry) [29,30]. The previous calculations suggest that SnTaS$_2$ has nodal-line structures with drumheadlike surface states around $E_F$ [31,32], making it a good candidate to further detect the TSCs and Majorana fermions. However, so far, direct ARPES measurements of the low-energy electronic states are still absent.

In this paper, we demonstrate the existence of topological nodal-line states and nontrivial surface states in a type-II BCS superconductor SnTaS$_2$ by employing ARPES, scanning...
tunneling microscopy/spectroscopy (STM/S), and in combination with first-principles calculations. STS measurements indicate that the superconducting gap of about 0.35 meV at T = 0.4 K can be suppressed by an applied magnetic field of 0.013 T perpendicular to the sample surface, which is consistent with the transport measurements. The calculations show that the nodal lines are formed by the crossings of the Ta 5d orbitals and the Sn 5p orbitals in the vicinity of $E_F$ without the inclusion of SOC. If SOC is considered, nodal lines are gapped out. The surface bands connecting to each nodal line indicate the topological nontrivial states. ARPES observations of the features are in good agreement with the band calculations. The observed surface state can be clearly distinguished from the bulk states near $E_F$. These results uncover the topological electronic states in superconducting SnTaS$_2$, offering a new platform for further studies into Dirac nodal-line physics as well as TSCs.

II. METHODS

The single crystals were grown by the chemical vapor transport method as described elsewhere. STM experiments were carried out with a Unisoku low-temperature STM system. SnTaS$_2$ single crystals were cleaved in situ at $T = 77$ K under ultra-high vacuum, and transferred immediately into STM head under the vacuum of $2 \times 10^{-10}$ Torr. STS measurements were done using standard lock-in technique with a bias modulation of 0.1 mV at the frequency of 741 Hz. ARPES measurements were performed at Dreamline and 03U beamlines of Shanghai Synchrotron Radiation Facilities (SSRF). Samples smaller than 1 x 1 mm$^2$ were cleaved in situ, exposing flat mirror-like (001) surfaces. During measurements, the temperature was kept at $T = 20$ K. The pressure was maintained less than $4 \times 10^{-11}$ Torr. The first-principles calculations based on the density functional theory (DFT) were performed by using the Vienna Ab initio Simulation Package [34, 35], with the generalized gradient approximation in the Perdew-Burke-Ernzerhof type as the exchange-correlation functional [36, 37]. The plane-wave cutoff energy was set to be 420 eV in all first-principles calculations, and the first Brillouin zone (BZ) was sampled using a 13 x 13 x 5 Monkhorst-Pack grid. The experimental lattice constants $a = b = 3.309$ Å and $c = 17.450$ Å [31] were used in the calculations.

III. RESULTS AND DISCUSSIONS

The crystal structure of SnTaS$_2$ is illustrated in Figs. [a] and [b], which crystallizes in a layered hexagonal structure with the space group of P6$_3$/mmc (No. 194). The iso-electronic PbTaSe$_2$ [P6$_3$mmc (No. 187)] has a similar layered hexagonal structure. SnTaS$_2$ is a centrosymmetric crystal with $T$-P symmetry, however, noncentrosymmetric PbTaSe$_2$ without $T$-P symmetry has a reflection symmetry caused by Ta atomic plane [21, 22]. The corresponding three-dimensional (3D) and projected two-dimensional (2D) BZs ($\Gamma$ - $K$ - $M$) are shown in Fig. [c], where the $\Gamma$, $K$, and $M$ points serve as the high symmetry points of the $k_z$ = 0 plane, and the $A$, $H$, and $L$ points of the $k_z$ = $\pi$ plane.

