Three-dimensional time-reversal invariant topological superconductivity in doped chiral topological semimetals

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Chiral topological semimetals host multifold degenerate band crossing points under the protection of crystalline symmetries. In this paper, we suggest the recently discovered chiral topological semimetals in space group $P\overline{2}13$ (No. 198), parts of which are superconducting upon doping, can be new candidates of time-reversal-invariant topological superconductors. By investigating the Fermi surfaces around the band crossing points, we clarify how the nontrivial topology of chiral topological semimetals affects their superconducting state and show the existence of topological superconductivity with surface Majorana fermions. We further demonstrate that the topological superconductivity is favored by inter-unit cell phonon-mediated electron-electron interaction.

Over the last decade, the interplay of superconductor pairing and band topology has paved a route to topological superconductors (TSC) hosting Majorana modes, which have potential applications in topological quantum computation \cite{11,12}. This intriguing interplay can be realized as a result of the proximity of conventional $s$-wave superconductor (SC) and one dimensional (1D) spin-orbit coupled semiconductor \cite{13,14} or 2D topological insulator \cite{16}. Despite the fact that experimental progress have been made \cite{17,18,19}, the heterostructures make confirmation and further application complicated. On the other hand, superconductivity is allowed to exist in topological (crystalline) insulator under doping, pressure, or low temperature. The famous examples include CuBi$_2$Se$_3$ \cite{20,21} and Sn$_{1-x}$In$_x$Te \cite{23}. This mechanism also applies to gapless topological matters (e.g., doped Weyl and Dirac semimetals) \cite{24,25}. Although zero-bias conductance peaks have been experimentally observed \cite{28,32} in iron-based superconductors in gapless system, further investigation on superconducting topological matter is necessary.

Recently, another type of gapless topological matters in crystals with specific non-symmorphic space group symmetry, dubbed as “chiral topological semimetals” or chiral crystals \cite{33,35}, have attracted a lot of experimental attentions \cite{36,37}. The chiral topological semimetals can be viewed as natural generalization of the well-studied Weyl semimetal. In particular, in low-energy Hamiltonian of Weyl semimetal $H = \delta \mathbf{k} \cdot \mathbf{S}$, the spin-1/2 vector $\mathbf{S}$ is replaced by spin-1 or -3/2 matrices in chiral topological semimetals \cite{33,35}. However, the chiral topological semimetal have distinguished bulk and edge topological properties. Different from the chiral fermion in spin-1/2 Weyl fermion with a topological charge (Chern number) $C = \pm 1$, the chiral fermions in chiral topological semimetals are multifold and carry topological charge $C$ larger than 1. For instance, the chiral topological semimetals in space group $P\overline{2}13$ host 4- and 6-fold chiral fermions as shown in Fig. 1(a) and (b). While the band crossings of Weyl semimetal are positioned at Weyl points away from the high-symmetry points of the Brillouin zone, the high-order degenerated band crossing point of chiral topological semimetal are located at high-symmetry points. In space group $P\overline{2}13$, the multifold nodes at $\Gamma$ and $R$ point are connected by a long Fermi arcs [see Fig. 1(c)].

In analog with TSC in doped Weyl semimetal, it is natural to expect interesting superconducting states to emerge in these topological chiral semimetal systems upon doping. In this paper we address the the effect of the nontrivial topology, i.e., the high symmetric points and Fermi arcs, on the superconducting properties. The fact that the source (positive Chern number) and sink (negative Chern number) of Berry curvature are located at high symmetric points (e.g., in space group $P\overline{2}13$,...
s \text{ical superconductivity requires a momentum-dependent semimetal and reveal that the realization of topolog-
tic charge at \( \Gamma \) and \( R \) point. To investigate the possible topolog-
class DIII is characterized by an ant superconductor in class DIII is characterized by an integer (\( Z \)) topological invariant, which can be written as a winding number over the entire momentum space. To characterize the topological properties of bulk wave function, the winding number for a 3D topological superconductor is defined as \[ \nu = \frac{1}{24 \pi^2} \int d^3 k \epsilon^{ijk} \text{Tr} \left[ Q_k^j \partial_i Q_k Q_k^i \partial_j Q_k Q_k^j \partial_k Q_k \right]. \]

Here, \( Q_k \) is related to the projection operator of occupied state \( p_k = \sum_{n \in \text{filled}} |u_{nk} \rangle \langle u_{nk}| \) as \( Q_k = 1 - p_k \) with \( |u_{nk} \rangle \) being the \( n \)-th Bloch wave function at \( k \).

