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Detailed Terms
Topological superconductor in quasi-one-dimensional Tl$_{2-x}$Mo$_6$Se$_6$

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We propose that the quasi-one-dimensional molybdenum selenide compound Tl$_{2-x}$Mo$_6$Se$_6$ is a time-reversal-invariant topological superconductor induced by intersublattice pairing, even in the absence of spin-orbit coupling (SOC). No noticeable change in superconductivity is observed in Tl-deficient (0 ≤ x ≤ 0.1) compounds. At weak SOC, the superconductor prefers the triplet d vector lying perpendicular to the chain direction and two-dimensional $E_u$ symmetry, which is driven to a nematic order by spontaneous rotation symmetry breaking. The locking energy of the $d$ vector is estimated to be weak and hence the proof of its direction would rely on tunneling or phase-sensitive measurements.

I. INTRODUCTION

Topological superconductivity stands out among all the topological phases in part because the Majorana fermions it allows at boundaries are not only fundamentally fascinating but also have potential applications in quantum computation [1–5]. A crucial element for such superconductors is spin-triplet pairing, or odd-parity pairing in the presence of inversion symmetry [6,7]. Prime examples are unconventional superconductors Sr$_3$RuO$_4$ [8,9] and UPt$_3$ [10], and both of them act as chiral superconductors [11–13]. However, their complex or nodal Fermi surface properties make it difficult to host distinct topological phases in part because the Majorana fermions it allows at boundaries are not only fundamentally fascinating but also have potential applications in quantum computation [1–5].

Tl$_2$Mo$_6$Se$_6$ has a hexagonal lattice with inversion symmetry, characterized by the space group $P6_3/m$ (no. 176). Having highly anisotropic lattice constants (a = 8.934 Å, c = 4.494 Å), its crystal structure is quasi-one-dimensional (quasi-1D), with Mo$_3$Se$_3$ chains arranged in a triangular lattice, as shown in Figs. 1(a) and 1(b). A Tl atom is centered in each triangle to couple the Mo$_3$Se$_3$ chains. Owing to neighboring three Se anions and one Tl cation, three Mo atoms of a triangle have to share five 4$d$ valence electrons, which implies a half-filled band in the absence of Tl deficiency.

II. CRYSTAL SYMMETRY AND ELECTRONIC STRUCTURE

Nonsymmorphic compound Tl$_{2-x}$Mo$_6$Se$_6$ has a hexagonal lattice with inversion symmetry, characterized by the space group $P6_3/m$ (no. 176). Having highly anisotropic lattice constants (a = 8.934 Å, c = 4.494 Å), its crystal structure is quasi-one-dimensional (quasi-1D), with Mo$_3$Se$_3$ chains arranged in a triangular lattice, as shown in Figs. 1(a) and 1(b). A Tl atom is centered in each triangle to couple the Mo$_3$Se$_3$ chains. Owing to neighboring three Se anions and one Tl cation, three Mo atoms of a triangle have to share five 4$d$ valence electrons, which implies a half-filled band in the absence of Tl deficiency.

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pointing toward nearby Se atoms [see Fig. 1(c)]. They are the basis states from which we construct the low-energy Hamiltonians. Two \( A \) and \( B \) sublattice states can interchange under inversion \( I \), the center of inversion being in the middle of the two sublattices. They can also interchange by a twofold screw operation \( S_2 \) along the \( z \) direction, plus a translation by \( \bar{c}/2 \).

Consider first a simple 1D \( \text{Mo}_3 \text{Se}_3 \) chain in the \( z \) direction. (Throughout the paper, we shall set lattice constants to unity.) The two sublattices in a unit cell form symmetric and antisymmetric states and they modulate with phase \( e^{ikz} \) to be bonding and antibonding bands. At \( k_z = \pi \), the Bloch-state modulating phase is equal to \((-1)^z\) and the bonding and antibonding states become identical under inversion, \( T \Psi_{\text{Bond}} = \Psi_{\text{Antibond}} \) (up to a phase), so that two bands touch. Extending to three dimensions through introducing interchain coupling, the band crossing evolves into a two-dimensional (2D) nodal surface at \( k_z = \pi \) [31]. The two-band Hamiltonian reads

\[
H_c(\mathbf{k}) = \epsilon_0(\mathbf{k})\sigma_0 + \epsilon_1(\mathbf{k})\sigma_1 + \epsilon_2(\mathbf{k})\sigma_2,
\]

where \( \sigma_0 \) and \( \sigma_1 \) are the identity and Pauli matrices for sublattices. The \( \sigma_3 \) term is forbidden by the \( T \bar{T} \) symmetry (refer to Appendix A). Furthermore, \((TS_2)^2 = 1\) is a unit lattice translation by \( \bar{c} \) and gives \( e^{-ik} \) by acting on a Bloch eigenstate. Particularly, \((TS_2)^2 = -1\) at \( k_z = \pi \), leading to a double degeneracy for all states, analogous to the Kramers degeneracy [31]. As a result, \( \epsilon_1(\mathbf{k}) = \epsilon_2(\mathbf{k}) = 0 \) at \( k_z = \pi \). As shown in Fig. 2(a), states along the \( A-L-H-A \) path on the \( k_z = \pi \) plane are degenerate.

