Observation of Dirac-like energy band and unusual spectral line shape in quasi-one-dimensional superconductor \( \text{Tl}_2\text{Mo}_6\text{Se}_6 \)

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We have performed high-resolution angle-resolved photoemission spectroscopy of the quasi-one-dimensional (1D) topological superconductor candidate \( \text{Tl}_2\text{Mo}_6\text{Se}_6 \) consisting of weakly-coupled \( \text{Mo}_3\text{Se}_3 \) chains. We found a quasi-1D Fermi surface arising from a Dirac-like energy band, which is associated with the nonsymmorphic screw symmetry of the chains and predicted to trigger topological superconductivity. We observed a significant spectral-weight reduction over a wide energy range, together with a tiny Fermi-edge structure which exhibits a signature of a superconducting-gap opening below the superconducting-transition temperature. The observed quasi-1D Dirac-like band and its very small density of states point to an unconventional nature of superconductivity in \( \text{Tl}_2\text{Mo}_6\text{Se}_6 \).

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The interplay between low dimensionality and superconductivity is one of the central issues in condensed-matter physics. The reduction of dimensionality triggers the rearrangement of lattice, charge, spin, and orbital degrees of freedom, leading to the competition or cooperation among various ordered phases as well as phase fluctuations. Since these rich properties and their interplay often give rise to unconventional superconductivity beyond the Bardeen-Cooper-Schrieffer (BCS) theory, low-dimensional electron systems are a fertile playground for the research of exotic superconductivity. Well-known examples of low-dimensional superconductors include quasi-two-dimensional (2D) copper oxides and iron pnictides/chalcogenides which show superconductivity at unexpectedly high temperatures [1, 2]. Interfaces and atomically thin films [3, 4] regarded as the ultimate of 2D materials, are now intensively investigated for the search of novel superconductivity that cannot be found in quasi-2D materials. On the other hand, superconductivity in one-dimensional (1D) or quasi-1D materials is relatively scarce, because of the difficulty in realizing a superconducting state in such systems owing to the Peierls instability as well as strong fluctuations.

Among known quasi-1D superconductors [3, 5, 6, 7, 8, 9], molybdenum selenide \( \text{Tl}_2\text{Mo}_6\text{Se}_6 \) [8, 9] is an ideal platform for studying quasi-1D superconductivity because of a high chemical stability, a relatively high superconducting transition temperature \( T_c = 6.5 \text{ K} \), and a strong 1D anisotropy in the normal and superconducting states as seen in the electrical resistivity and upper critical field [5, 10, 12]. A basic unit of the crystal structure in \( \text{Tl}_2\text{Mo}_6\text{Se}_6 \) is an infinitely long Mo\(_3\)Se\(_3\) chain situated along the \( c \) axis [Fig. 1(a)]. Each 1D chain is separated by Tl atoms which prevent direct chemical bonding between adjacent chains [Fig. 1(b)]. The resultant weak inter-chain interaction provides the crystal a quasi-1D character. The quasi-1D electronic properties of \( \text{Tl}_2\text{Mo}_6\text{Se}_6 \) provide a rare opportunity to search for the Tomonaga-Luttinger-liquid (TLL) state. Furthermore, in addition to these basic interests in the 1D properties, \( \text{Tl}_2\text{Mo}_6\text{Se}_6 \) is now attracting great attention as a topological material candidate [13, 14]. In fact, first-principles band-structure calculations suggested that \( \text{Tl}_2\text{Mo}_6\text{Se}_6 \) is a Dirac semimetal characterized by a nonsymmorphic symmetry [13, 14], which originates from the presence of two sublattices (A and B) connected to each other by a two-fold screw operation [Fig. 1(a)]. In particular, one of the Dirac-cone energy bands represents a novel Dirac fermion termed a cubic Dirac fermion which...
shows a cubic (linear) dispersion perpendicular (parallel) to the chain [14]. Further, a very recent theory proposed that Tl₂Mo₆Se₆ may realize time-reversal-invariant topological superconductivity associated with the symmetry-protected Dirac cones even in the absence of spin-orbit coupling [15]. To examine the origin of quasi-1D properties and theoretical predictions for Dirac-semimetal and topological-superconductor phases, the experimental determination of the electronic structure of Tl₂Mo₆Se₆ is urgently required.

In this Rapid Communication, we report high-resolution angle-resolved photoemission spectroscopy (ARPES) of Tl₂Mo₆Se₆ single crystal. By utilizing energy-tunable photons from synchrotron radiation, we obtained definitive evidence for the formation of a quasi-1D Fermi surface (FS) originating from the linearly-dispersive Dirac-like band. We also observed a significant suppression of the density of states (DOS) near the Fermi level (E_F) which coexists with superconductivity. We discuss the implications of our observations in relation to the superconducting and topological properties.