To relate the winding number to the Chern numbers on Fermi surfaces, we consider a simple case: When the superconducting gap is much smaller than the Fermi energy, the topological properties of the possible superconductor pairing completely determined by the properties in the neighborhood of the Fermi surface \[ \nu = \frac{1}{2} \sum_{j \in \text{FS}} C_j \text{sgn}(\Delta_j). \]

Under the time-reversal symmetry, the SC pairing gap function \( \Delta_j \) on the \( j \)-th surface is real and is well-defined for a gapped system.

The huge separation of \( \Gamma \) and \( R \) critically affects the possible superconductor pairing between electrons. Indeed, we can show that \( s \)-wave pairing local in space is topological trivial. The \( s \)-wave SC pairing gap functions on all the Fermi surfaces are all positive or all negative. Since the total Chern number for all the Fermi surfaces in the BZ is zero guaranteed by the no-go theorem \[ \nu = \frac{1}{2} \sum_{j \in \text{FS}} C_j \text{sgn}(\Delta_j). \]

In noncentrosymmetric superconductors whose inversion symmetry is broken, parity is ill-defined. Here, \( d(k) \) is an even functions of \( k \) and forms an irreducible representation of space group. For simplify, it can be chosen to be \( d(k) = \Delta_0 (\cos(k_x) + \cos(k_y) + \cos(k_z)) \) corresponding to \( A \) representation of space group \( P2_13 \). As anticipated, the \( s \pm \)-wave SC pairing gives a TSC with \( \nu = 4 \).
Note that since the inversion symmetry is broken in the system, one cannot apply the criterion for odd-parity superconductor. And for a 3D time-reversal-invariant TSC in class DIII, the \( Z \) classification of band theory reduces to a \( Z_{16} \) classification with interactions [47].

**Low-energy analysis.** – For definiteness, we study a low-energy effective Hamiltonian respects time-reversal symmetry \( \mathcal{T} \) and non-symmorphic symmetries. The generators are described by a point group \( \mathbb{T} \) in combination with the translational parts. In the presence of the translational parts, the generators at different high-symmetric points are distinguished. In particular, the generators at \( \Gamma \) point are \( s_{2x} = \{ C_{2x} | \frac{1}{2} \frac{1}{2} \frac{1}{2} \} , s_{2z} = \{ C_{2z} | \frac{1}{2} \frac{1}{2} \frac{1}{2} \} , s_{3,111} = \{ C_{3,111} | 000 \} \) with \( K \) the complex conjugation. At \( R \) point, the generators become \( s_{2x} = \{ C_{2x} | \frac{1}{2} \frac{3}{2} \frac{3}{2} \} , s_{2z} = \{ C_{2z} | \frac{1}{2} \frac{1}{2} \frac{3}{2} \} , s_{3,111} = \{ C_{3,111} | 010 \} \). Thus, to capture the topological properties of the Fermi surfaces around \( \Gamma \) and \( R \) point, the Hamiltonian should be allowed by the space group symmetries instead of a little group symmetries near one of the band touching points.