Under time-reversal and inversion symmetries, the Hamiltonian that includes SOC reads, as derived in Appendix A,

\[
\mathcal{H}(\mathbf{k}) = s_0 H_c(\mathbf{k}) + \zeta(\mathbf{k} \cdot \vec{s}) \sigma_3,
\]

where \( s_0 \) and \( \vec{s} = (s_1, s_2, s_3) \) are the identity and Pauli matrices for spin. As a consequence of \( T \) and \( I \) symmetries, \( \zeta \)'s must be odd in \( \mathbf{k} \). This \( \sigma_3 \) term will gap out the surface node. According to first-principles calculations, the SOC is quite weak for \( \text{Tl} \) atom, especially along \( A-L \), but gets larger for heavier \( M \) atom [see Fig. 2(b)]. Since SOC vanishes at time-reversal invariant momenta, residual pointlike band crossings appear at \( A \) and \( L \) points, namely three-dimensional (3D) Dirac nodes. In particular, the band crossing at \( A \) point is a cubic Dirac fermion due to its sixfold symmetry [32].

III. THEORY OF SUPERCONDUCTIVITY

Under time-reversal symmetry, the \( \text{Tl}_2\text{Mo}_6\text{Se}_6 \) superconducting states, described by the mean-field Hamiltonian

\[
\mathcal{H}_{SC}(\mathbf{k}) = \begin{pmatrix}
\mathcal{H}(\mathbf{k}) - \mu & \Delta(\mathbf{k}) \\
\Delta(\mathbf{k})^\dagger & -[\mathcal{H}(\mathbf{k}) - \mu]
\end{pmatrix}
\]

where \( \mathcal{H}(\mathbf{k}) = \begin{pmatrix}
\psi_{\mathbf{k}1}^T, & \psi_{\mathbf{k}1}^T, & \psi_{\mathbf{k}1}^T - \psi_{\mathbf{k}1}^T
\end{pmatrix}^T
\]

is classified into even-parity (spin singlet) and odd-parity (spin triplet) pairing by \( T\Delta(\mathbf{k})^T = \pm \Delta(-\mathbf{k}) \). For a DIII topological superconductor, the parity of the superconducting gap has to be odd [6]. In conventional superconductivity, spin singlet (triplet) imposes that the gap function is even (odd) in \( \mathbf{k} \). However, additional sublattice degrees of freedom play roles much like
in the orbital pairing theory in Fe-based superconductors [33]: For spin singlet, to make parity even, we can have sublattice and $\mathbf{k}$ parts to be both even or both odd. For spin triplet, to make parity odd, we can have sublattice even and $\mathbf{k}$ odd, or sublattice odd and $\mathbf{k}$ even. Since $\mathcal{I}$ is a combination of the twofold screw operation $S_2$ and mirror operation $M_z$, (i.e., $z \rightarrow -z$), we can further classify the superconducting states in each parity into screw even (+) and screw odd (−), according to

$$S_2(k_z)\Delta(k_x, k_y, k_z)S_2(k_z)^T = \pm \Delta(-k_x, -k_y, k_z),$$

and similarly for $M_z$. The full classification of the gap functions according to $C_{6h}$ group is shown in Table I.

We consider attractive, intra- and intersublattice interactions for pairing,

$$H_{int} = -\sum_{\mathbf{r}} \left[ U[n_{A_1}(\mathbf{r})n_{A_1}(\mathbf{r}) + n_{B_1}(\mathbf{r})n_{B_1}(\mathbf{r})] + V[n_{A_1}(\mathbf{r})n_{B_2}(\mathbf{r} + \vec{c}/2) + n_{A_1}(\mathbf{r})n_{B_2}(\mathbf{r} - \vec{c}/2)] \right],$$

where $\mathbf{r}$ runs over the Bravais lattice and $n_X(\mathbf{r}) = n_X(\mathbf{r}) + n_{X_1}(\mathbf{r})$ is the electron density for sublattice $X$. Interactions between chains are neglected since we expect pairing to be the strongest within a chain. Table I lists six possible pairing symmetries. While the intra sublattice interactions participate in the $A_g$ pairing, the intersublattice interactions contribute to all six pairing states. Details are in Appendix A. Their critical temperatures $T_c$ are determined by

$$\det \left[ \begin{array}{cc} \frac{U}{2} \chi(0)(T_c) & \frac{U}{2} \chi(1)(T_c) \\ \frac{V}{2} \chi(0)(T_c) & \frac{V}{2} \chi(1)(T_c) \end{array} \right] = 0, \quad \text{for } \Delta_1,$$