High-quality Tl₂Mo₆Se₆ crystals with T_c = 6.3 K were grown from elemental Tl shot (purity 99.999%), Mo powder (purity 99.999%), and Se powder (purity 99.999%) [16, 17]. ARPES measurements were performed at UE112_PGM-2b of BESSY, Helmholtz-Zentrum Berlin. The ARPES end station is equipped with an Omicron-Scienta R4000 electron analyzer with a Janis 1-K cryostat which enables access to the superconducting phase of Tl₂Mo₆Se₆. The energy and angular resolutions were set at 4-30 meV and 0.3°, respectively. Samples were cleaved in situ along the (1100) crystal plane in an ultrahigh vacuum of better than 1×10⁻¹⁰ Torr. Corresponding bulk and surface Brillouin zones (BZs) are shown in Fig. 1(c). Details of the sample geometry and the core-level spectrum are described in the Supplemental Material [17].

To discuss the valence-band (VB) structure, we performed ARPES measurements along the ΓY cut (parallel to the Mo₃Se₃ chain) of the surface BZ with \( \hbar \nu = 50 \) eV [Figs. 1(d) and 1(e)]. At a binding energy (\( E_B \)) of 2.5-4.0 eV, one can find several dispersive bands such as two holelike bands (S1-2) at the \( \bar{\Gamma} \) point and another holelike band (S3) with the top of the dispersion slightly away from the \( \bar{Y} \) point. According to the first-principles calculations, these bands have a dominant Se 4p character with a finite admixture of Mo 4d [12, 18]. More intense features are observed at \( E_B = 1.0-2.5 \) eV (M1 and M2), which mainly stem from the bonding states of Mo 4d orbitals. The antibonding counterparts of the Mo 4d states contribute to conduction bands above \( E_F \) [12, 18].

To see more clearly the electronic states near \( E_F \), we mapped out the band structure in the 3D bulk BZ. In Figs. 2(a) and 2(b), we show FS in the \( k_x-k_z \) plane and representative band dispersions around the BZ corner, respectively. As seen in Fig. 2(b), the \( d_{xz} \) band linearly disperses and crosses \( E_F \) in a momentum region slightly away from the YM line, consistent with the metallic property of Tl₂Mo₆Se₆. More importantly, the Fermi wave vector (\( k_F \)) is stationary to the variation of \( k_z \), as recognized from a nearly straight FS shape in Fig. 2(a) (note that there is a finite ambiguity for the position of \( k_z = 0 \) because of the lack of periodic band dispersion as a function of \( k_z \)). Large anisotropy of the electronic structure is also observed in the \( k_y-k_z \) plane [Figs. 2(c) and 2(d)]; namely, there is no large FS warping nor clear change in the band dispersion along \( k_y \). To quantitatively discuss the anisotropy of the electronic structure, we compared in Fig. 2(e) the band dispersions extracted at various \( k_z \) and \( k_y \).
$k_y$ cuts. Apparently, the linear band dispersion is robust against the variations of $k_x$ and $k_y$. Linear fittings to the band dispersions at various cuts give only small changes in $k_F$ (0.65-0.67 Å$^{-1}$) and the Fermi velocity $v_F$ (3.8-4.7 eVÅ). The magnitude of the band dispersion along the $k_x$ and $k_y$ axes is at most ~100 meV, as estimated from the energy difference of band dispersions at different $k_x$ and $k_y$ cuts [see an arrow in Fig. 2(e)]. This value is ten times smaller than that along $k_z$ (> 1 eV). These results unambiguously demonstrate the quasi-1D nature of the electronic structure in Tl$_2$Mo$_6$Se$_6$. Since other bands except for the quasi-1D band do not cross $E_F$, the FS of Tl$_2$Mo$_6$Se$_6$ consists only of almost flat sheets near the BZ boundary, as illustrated in the upper right inset to Fig. 2(c). The carrier concentration estimated from the FS volume is $3.7 \times 10^{20}$ cm$^{-3}$, which shows a good agreement with that from the Hall coefficient ($\sim 3 \times 10^{20}$ cm$^{-3}$) [11].