To reveal the surface topography and the superconductivity, STM/S measurements were carried out on the (001) surfaces of SnTaS$_2$. The high-resolution STM topography taken on the area of the cleaved surface [Fig. [d]] shows flat TaS$_2$ plane decorated with islands of Sn. The atomic-resolved STM topography taken on the TaS$_2$ surface [inset of Fig. [d]] shows a clear hexagonal atomic structure with the lattice parameter of $a = 3.3$ Å. Figure [e] displays the scanning tunneling spectrum (dI/dV) at $T = 0.4$ K under the magnetic field of 0 (blue) and 0.013 T (red) perpendicular to the sample surface, respectively. To determine the gap size more precisely, we fit the tunneling spectrum with the Dynes function. The fitting curve is obtained by the thermal broadened density of states (DOS), which was calculated from the tunneling current expression [38, 39]:

$$I(V) \propto \int_{-\infty}^{\infty} \left| \text{Re} \frac{e^{-E-E_F}}{\sqrt{(E-E_F)^2}} [f(E) - f(E + eV)] dE \right|$$

where $f(E)$ is the Fermi-Dirac distribution function. The superconducting gap of about 0.35 meV at $T = 0.4$ K is estimated based on the fitting curve [blue curve in Fig. [e]]. By applying a magnetic field of 0.013 T perpendicular to the
We performed orbital-projected DFT calculations to study the low-energy electronic structure with their orbital characters. Figure 2(a) shows total and orbital-projected DOS within ±2 eV at $E_F$. The obvious dip-off of DOS near $E_F$ suggests a semimetallic character. Figures 2(b) and 2(c) show orbital-projected dispersions along the high-symmetry directions without and with SOC, respectively. The electronic structure near $E_F$ is mainly dominated by Ta 5$d$ (red) and Sn 5$p$ (blue) orbitals mixed with less S 3$p$ (green). The hole-like Ta 5$d$ bands and the electronlike Sn 5$p$ bands cross each other, forming several band-crossings around the $K$ point near $E_F$, as shown in Fig. 2(b). When SOC is taken into account, band gaps open at the crossing points, as shown in Fig. 2(c). In order to see the crossing points clearly, we enlarge the view around the $K$ point near $E_F$, as shown in Figs. 2(d) and 2(e). Without the inclusion of SOC, there are two crossing points considered as nodes along the $\Gamma$-$K$ direction, namely N1 and N2. The corresponding crossing points of N2 along the $\Gamma$-$M$ direction is marked with N2’. With the inclusion of SOC, the nodes are all gapped out. The sizes of SOC gaps at D1 and D2 (D2’) are about 40 and 80 meV [Fig. 2(e)], respectively, which are comparable with typical nodal-line materials such as PbTaSe$_2$, CaAgAs, TiB$_2$, ZrSiS and CaP$_3$ families [22, 40–47]. To carefully check whether the band-crossings form the nodal lines in the momentum space, we calculate constant energy surfaces without SOC at $E_F$ and $E_F$-0.39 eV, respectively. The nodal lines formed by N1 and N2 (N2’) are indicated by the arrows as shown in Figs. 2(f) and 2(g). Because the energy positions of crossing points of N2 nodal lines are different around the $K$ points, the N2 shows various thicknesses at different momentum points on the constant energy surfaces.