![Diagram](image)

*FIG. 2. (Color online) (a) The lattice structure in real space. The orbitals \( A(0,0,0), B(\frac{1}{2}, \frac{1}{2}, 0), C(\frac{1}{2}, 0, \frac{1}{2}) \) and \( D(0, \frac{1}{2}, \frac{1}{2}) \) in the same unit cell are marked in green, while the orbital in the adjacent unit cells are in purple. (b) Reproduction the band dispersion of RhSi [31] along a typical high symmetric cut in the BZ.*

The insulating filling constraint for spin-orbit coupled insulators in space group \( P2_13 \) is \( \nu \in 8Z \) according to Ref. [35]. It indicates the tight-binding model should be described by a \( 8 \times 8 \) matrix Hamiltonian. The Hamiltonian can be written in a basis of spin \( \sigma \) and four Wannier orbitals in a unit-cell shown in Fig. 2(a). The Pauli matrix \( \sigma^x \) represents hopping between orbitals \( A \) and \( B \), or between orbitals \( C \) and \( D \). Similarly, \( \mu^x \) represents hopping between \( A \) and \( C \), or \( B \) and \( D \). Under the basis \( \{ e^A, e^C, e^B, e^D \} \), the operations can be written as \( s_{2x} = i \tau^x \sigma^x \otimes (k_{y,z} \rightarrow -k_{y,z}) , s_{2z} = i \mu^x \sigma^z \otimes (k_{x,y} \rightarrow -k_{x,y}) , T = i \sigma^y K \otimes (k_{x,y} \rightarrow -k_{x,y,z}) \) and \( C_{3,111} =
\begin{bmatrix}
1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & 1 & 0 \\
0 & 0 & 0 & 1
\end{bmatrix}
\begin{bmatrix}
0 \\
0 \\
0 \\
0
\end{bmatrix}
\end{bmatrix}
\begin{bmatrix}
\varepsilon_{3,111}/3 \otimes (k_x \rightarrow k_y , k_y \rightarrow k_z , k_z \rightarrow k_x )
\end{bmatrix}
\]
with \( \sigma_{111} = (\sigma_x + \sigma_y + \sigma_z) / \sqrt{3} \). The full expression for the lattice model \( H_0 \) is given in the Supplemental Materi-
effective intra-orbital onsite interaction $U$, the effective inter-orbital interaction $V$, and effective intra-orbital interaction between adjacent unit cells $W$. The effective interaction parameters are given by the difference between electron-phonon coupling $I_{ph}$ and Coulomb repulsion $I_{coul}$ as $I = I_{ph} - I_{coul}$, $U, V, W$. The interactions as follows,

$$H_{int} = -U \sum_{i,l} n_{i\uparrow} n_{i\downarrow} - V \sum_{i,l \neq j,l} n_{i\downarrow} n_{i'\uparrow} - W \sum_{\langle i,l \rangle, \sigma \neq \sigma'} C_{il\sigma}^\dagger C_{il'\sigma} C_{il'\sigma'} C_{il\sigma'}$$

where $l$ indices are summed over all the $s$-wave orbitals in one unit cell ($l = A, B, C, D$). $n_{i\sigma} = \sum_{\sigma} C_{il\sigma}^\dagger C_{il\sigma}$ is the electron density with spin $\sigma = \uparrow, \downarrow$ locating at sublattice $l$ in the unit cell $i$.

In the BCS theory, if we start from a free electron gas, and turn on an attractive interaction. The system becomes unstable and the electrons will group themselves and turn on an attractive interaction. The system be-

Supplemental Material (SM).

The effective interaction, we obtain the pairing order parameter by solving the linearized gap equation

$$\sum_j \int_k' \delta(\epsilon_j \delta k') \chi^{ij}(k, k') \Delta_j(k') = \lambda \Delta_i(k)$$

where $\int' = \int \frac{d^3k'}{(2\pi)^3}$ sum over the fermi surface. The most negative eigenvalue $\lambda$ gives the highest $T_c \propto \exp(-1/\lambda)$ and determines the dominant pairing. And its corresponding eigenvector gives the pairing order parameter $\Delta_j$. In particular, the signs of the pairing order on different Fermi surfaces and the winding number are related by Eq. (2), which characterizes the SC pairing phase.