The observed quasi-1D electronic structure shows a reasonable agreement with band structure calculations [12, 15, 18] when the chemical potential is located ~200 meV below the calculated $E_F$ (likely due to Tl deficiencies) [compare Figs. 2(c) and 2(f)]. In particular, $k_F$ and $v_F$ show a quantitatively good agreement between the experiment and calculations, indicating the bulk nature of the observed band structure. Moreover, our observation of a linearly dispersive feature is a signature of the non-trivial electronic structure in Tl$_2$Mo$_6$Se$_6$. According to the theoretical calculations [12, 15, 18], the two-fold screw symmetry of the Mo$_3$Se$_3$ chains forces the degeneracy of the bonding and antibonding Mo 4$d_{xz}$ bands at the A and H points [the resulting Dirac points are marked by black arrows in Fig. 2(f)] and hence results in a Dirac-semimetal phase with anisotropic Dirac-cone-like dispersions near $E_F$. By linearly extrapolating the experimental band dispersions (lower branch of the Dirac cone), we estimate the energy position of the Dirac point ($E_{F\text{DP}}$) to be 100-200 meV above $E_F$. The observed quasi-1D electronic structure indicates a highly anisotropic nature of the Dirac-cone dispersion: as illustrated in the lower inset to Fig. 2(e), the Dirac cone would have a relatively large dispersion in the $k_z$ direction compared with the negligible $k_x/k_y$ dispersion. This large anisotropy corresponds to the $k_F$ value almost independent of $k_x/k_y$, creating sheet-like FSs (red lines in the lower inset).

A hallmark of a quasi-1D electron system appears in the spectral line shape. Figures 3(a)-3(c) display representative ARPES spectra measured around the $k_F$ point at $T = 30$ K, their symmetrized curves, and corresponding intensity plot, respectively. As recognized from Figs. 3(a) and 3(b), a quasiparticle peak is not well defined at the $k_F$ point, indicating a marked suppression of spectral weight in the normal state [also see Fig. 3(c)]. Correspondingly, DOS [red curve in Fig. 3(d)] starts to decrease at ~50 meV and is continuously reduced with approaching $E_F$ in a power-law-like manner ($|x|E^{0.42}$; see the green curve and the inset), in contrast to a steep Fermi edge in a 3D metal (gray curve). Such a suppression of DOS over a relatively wide energy range is characteristic of quasi-1D materials [20, 24]. The observed power-law-like suppression persists down to $T = 1$ K (not shown) well below $T_c$, suggesting the coexistence with superconductivity. It is remarked here that while the DOS is significantly suppressed, our high-resolution measurements in close vicinity of $E_F$ reveal a very small but finite step edge at low temperatures [Fig. 3(e)]. This remaining tiny DOS at $E_F$ must be responsible for superconductivity in Tl$_2$Mo$_6$Se$_6$. In fact, we found a finite leading-edge shift by ~0.2 meV across $T_c$ which suggests the superconducting-gap opening [Fig. 3(e)]. A signature of gap opening below $T_c$ is more clearly seen by comparing the symmetrized spectra shown in the inset to Fig. 3(e) [see magenta and blue curves for $T = 8$ K and $1$ K, respectively]. To cancel out the background from the V-shaped DOS, we divided the intensity of symmetrized curves at 1 K by that at 8 K (unity is indicated by gray dashed line).

Now we discuss the origin of the unusual spectral-weight loss in the normal state. Similar behavior has been observed in several quasi-1D materials and regarded as a hallmark of TLL [24, 24], where a confinement of correlated electrons in 1D breaks down the single-particle
In the TLL picture, the DOS is significantly suppressed as $\propto |E|^\alpha$ and becomes vanishingly small near $E_F$. The present observations of a quasi-1D band structure and a power-law-like suppression of DOS ($\alpha = 0.42$) seem consistent with the TLL picture. However, we also found a small but finite Fermi edge which is not expected in the TLL theory. This discrepancy suggests a departure from an ideal 1D TLL state, possibly due to finite inter-chain interactions. The suppression of DOS may be also explained in terms of the formation of a pseudogap by charge-density-wave (CDW) fluctuations. While there is no clear indication for a CDW order, Tl$_2$Mo$_6$Se$_6$ would have a large CDW susceptibility because of the observed strong quasi-1D electronic structure. This is supported by the stabilization of a CDW order under uniaxial strain.[27] Such a proximity to the TLL and CDW-fluctuation pictures, the presence of finite DOS at $E_F$ is a consequence of the deviation from the ideal 1D system and would be responsible for the coexistence with the superconductivity. While direct evidence for a deviation from the pure-1D system may be seen as a finite band dispersion along $k_x/k_y$ and a wiggling of FS, possible differences in the band dispersions in Fig. 2(e) ($\sim 100$ meV and $\sim 0.02$ Å$^{-1}$) are comparable to the present experimental uncertainties, requiring higher-resolution ARPES measurements to settle this issue. Also, further complementary experiments are desired to clarify the origin of the suppressed DOS and its link to the normal-state physical properties.