$$\frac{V}{2} \chi(1)(T_c) = 1, \quad \text{for } \Delta_{i=2,3,4,5,6}.$$  

The pair susceptibility $\chi_i$ is given by

$$\chi_i = \frac{T}{N} \sum_{\mathbf{k}, \omega_n} \text{Tr}(\Gamma_i(\mathbf{k})G(\mathbf{k}, i\omega_n)\Gamma_i(\mathbf{k})G(\mathbf{k}, -i\omega_n)),$$

where $G(\mathbf{k}, i\omega_n) = [i\omega_n - \mathcal{H}(\mathbf{k}) + \mu]^{-1}$ with $\omega_n = (2n + 1)\pi k_BT$ being the fermion Green’s function, and $N$ is the number of lattice sites. The chemical potential $\mu$ is used to simulate doping effect. The vertex functions are $\Gamma_0(\mathbf{k}) = s_0\sigma_0$, $\Gamma_1(\mathbf{k}) = s_0\sigma_3\cos(k_z/2)$, $\Gamma_2(\mathbf{k}) = s_0\sigma_1\sin(k_z/2)$, $\Gamma_3(\mathbf{k}) = s_0\sigma_1\sin(k_z/2)$, $\Gamma_4(\mathbf{k}) = s_0\sigma_1\cos(k_z/2)$, and $\Gamma_5(\mathbf{k}) = s_1\sin(k_z/2)$. $\chi_0$ is obtained by replacing the first $\Gamma_1(\mathbf{k})$ in Eq. (6) by $\Gamma_0(\mathbf{k})$ and the second by $\Gamma_1(\mathbf{k})$.

Adopting the fitting parameters for the band structure in Fig. 2(b), we computed the pair susceptibility for these six channels [see Fig. 3(a)]. Three dominant channels are $\chi_0$, $\chi_3$, and $\chi_6$ for, respectively, 1D $A_g$ and $A_u$, and 2D $E_{2u}$ irreducible representations, all having sublattice-even and screw-even pairings. In Table I, those for gapful superconductivity show the conventional logarithmic behavior, $\chi \sim N_{eff} \ln(\Lambda/k_BT)$, where $N_{eff}$ stands for the effective density of states at the Fermi energy and $\Lambda$ is the energy cutoff. The logarithmic law taken into Eq. (5) determines the critical temperature for superconductivity.

We first consider $A_g$ and $E_{2u}$ states. Depending on the interaction strength ratio $U/V$, the superconductor can fall into $A_g$ or $E_{2u}$ states. From Eq. (5), the condition for $E_{2u}$ to dominate over $A_g$ is

$$\frac{U}{2V} \leq \frac{\chi_1 - 1}{\chi_0(1) - 1},$$

where $\chi_{0,0.011} = \chi_{0,0.1}(T_c)/\chi_0(T_c)$; otherwise, $A_g$ dominates over $E_{2u}$. The phase diagram is shown in Fig. 3(b). Doping would only slightly shift the phase boundary and reduce $T_c$. At present, little is known about the origin of pairing and the values of $U$ and $V$. If the attractive interactions are phonon mediated, the spin triplet state could be stabilized by a weak electronic correlation, as proposed for Cu$_2$B$_2$Se$_3$ [34]. Then, considering that strong onsite repulsion is common in 4$d$ transition metals, the $E_{2u}$ state is likely the winner.

The critical temperatures for $A_u$ and $E_{2u}$ states are very close since their $\chi$ difference is small (the estimation is found in Appendix B). In the absence of SOC, the $E_{2u}$ state will be triply