Besides, the drumheadlike surface state is a typical characteristic in nodal-line semimetals and could bring varieties of unusual intriguing properties. To study the surface states, we performed the slab calculation with 30-unit-thickness layers [Figs. 2(h) and 2(i)]. The gradual changing bands present the bulk bands and the rest are surface bands in Fig. 2(h).
To directly detect the topological features near $E_F$, we performed ARPES measurements on (001) surfaces of SnTaS$_2$. Since the nodal lines are located on the $k_z = 0$ plane according to the calculation, we carried out the photon-energy-dependent ARPES measurement to investigate the detailed $k_z$ dispersions. With empirical value of inner potential ~11 eV and $c' = c/2 = 8.725$ Å (due to bilayer in the conventional unit cell), we found that $h\nu = 60$ and 84 eV are close to the $\Gamma$ point, and 48 and 72 eV are close to the $A$ point, according to the free electron final-state model [48]. Despite the bands near $E_F$ show weak $k_z$ dispersions in Figs. 3(a) and 3(b), a periodic modulation along the $k_z$ direction can still be found, as the dispersions marked by the red line in Fig. 3(b). Figures 3(c) and 3(d) show corresponding energy-momentum plots along the $A-H$ line (48 eV), and the marks on the momentum distribution curve (MDC) taken at the binding energy of about 0.2 eV refer to the bands crossing at $E_F$. This band structure looks more like the slab calculation with Sn-terminated (001) surface states of Fig. 2(i), rather than the bulk states of Fig. 2(c). Especially, the bands around BZ center with weak intensities seem to be stuck together, which are different from the clean bulk-calculation bands with strong dispersions along the $\Gamma-A$ direction in Fig. 2(c). This discrepancy is mainly caused by the $k_z$-limitation and matrix element effects in the ARPES spectra, which reflect the electronic states integrated over a certain $k_z$ region of bulk BZ, and the electronic states at $k_z = 0$ and $\pi$ contribute greatly [49]. In recent studies on the topological semimetals [22, 41–44], it is prominent that the states from $k_z = 0$ and $\pi$ can be detected on other $k_z$ planes in the ARPES measurements. Thus, ARPES data is usually compared with the calculation results of the slab and the surface states. As an evidence shown in Figs. 3(c) and 3(g), the Fermi surfaces of the $k_z \sim 0$ and $\pi$ planes are almost the same. The Fermi surfaces are similar to those of PbTaSe$_2$, which can be more precisely figured out with the help of calculations and quantum oscillations [26]. We extract the Fermi surfaces from the experimental observation on the $k_z \sim 0$ plane, as shown.
FIG. 4. (a)-(c) Photoemission intensity plots along the Γ-K, K-M, and Γ-M directions, respectively. (d)-(f) DFT-projected bulk bands and surface bands of the Sn-terminated (001) surface along the Γ-K, K-M, and Γ-M directions, respectively, correspond to (a)-(c). The surface states and the Dirac nodes are indicated by the black arrows and the transparent dots, respectively. (g) MDCs around the nodal-line feature near the K point along Γ-K, as indicated by the dashed square in (a). (h) MDCs around the nodal-line feature near the K point along K-M, as indicated by the dashed square in (b). The dashed lines are guides to the bands.

In Fig. 4 we detailedly compare the observed dispersions with the surface states calculation along the high-symmetry lines. Figures 4(a), 4(c) show ARPES intensity plots along the Γ-K, K-M, and Γ-M directions, respectively. The band-crossings are clearly shown in the dashed square of Figs. 4(a) and 4(b). As discussed above, the observed bands look more like the slab calculation of Sn-terminated (001) surface states in Fig. 2(i). We thus show DFT-projected bulk bands and surface bands of the Sn-terminated (001) surface along the three corresponding directions in Figs. 4(d)-4(f), respectively. The surface states and the Dirac nodes are indicated by the black arrows and the transparent dots, respectively. The calculation results are consistent well with the ARPES measurements including $k_z$ integration, except that the calculated hole-like bands near $M$ need to be shifted down and the calculated nodal-line features near $K$ need to be shifted up due to the reasons mentioned above. Combining the measured and calculated bands along Γ-K [Figs. 4(a) and 4(d)], one can figure out the surface state (SS1) and the Dirac node (D1), which can be more clearly seen on MDCs plot of Fig. 4(g). D1 is located at about -0.3 eV below $E_F$, and SS1 corresponds to the red Fermi surface in Fig. 3(h). Because of the upward shifting band, the SS2 and D2 should be located above $E_F$ and cannot be detected along Γ-K [Figs. 4(d) and 4(g)] and K-M [Figs. 4(e) and 4(h)]. However the consistency between experiment and calculation provides solid evidence for the existence of SS2 and D2 near $E_F$. Compared with other nodal-line semimetals, the surface state (SS1) can be more clearly distinguished from the bulk states near $E_F$. The results will supply valuable information for a further study on the Dirac nodal-line fermions.
By presenting an investigation of the low-energy electronic structures both in experiments and calculations, we provide evidence of topological nodal lines and surface states in centrosymmetric superconducting SnTaS$_2$. STS measurements indicate that the superconducting gap of about 0.35 meV at $T = 0.4$ K is suppressed by a magnetic field of 0.013 T perpendicular to the sample surface. The vortex states have not been found under such a small applied magnetic field possibly due to the low vortex density. As the typical characteristics in nodal-line semimetals, however, the surface states connect due to the low vortex density. As the typical characteristics in topological nodal-line fermions. Our findings are also beneficial for studies on TSCs.

IV. CONCLUSION

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