Finally, we discuss implications of the present results in relation to the superconductivity in Tl$_2$Mo$_6$Se$_6$. Our ARPES measurements show that the starting point for understanding the superconductivity in the present system is a quasi-1D electronic structure with a very small DOS at $E_F$. It is surprising that, although the BCS theory predicts that $T_c$ decreases with the suppression of DOS (since $T_c$ is proportional to $\exp(-1/\text{DOS}(E_F)V)$ where DOS($E_F$) is the DOS at $E_F$ and $V$ is the interaction potential), our sample shows a relatively high $T_c$ value of 6.3 K. In this regard, the parameter $V$ in the BCS equation is not likely to be the cause of the high $T_c$, because $V$ is essentially governed by the Debye energy which in Tl$_2$Mo$_6$Se$_6$ is expected to be no larger than 27 meV reported for an isostructural compound K$_2$Cr$_6$As$_6$.[31] consisting of lighter-mass elements; note that 27 meV is just an ordinary value for conventional low-$T_c$ superconductors. Therefore, regardless of the origin of the small DOS is (TLL behavior or CDW fluctuations), an unconventional superconducting mechanism may be at work in Tl$_2$Mo$_6$Se$_6$.

The unconventional pairing could be playing a role in determining the shape of the DOS in the superconducting state. It has been reported that the gap anisotropy or nodes exist in various quasi-1D superconductors such as organic superconductors and metallic-chain-based systems.[28–29] Such commonality suggests that the low dimensionality plays an important role for promoting anisotropic superconductivity. In addition, the gap anisotropy may be related to odd-parity topological superconductivity, because Tl$_2$Mo$_6$Se$_6$ is predicted to be such a topological superconductor[15] and the origin of its topological nature (i.e., inter-orbital pairing) is similar to that in Cu$_2$Bi$_2$Se$_4$ where a clear gap anisotropy has been observed.[31 32] Given the quasi-1D nature and the possible odd-parity superconductivity, an anisotropic gap opening in Tl$_2$Mo$_6$Se$_6$ is not surprising, and an anisotropic gap is expected to weaken the coherence peak [note that the experimental curves in Fig. 3(e) (blue and pink circles) are not simple ARPES spectra at a specific $k_F$ point, but are angle-integrated PES spectra to mimic the total DOS][33]. Furthermore, fluctuation effects would be enhanced at the surface in a quasi-1D superconductor (because the superconducting fluctuations in each chain are stabilized by the existence of neighboring chains), which would smear a coherence peak. Nevertheless, the lack of a coherence peak may simply be due to the lack of resolutions or unfavorable matrix elements, and one cannot make a conclusive statement at this point.

It is also remarked that the observed Dirac-cone-like band has been predicted to be responsible for the time-reversal-invariant topological superconductivity. The presence of a Dirac-cone-like band, which is protected by a nonsymmorphic screw symmetry interchanging the two sublattices A and B [Fig. 1(a)], indicates that the sublattice degrees of freedom are of crucial importance to classify superconducting states in Tl$_2$Mo$_6$Se$_6$. Theoretically, there exist six possible pairing states categorized by the difference in the sublattice symmetries, and the spin-triplet $E_{2u}$ state promoted by the inter-sublattice pairing is likely stable.[15] Intriguingly, this topological superconducting state breaks the rotational symmetry in the $a$-$b$ plane because of a nematic order observed in Cu$_2$Bi$_2$Se$_4$.[31 32]. It has been also predicted that a pair of Majorana flat bands emerges on the (001) surface of Tl$_2$Mo$_6$Se$_6$. The predicted topological superconducting phase is stable over a wide parameter range even when the chemical potential is close to the present value ($\sim 0.2$ eV below the calculated $E_F$).[15] Therefore, Tl$_2$Mo$_6$Se$_6$ is a promising platform to realize topological superconductivity. All these intriguing aspects strongly suggest the occurrence of unconventional superconductivity in Tl$_2$Mo$_6$Se$_6$.

In conclusion, we have presented high-resolution ARPES results on Tl$_2$Mo$_6$Se$_6$ superconductor. We revealed a linear band dispersion near the BZ corner, in agreement with the presence of Dirac cones protected by nonsymmorphic screw symmetry. The observed Dirac-like energy band shows a quasi-1D characteristic such as the formation of nearly-flat FS sheets and a power-law-like suppression of the DOS upon approaching $E_F$.

We also observed a signature of an unusual DOS shape in the superconducting phase. These results lay the foundation for understanding the superconducting and topological properties of Tl$_2$Mo$_6$Se$_6$. 
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[19] The experimental curves in Fig. 3(e) are obtained by integrating the ARPES intensity from $k_y = 0.5$ to $0.9 \, \AA^{-1}$ to mimic the total DOS. We note that there must be a momentum broadening in the $k_y$ direction (perpendicular to the sample surface), which is inevitable in the ARPES measurements with vacuum-ultraviolet photons as in the present case. Considering these facts, the coherence peak may be substantially broadened in the curves as those in Fig. 3(e) when the gap size is highly anisotropic in the momentum space.