The phase diagrams as a function of onsite interactions $U(V)$ and neighbor unit-cell interaction $W$ are shown in Fig. 4. First, the phase diagram for onsite intra-orbital interaction $U$ is plotted in Fig. 4(a). The $s_\pm$-wave SC pairing is favored by negative $U$ and positive $W$. This indicates that the topological nontrivial $s_\pm$-wave pairing exists only when the onsite Coulomb repulsion is stronger than electron-phonon coupling and the inter-unit-cell electron-phonon coupling is stronger than Coulomb interaction. In contrast, the conventional $s$-wave pairing which is inter-orbital spin-singlet, it is favored by the attractive onsite intra-orbital interaction. And the system is in a metal phase with $\Delta = 0$ when there is no correlations. Second, in Fig. 4(b), the inter-unit-cell $s_\pm$ phase wins as long as the inter-unit cell interaction is positive and exceeds the onsite inter-orbital interaction $W > |V|$. Therefore, when there is electron correlation between neighbor electron correlation and the onsite interaction is constrained, the $s_\pm$-wave SC pairing is preferred.

Materials. – The chiral topological semimetals can be realized in materials with time-reversal symmetry and spin-orbit coupling and their host of crystal symmetry-protected fermionic excitations are stabilized by non-symmorphic symmetries [33]. The most considered chiral crystals are in space group $P2_13$ (No. 198) primitive cubic lattice [34, 35]. Recently, chiral topological

FIG. 3. (Color online) The low-energy BdG spectra for (0 1 0) surface with SC pairing amplitude $\Delta = 0.2$. The red solid lines indicates the helical electron edge modes. The parameters are the same with Fig. 2.

FIG. 4. (Color online) The phase diagram for inter-unit cell interaction $W$ and onsite (a) intra-orbital interaction $U$ and (b) inter-orbital interaction $V$ respectively. Only the most leading channel at each point is indicated: $s_\pm$-wave pairing(red), $s$-wave pairing(purple).
semimetals have been experimental found with the observation of long Fermi arcs by angle-resolved photoemission spectroscopy (ARPES) in several materials of space group $P2_13$, including CoSi, RhSi, PtGa, PdGa, AIPt, and PbBiSe.

Superconducting phase transitions were reported in AuBe and PbBiSe, two compounds in the cubic $P2_13$ space group. AuBe, a transition metal compound, has been predicted to host unconventional fermions due to its calculated electronic structure [51]. It exhibits superconductivity under low temperature (3.3K) with time-reversal symmetry being preserved [52]. On the other hand, ARPES measurement has observed multiple unconventional fermions in PbBiS, an Ullmannite-type compound [40]. And bulk PbBiSe has been claimed to undergoes a superconducting transition below 1.8 K [53].

**Conclusion.**—We have revealed that 3D time-reversal-invariant TSC phase can be realized in a doped chiral topological semimetal. In particular, we have shown the existence of TSC phase with $\nu = 4$ in chiral topological semimetals of space group $P2_13$ by calculating topological invariant and BdG spectrum. Our work on realizing TSC in topological chiral semimetal opens the door to advances in the study of spin triplet pairing and their application to quantum information technology. The possible Majorana excitations hosing in the chiral topological semimetal can be detected by angle-resolved photoemission spectroscopy or scanning tunneling microscope.

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Supplemental Material

I. THE EFFECTIVE TIGHT-BINDING MODEL

To characterize the chiral topological semimetals protecting by non-symmorphic space group symmetries, it is necessary to construct an effective tight-binding model instead of $k \cdot p$ models around high-symmetry points. Although the $k \cdot p$ models manifest the degeneracies of the high-spin fermions hosting in a material, it does not determine all the key properties of the material. The band dispersion away from the high-symmetry point, and any band crossings in the dispersion are also fundamental properties of the material.