<table>
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<tr>
<th>$\Delta_k$</th>
<th>$\mathcal{S}_2$</th>
<th>$M_z$</th>
<th>Basis functions</th>
<th>$\Delta(k)$</th>
<th>Susceptibilities</th>
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<td>$A_g$ ($\Delta_1$)</td>
<td>+</td>
<td>+</td>
<td>$1$</td>
<td>$s_0 \otimes s_0; \cos \frac{\pi}{3}\sigma_0 \otimes \sigma_1$</td>
<td>$\chi_0$, $\chi_{0.011}$</td>
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<td>$B_y$ ($\Delta_2$)</td>
<td>-</td>
<td>-</td>
<td>Re $k_{1x}k_z \pm \Im k_{1z}k_z$</td>
<td>$s_0 \otimes \sin \frac{\pi}{3}\sigma_2$</td>
<td>$\chi_2$</td>
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<tr>
<td>$E_{1g}$</td>
<td>-2</td>
<td>-2</td>
<td>${k_{1x}^2 - k_{1z}^2}$</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>$E_{2g}$</td>
<td>+2</td>
<td>+2</td>
<td>${k_{1x}^2 - k_{1z}^2}$</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>$A_u$ ($\Delta_3$)</td>
<td>+</td>
<td>-</td>
<td>$k_{1x}k_z + k_{1z}k_x - k_yk_z$</td>
<td>$s_1 \otimes \sin \frac{\pi}{3}\sigma_1$</td>
<td>$\chi_3$</td>
</tr>
<tr>
<td>$B_u$ ($\Delta_4$)</td>
<td>-</td>
<td>+</td>
<td>$k_{1x}k_z \pm \Im k_{1z}k_z$</td>
<td>$s_1 \otimes \cos \frac{\pi}{3}\sigma_2$</td>
<td>$\chi_4$</td>
</tr>
<tr>
<td>$E_{1u}$ ($\Delta_5$)</td>
<td>-2</td>
<td>+2</td>
<td>${k_{1x}^2 - k_{1z}^2}$</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>$E_{2u}$ ($\Delta_6$)</td>
<td>-2</td>
<td>-2</td>
<td>${k_{1x}^2 - k_{1z}^2}$</td>
<td>${s_1 \otimes \cos \frac{\pi}{3}\sigma_2}$</td>
<td>$\chi_5$</td>
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</table>
to 1000 K (nonlinear relation). The SOC lifts their degeneracy, favoring $E_{2u}$. The solution to the fact is that the highest $T_c$ is obtained when the triplet $d$ vector aligns with the SOC field $\tilde{\xi}(k)$ in Eq. (2) [35]. For the Fermi surface located around $k_z = \pi, \tilde{\xi}(k)$ and hence the $d$ vector in principle are on the $x$-$y$ plane.

IV. NEMATIC ORDER

To study spontaneous time-reversal and rotation symmetry breaking, we consider the phenomenological Ginzburg-Landau free energy for the spin-triplet $E_{2u}$ state, which reads

$$F = \alpha(\Psi^+|^2 + |\Psi^-|^2) + \beta_1(|\Psi^+|^2 + |\Psi^-|^2)^2 + \beta_2|\Psi^+|^2|\Psi^-|^2,$$

(8)

where $\Psi^\pm = \Psi_i \pm i\Psi_2$. The two order parameters for $E_{2u}$, $\Psi_1$ and $\Psi_2$, correspond to the pairing states $i(c_{A1}^\dagger c_{B1}^\dagger - c_{A1}^\dagger c_{B1}^\dagger)$ and $(c_{A1}^\dagger c_{B1}^\dagger + i c_{A2}^\dagger c_{B1}^\dagger)$, respectively. Below $T_c$ ($\alpha < 0$), we obtain $\Psi_{1,2} \neq 0$ and superconductivity occurs. The sign of $\beta_2$ is crucial for determining whether time-reversal symmetry ($\beta_2 > 0$) or rotation symmetry ($\beta_2 < 0$) breaks [20]. We shall rule out the $T$-breaking scenario since no magnetic moment is found in Tl$_2$Mo$_6$Se$_6$ [24]. In order to determine the nematic angle $\theta$ in the crystal, we need the sixth-order term in the free energy, given by

$$\delta F_6 = -i(\gamma_1 + i\gamma_2)(\Psi^+_c \Psi^-_c)^3 + \text{H.c.},$$

(9)

where $(\gamma_1, \gamma_2)$ depend on microscopic models. This term is proportional to $-\sqrt{\gamma_1^2 + \gamma_2^2} \cos(6\theta - \phi)$ with $\phi = \text{arctan}(\gamma_2/\gamma_1)$; so, $\theta$ is pinned at $\phi/6 + 2n\pi/3$ with arbitrary integer $n$. (For a nematic order, $\theta$ and $\theta + \pi$ are equivalent.) In contrast to Cu$_2$Bi$_2$Se$_3$, whose nematic state is possibly nodal [20,36], Tl$_2$Mo$_6$Se$_6$ has a nematic state that is fully gapped for any $\theta$.

Regardless of the nematic angle, a Kramers pair of Majorana flat bands will harbor on the (001) surface, which is guaranteed by a nonzero 1D winding number over $k_{\perp} = (k_x, k_y)$ [37,38]. Although the Majorana surface states can be gapped out by disorder which breaks translational symmetry locally, they will be restored after disorder averaging, similar to weak or crystalline topological insulators [39,40]. Interestingly, there exists a kind of disorder which can host Majorana modes locally. At a nematic vortex core, where three degenerate nematic domain walls meet, the Majorana Kramers pair return and pin to it [28].