While the $k \cdot p$ Hamiltonian is constructed from the irreducible representations of the little group at high-symmetry invariant, the tight-binding model is based on the representations of the space group. The representations of space group is constructed from non-symmorphic symmetries operators, which are combining operators from a point group operation followed by a translation. In particular, the representations of space group $P_2_13$ are build on representations of point group $T$ (No. 23) and translational operators. To start, we can write down $T$ representations of point group $T$:

$$\{\sigma_x, \sigma_y, \sigma_z\}$$
$$\{\tau_x, \tau_x \mu_x, \mu_x\}$$
$$\{\tau_y, \tau_x \mu_y, \tau_z \mu_y\}$$
$$\{\tau_y \mu_z, \tau_y \mu_x, \mu_y\}$$
$$\{\tau_z \mu_z, -\tau_y \mu_y, \tau_z \mu_x\}$$

Here, the Pauli matrices $\sigma_\alpha$ and $\tau_\alpha$ ($\alpha = x, y, z$) are defined in the main text.

Based on the irreducible representation theory, we can obtain the terms preserving space group symmetry as product of $T$ representation of point group and momentum. With momentum up to second order, the tight-binding model
firstly represented in Ref. [34] is

\[
H_0 = v_1 [\tau^x \cos k_x/2 \cos k_y/2 + \tau^y \mu^x \cos k_y/2 \cos k_z/2 + \mu^x \cos k_z/2] \\
+ v_p [\tau^y \mu^z \cos k_x/2 \sin k_y/2 + \tau^y \mu^x \cos k_y/2 \sin k_z/2 + \mu^y \cos k_z/2] \\
+ v_r [\tau^y \mu^x \sigma^y \cos k_x/2 \cos k_y/2 + \tau^x \mu^x \sigma^y \cos k_y/2 \cos k_z/2 + \mu^x \sigma^y \cos k_z/2] \\
+ v_s [\tau^y \mu^x \sigma^z \cos k_x/2 \sin k_y/2 + \tau^x \mu^y \sigma^z \cos k_y/2 \sin k_z/2 + \mu^y \sigma^z \cos k_z/2] \\
+ v_3 [\tau^y \mu^z \sigma^z \cos k_x/2 \sin k_y/2 + \tau^y \mu^x \sigma^z \cos k_y/2 \sin k_z/2 + \mu^y \sigma^z \cos k_z/2] \\
+ v_2 [\cos(k_x) + \cos(k_y) + \cos(k_z)].
\]

The parameters in Figs. 2 and 3 are chosen following Ref. [34] as: \(v_1 = 0.55, v_p = -0.76, v_{s1} = -0.04, v_{s2} = 0, v_{s3} = 0, v_r = 0, v_{r2} = -0.03, v_r = 0.01, v_2 = 0.16, \mu = 0.2\).

II. CONSTRUCTION OF WAVEFUNCTION AT \(\Gamma\) AND \(R\) POINT

In this section, we are going to construct the wavefunctions at two high symmetry points \(\Gamma\) and \(R\), which are used to project the SC pairing onto the Fermi surfaces around the high symmetry points in the main text. At \(\Gamma\) and \(R\), the non-symmorphic symmetry can be treated as its point group component which is independent with momentum \(k\). Accordingly, we can use two \(k \cdot p\) models near \(\Gamma\) and \(R\) instead of the continuum model. However, the \(k \cdot p\) form is usually difficult to diagonalize. Accordingly to Ref. [33] the low energy Hamiltonian describing fourfold or sixfold degeneracies has a form \(k \cdot p\), where \(p\) is the vector of spin-3/2 or -1 matrices. Here, we will first project the \(k \cdot p\) model into a \(k \cdot S\) form and then project the corresponding eigenvectors onto the original \(k \cdot p\) form.