V. DISCUSSION

The nonsymmorphic crystal structure provides a proper electronic base for odd-parity pairing. Under time-reversal and inversion symmetries, the SOC is shown to favor equal-spin pairing and the $E_{2u}$ state in which the triplet $d$ vector is pinned to the $x$-$y$ plane. This 2D representation state would then spontaneously break the rotation symmetry and produce a nematic order, as in Cu$_2$Bi$_2$Se$_3$ [19–21], which has been ultimately confirmed by nuclear magnetic resonance (NMR) experiments [19]. However, NMR measurement would fail to answer the direction of the $d$ vector as in Sr$_3$RuO$_4$ because $E_{2u}$ and $A_u$ states are very close in energy ($T_c$ difference being less than 5%) and external magnetic fields can easily unpin the $d$ vector from the $x$-$y$ plane. Therefore, we suggest the proof can be realized in scanning tunneling spectroscopy or phase-sensitive measurements [41]. A salient point for this quasi-1D crystal is that it is a type-II superconductor with huge $\kappa$ [24], thus forbidding vortex formation, so that pure Zeeman effect can be used to study transitions between superconducting states.

Recently, similar quasi-1D $A_2$Cr$_3$As$_3$ ($A = K, Rb, Cs$) superconductors with comparable $T_c$ were reported [42–44] and suggested to be nodal unconventional superconductivity [44–47]. Although they share identical crystal structure as $M_2$Mo$_6$Se$_6$, their different electron valences [48] lead to completely different Fermi surface structures, and consequently distinct superconductivity theories. We also noted an unexpected superconductivity found in Na$_2$-$\_$.Mo$_6$Se$_6$ in which a large Na deficiency makes the localized system superconducting [49].
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APPENDIX A: TIGHT-BINDING MODEL

We build up the low-energy Hamiltonian for $\text{Mo}_3\text{Se}_3$ according to symmetry. There are 12 symmetry elements in space group of $P6_3/m$ (no. 176). To derive the Hamiltonian, it suffices to use the inversion center (1), the twofold screw axis about $z$ (2), and the threefold rotation axis about $z$ (3), since combinations of these three and their inverse elements can produce all possible operations. For example, the sixfold screw axis $6_3$ corresponds to a threefold rotation $3$ followed by the twofold screw $2_1$. Two $A$ and $B$ sublattices in this non-symorphic crystal interchange under inversion and twofold screw operations. Mathematically, the Hamiltonian follows

$$\mathcal{H}(k_x,k_y,k_z)\mathcal{Z}^{-1} = \mathcal{H}(-k_x,-k_y,-k_z),$$

$$\mathcal{S}_2\mathcal{H}(k_x,k_y,k_z)\mathcal{S}_2^{-1} = \mathcal{H}(-k_x,-k_y,k_z),$$

$$\mathcal{C}_3\mathcal{H}(k_x,k_y,k_z)\mathcal{C}_3^{-1} = \mathcal{H}(k_x',k_y',k_z'),$$

where $\mathcal{Z}$, $\mathcal{S}_2$, and $\mathcal{C}_3$ stand for inversion, twofold screw, and threefold rotation operators respectively. The momenta $k'$s in Eq. (A3) are given by

$$
\begin{pmatrix}
  k_x' \\
  k_y' \\
  k_z'
\end{pmatrix} =
\begin{pmatrix}
  \cos \frac{2\pi}{3} & \sin \frac{2\pi}{3} & 0 \\
  -\sin \frac{2\pi}{3} & \cos \frac{2\pi}{3} & 0 \\
  0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
  k_x \\
  k_y \\
  k_z
\end{pmatrix}.

In addition, time-reversal symmetry for the physical system requires

$$\mathcal{T}\mathcal{H}(k_x,k_y,k_z)\mathcal{T}^{-1} = \mathcal{H}(-k_x,-k_y,-k_z).$$

1. Spinless case

We consider first the spinless two-band Hamiltonian, given by

$$\mathcal{H}_i(k) = \sum_{j=0}^3 \epsilon_j(k)\sigma_j,$$

where $\sigma_0$ and $(\sigma_1,\sigma_2,\sigma_3)$ are the identity and Pauli matrices in sublattice subspace. This subspace, the symmetry operators are $\mathcal{I} = \sigma_1$, $\mathcal{S}_2 = e^{-i\hat{k}_z/2}\sigma_1$, $\mathcal{C}_3 = \sigma_0$, and $\mathcal{T} = \sigma_0K$. (acting on $\phi$ gives the complex conjugate $\phi^*$.)

Time-reversal symmetry (A5) imposes that $\epsilon_2(k)$ must be odd in $k$ and the other $\epsilon$'s even in $k$. Inversion symmetry (A1) imposes that both $\epsilon_2(k)$ and $\epsilon_3(k)$ must be odd in $k$. As a result, we have

$$\epsilon_3(k) = 0.$$ (A7)

Moreover, the twofold screw symmetry (A2) imposes that $\epsilon_2(k)$ must be odd in $k_\perp = (k_x,k_y)$, i.e., $\epsilon_2(-k_x,-k_y,k_z) = -\epsilon_2(k_x,k_y,k_z)$, and $[\epsilon_0(k),\epsilon_1(k)]$ even in $k_\perp$. Combining the time-reversal symmetry and twofold screw symmetry constraints on $\epsilon_i=0,1,2$, we find that they are all even in $k_\perp$.

Moreover, threefold symmetry (A3) requires that $\epsilon_{i=0,1,2}$ are threefold rotation invariant. So, $\epsilon_1(k)$ can be written as a product of $k_\perp$ and $k_z$ parts, namely $\sum_{j=1,2,3} f(k_\perp \cdot \bar{\delta}_j)g(k_z)$. The Bravais vectors $(\bar{\delta}_1,\bar{\delta}_2,\bar{\delta}_3)$ are interchangeable under $C_3$. As a result, we get

$$\epsilon_0(k) = E_0 + 2t_{01} \cos(k_z/2) + 2t_{02} \cos(3k_z/2) + 2t_{11} \cos(k_z/2) + 2t_{12} \cos(3k_z/2) + 2t_2 \cos(k_z/2) + 2t_4 \cos(3k_z/2),$$

(A8)

$$\epsilon_1(k) = -i \epsilon_2(k) = 2t_{11} \cos(k_z/2) + 2t_{22} \cos(k_z/2) + 2t_{12} \cos(3k_z/2) + 2t_{22} \cos(k_z/2) + 2t_{22} \cos(3k_z/2),$$

(A9)

where we consider finite hoppings up to second nearest neighbors in the $x$-$y$ plane and define

$$T_1(k_\perp) \equiv \sum_{i=1,2,3} \exp(i k_\perp \cdot a_i),$$

$$T_2(k_\perp) \equiv \sum_{i=1,2,3} \exp[i k_\perp \cdot (a_{i+1} - a_i)],$$

with primitive vectors $a_1 = a_4 = (\frac{\sqrt{3}}{2},-\frac{1}{2},0)$, $a_2 = (0,1,0)$, and $a_3 = (-\frac{\sqrt{3}}{2},\frac{1}{2},0)$. Equation (A9) is such that $\epsilon_1(k) = \epsilon_2(k) = 0$ at $k_z = \pi$, as required by the $T\mathcal{S}_2$ symmetry (see the main text).

2. Spinful case

Now, we introduce spin-orbital coupling. The spinful Hamiltonian then reads as $\mathcal{H}(k) = \sum_{i,j=0}^3 d_{ij}(k)\sigma_i\sigma_j$, where $s_0$ and $(s_1,s_2,s_3)$ are the identity and Pauli matrices for spin. The symmetry operators from Eqs. (A1) to (A5) in spin-sublattice subspace are $\mathcal{I} = s_0\sigma_1$, $\mathcal{S}_2 = i e^{-i\hat{k}_z/2}s_3\sigma_1$, $\mathcal{C}_3 = s_0e^{i\hat{k}_z/2}$, and $\mathcal{T} = i\mathcal{S}_2s_0K$.

The $s_0$ terms in the Hamiltonian immediately give $d_{00}(k) = \epsilon_j(k)$. For those $s_i$ terms with $i = (1,2,3)$, inversion symmetry
TABLE II. Hopping and spin-orbit coupling parameters in Eqs. (A8), (A9), (A19), and (A20) of the tight-binding model for Tl₂Mo₆Se₆. The site energy $E_0 = -0.1176$. All numbers are in units of eV.

<table>
<thead>
<tr>
<th>$\alpha$</th>
<th>$t_0$</th>
<th>$t'_0$</th>
<th>$t''_0$</th>
<th>$\lambda_0$</th>
<th>$\lambda'_0$</th>
<th>$\lambda''_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-0.0561</td>
<td>-0.0449</td>
<td>0.0023</td>
<td>1.0508</td>
<td>-0.0034</td>
<td>0.0001</td>
</tr>
<tr>
<td>0.01</td>
<td>-0.0561</td>
<td>-0.0449</td>
<td>0.0023</td>
<td>1.0508</td>
<td>-0.0034</td>
<td>0.0001</td>
</tr>
<tr>
<td>0.02</td>
<td>-0.0561</td>
<td>-0.0449</td>
<td>0.0023</td>
<td>1.0508</td>
<td>-0.0034</td>
<td>0.0001</td>
</tr>
</tbody>
</table>

(A1) gives

$$d_{ij}(-\mathbf{k}) = (-1)^{\delta_{i,j}} d_{ij}(\mathbf{k}),$$

(A12)

and time-reversal symmetry (A5) gives

$$d_{ij}(-\mathbf{k}) = (-1)^{\delta_{i,j} + \delta_{j,i}} (-1)^{\delta_{ij}} d_{ij}(\mathbf{k}).$$

(A13)

So, they lead to

$$d_{i0}(\mathbf{k}) = d_{i1}(\mathbf{k}) = d_{i2}(\mathbf{k}) = 0,$$

(A14)

$$d_{i3}(-\mathbf{k}) = -d_{i3}(\mathbf{k}).$$

(A15)

Considering twofold screw symmetry in Eq. (A2), we have for $i = 1, 2, 3$

$$d_{i3}(-\mathbf{k}, -k_y, k_z) = (-1)^{\delta_{i,j}} d_{i3}(k_y, k_z),$$

which imposes that $[d_{i3}(\mathbf{k}), d_{23}(\mathbf{k})]$ are even in $k_z$ and odd in $k_y$, while $d_{23}(\mathbf{k})$ is odd in $k_y$ and even in $k_z$. Finally, the threefold rotation symmetry (A3) imposes

$$d_{13}(\mathbf{k'}) = i d_{35}(\mathbf{k}),$$

(A16)

$$d_{35}(\mathbf{k'}) = d_{35}(\mathbf{k}).$$

(A17)

We can use the rotation relations in Eq. (A4) to write down all possible forms for $d_{i3}$.

Let us define $\zeta_i(\mathbf{k}) = d_{i3}(\mathbf{k})$ ($i = 1, 2, 3$). The full Hamiltonian reads

$$\mathcal{H}(\mathbf{k}) = s_0 \mathcal{H}_c(\mathbf{k}) + \sum_{i=1,2,3} \zeta_i(\mathbf{k}) s_i \sigma_3,$$

(A18)

where $\mathcal{H}_c$ is given in Eq. (A6). Again by writing $\zeta_i$ as a product of $k_\perp$ and $k_z$ parts, we get

$$\zeta_1(\mathbf{k}) = i \zeta_2(\mathbf{k}) = 4 R_1(\mathbf{k}_\perp) [\lambda_{11}(\mathbf{k}_\perp) \sin(k_z) + \lambda_{12}(\mathbf{k}_\perp) \sin(2k_z)],$$

(A19)

$$\zeta_3(\mathbf{k}) = 2 \text{Im}[T_1(\mathbf{k}_\perp)] [\lambda_{00}(\mathbf{k}_\perp) + 2 \lambda_{01}(\mathbf{k}_\perp) \cos(k_z) + 2 \lambda_{02}(\mathbf{k}_\perp) \cos(2k_z)],$$

where in-plane functions $R_{1,2}$ are

$$R_1(\mathbf{k}_\perp) = \sum_{i=1,2,3} e^{-i\theta_i} \cos(\mathbf{k}_\perp \cdot \mathbf{a}_i),$$

(A21)

$$R_2(\mathbf{k}_\perp) = \sum_{i=1,2,3} e^{-i\theta_i} \cos(\mathbf{k}_\perp \cdot (\mathbf{a}_{i+1} - \mathbf{a}_i)).$$

(A22)

where $\theta_i$ ($\theta'_i$) is the angle of $\mathbf{a}_i$ ($\mathbf{a}_{i+1} - \mathbf{a}_i$) relative to the $x$ axis. Table II lists the hopping and spin-orbit coupling parameters for our band fitting results for Tl₂Mo₆Se₆.

APPENDIX B: ESTIMATE $T_D$ DIFFERENCE BETWEEN $A_g$ AND $E_{2u}$ STATES

For the short-range interaction Hamiltonian

$$H_{int} = - \sum_{\mathbf{r}} [U[n_{A\uparrow}(\mathbf{r}) n_{A\downarrow}(\mathbf{r}) + n_{B\uparrow}(\mathbf{r}) n_{B\downarrow}(\mathbf{r})]$$

$$+ V[n_{A\uparrow}(\mathbf{r}) n_{B\downarrow} + \bar{c}(\mathbf{r})/2 + n_{A\uparrow}(\mathbf{r}) n_{B\downarrow}(\mathbf{r}) - \bar{c}(\mathbf{r})/2)],$$

(B1)

where $\bar{c}(\mathbf{r})$ runs over the Bravais lattice and $n_{X\uparrow}(\mathbf{r}) + n_{X\downarrow}(\mathbf{r})$ is the electron density for sublattice $X$, the possible order parameters are defined as follows:

$$A_g : \Delta_1 = \frac{U}{4} \sum_{s=\uparrow,\downarrow} \sum_{j} s \langle c^\dagger_{As}(\mathbf{r}) c^\dagger_{As}(\mathbf{r}) + c^\dagger_{Bs}(\mathbf{r}) c^\dagger_{Bs}(\mathbf{r})$$

$$+ V \sum_{j \neq \bar{j}} \sum_{\eta = \pm} \langle c^\dagger_{As}(\mathbf{r}) c^\dagger_{Bs}(\mathbf{r} + \bar{\mathbf{c}}/2) \rangle, \quad \Delta_2 = \frac{V}{2} \sum_{s=\pm} \sum_{\eta = \pm} \langle c^\dagger_{As}(\mathbf{r}) c^\dagger_{Bs}(\mathbf{r} + \bar{\mathbf{c}}/2) \rangle,$$

$$A_u : \Delta_3 = \frac{V}{2} \sum_{s=\pm} \sum_{\eta = \pm} \langle c^\dagger_{As}(\mathbf{r}) c^\dagger_{Bs}(\mathbf{r} + \bar{\mathbf{c}}/2) \rangle,$$

$$B_u : \Delta_4 = \frac{V}{2} \sum_{s=\pm} \sum_{\eta = \pm} \langle c^\dagger_{As}(\mathbf{r}) c^\dagger_{Bs}(\mathbf{r} + \bar{\mathbf{c}}/2) \rangle,$$

$$E_{1g} : \Delta_5 = \frac{V}{2} \sum_{s=\pm} \sum_{\eta = \pm} \langle c^\dagger_{As}(\mathbf{r}) c^\dagger_{Bs}(\mathbf{r} + \bar{\mathbf{c}}/2) \rangle,$$

$$E_{2u} : \Delta_6 = \frac{V}{2} \sum_{s=\pm} \sum_{\eta = \pm} \langle c^\dagger_{As}(\mathbf{r}) c^\dagger_{Bs}(\mathbf{r} + \bar{\mathbf{c}}/2) \rangle. \quad \text{(B2)}$$

The pair susceptibilities $\chi$'s are defined in the main text. Their numerical results are shown in Fig. 4, in which undoped ($x = 0$) and 5% hole doping ($x = 0.1$) are considered. No qualitative change in pairing susceptibilities by doping is observed. Three prominent channels $\chi_0$, $\chi_3$, and $\chi_6$ correspond to $A_g$, $A_u$, and $E_{2u}$ symmetries, respectively, all for
FIG. 4. Pair susceptibilities of Tl$_{2-x}$Mo$_6$Se$_6$ for all channels for different dopings: (a) $x = 0$ ($\mu = 0$) and (b) $x = 0.1$ ($\mu = -0.176$ eV). The most dominant channel $\chi_0$ corresponds to the $A_g$ state, followed by $\chi_3$ and $\chi_6$ for $A_u$ and $E_u$ states, respectively. Differences of $\chi_3$ and $\chi_6$ are shown in the insets.

Interestingly, the pairing susceptibilities for the $A_u$ and $E_u$ channels are very close, as shown in the insets of Fig. 4. Pair susceptibilities for the gap functions in the form of $\cos(k_z/2)$, like $B_u$, are very weak since the normal-state Fermi surface is close to or even beyond the $k_z = \pi$ plane where gap functions vanish. Those for gapful sublattice-even pairing. The resulting fitting parameters are given in Table III. We have chosen to fit the high temperature range above $k_B T = 10^{-3}$ eV due to numerical limit.
superconductivity show the conventional logarithmic behavior, $\chi \sim N_{\text{eff}} \ln (\Lambda/k_B T)$, where $N_{\text{eff}}$ stands for the weighted density of states and $\Lambda$ is the energy cutoff.

To estimate the critical temperatures $T_{c,3}$ and $T_{c,6}$ for the $A_u$ and $E_{2u}$ channels, we shall adopt the simple BCS phenomenological formula,

$$\chi = N_{\text{eff}} \ln (\Lambda/k_B T),$$

(B3)
to fit $\chi_3$ and $(\chi_6 - \chi_3)$ calculated from the tight-binding model, as shown in Fig. 5. The resulting fitting parameters are given in Table III. A simple way to estimate their critical temperatures is to use

$$k_B T_{c,3} = \Lambda \exp\left(-\frac{1}{V (N_{\text{eff},6} - N_{\text{eff},3})}\right)$$

$$\simeq \Lambda \exp\left(-\frac{1}{V N_{\text{eff},6} (1 + \Delta N_{\text{eff}}/N_{\text{eff},6})}\right)$$

$$= \Lambda \left(\frac{k_B T_{c,6}}{\Lambda}\right)^{(1 + \Delta N_{\text{eff}}/N_{\text{eff},6})} = k_B T_{c,6} \times \left(\frac{k_B T_{c,6}}{\Lambda}\right)^{(\Delta N_{\text{eff}}/N_{\text{eff},6})},$$

(B4)

where we take $\Delta N_{\text{eff}} = N_{\text{eff},6} - N_{\text{eff},3} \ll N_{\text{eff},6}$, and assume $\Lambda$ is the same for both susceptibilities (but at fitting it is treated differently). By using the fitting parameters given in Table III, we can estimate the $T_c$ difference for $A_u$ and $E_{2u}$ states. If we take $T_{c,6} = 6 \, \text{K}$, $T_{c,3}/T_{c,6} \simeq 0.95$ for $x = 0$ and $T_{c,3}/T_{c,6} \simeq 1$ for $x = 0.1$ in $\text{Tl}_2-\text{Mo}_6\text{Se}_6$. So, within this doping range, the $T_c$ difference is less than 5%.