After choosing linear terms originating from the tight-binding Hamiltonian expanded around \(\Gamma\) point (\(H_\Gamma = H|_{k_x=k_y=k_z=0} + \frac{\partial H}{\partial k_x}|_{k_x=1, k_y=k_z=0} + \frac{\partial H}{\partial k_y}|_{k_x=0, k_y=1, k_z=0} + \frac{\partial H}{\partial k_z}|_{k_x=0, k_y=0, k_z=1}\)), we obtain a \(k \cdot p\) Hamiltonian near \(\Gamma\) as

\[
H_\Gamma = v_1 (\tau_x + \tau_x \mu_x + \tau_x) \\
+ v_p (\mu_y k_x + \tau_y \mu_z k_y + \tau_y k_z) \\
+ v_r (\tau_y \mu_z \sigma_y + \tau_x \mu_x \sigma_z + \mu_x \sigma_x) \\
+ v_s (\tau_y \mu_z \sigma_x k_x + \tau_x \mu_x \sigma_y k_y + \mu_x \sigma_z k_z) \\
+ v_3 (\tau_y \mu_z \sigma_y k_x + \tau_x \mu_z \sigma_y k_y - \tau_y \mu_y \sigma_z k_z) \\
+ 3v_2 - \mu r.
\]

which is constraint by the Little group isomorphic to point group \(\mathbb{T}\).

Before deriving the eigenvector of Eq. (S-2), we construct the projection operator connect the \(k \cdot p\) form to the \(k \cdot S\) form with \(S\) being the vector of spin-3/2 matrices. The spin-3/2 matrices can be view as a total angular momentum as a mixture of the \(p\)-orbital momentum \(l=1\) and the electron spin momentum 1/2. The \(p\)-orbital momentum can be constructed from the matrix representations of the three generators at \(\Gamma\). In particular, the representation \(G_1\) and \(G_2\) of the spinless screws operator \(S_{2x}\) and \(S_{2y}\) are commute with the representation \(G_3\) of spinless threefold rotation \(C_{3,111}\). The commutation relations read \(G_1^2 = G_2^2 = G_3^2 = 1\), \([G_1, G_2] = 0\), \(G_1G_3 = G_3G_2\), \(G_2G_3 = G_3G_1G_2\).
We find that these commutation relations are satisfied by the following spinless matrices

\[ G_1 = \tau^x, \quad G_2 = \mu^x \quad \text{and} \quad G_3 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \end{pmatrix}. \] (S-3)

Here, the eigenvalues of \( G_1(G_2) \) are \( m_x(m_z) = \pm 1 \) and the corresponding eigenvectors are analogous to three \( p \) orbitals and one \( s \) orbital. The \( s \) orbital with \( (m_x, m_z) = (-1, 1) \) corresponds to a trivial representation and the three \( p \) orbitals under SU(2) invariance form a 3d irreducible representation: \( p_x \) orbital with \((1, -1), p_y \) orbital with \((-1, -1), p_z \) orbital with \((-1, 1)\), which can be

\[ p_x = \frac{1}{2}(-1, 1, 1, -1) \]
\[ p_y = \frac{1}{2}(-1, -1, 1, 1) \]
\[ p_z = \frac{1}{2}(-1, -1, 1, 1) \] (S-4)

We express the three \( p \) orbitals as linear combinations with distinct angular momentum eigenvalues \((l, m_l) : p_z \) orbital with \( l = 0, m_l = 0; p_{\pm} = \frac{1}{\sqrt{2}}(p_x \pm ip_y) \) orbitals with \( l = 1, m_l = \pm 1 \). When coupled to the spin, the component of the total angular momentum along \( z \) direction \( m_j = \pm \frac{3}{2}, \pm \frac{1}{2} \) is good quantum number to characterize the fourfold degenerate state at \( \Gamma \). And the Clebsch-Gordan coefficients are assigned as \( p_{\pm}^2 = \hat{p}_+ \otimes | \uparrow \rangle, p_{\pm}^0 = \sqrt{\frac{3}{2}}\hat{p}_+ \otimes | \downarrow \rangle \) + \( \sqrt{\frac{3}{2}}\hat{p}_- \otimes | \uparrow \rangle \) + \( \sqrt{\frac{3}{2}}\hat{p}_- \otimes | \downarrow \rangle \). Then we obtain the spin-3/2 matrices

\[ p_{\pm}^2 = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & \frac{i}{2} + i \frac{i}{2} & 0 & -1 + i \frac{i}{2} & 1 & 0 & -1 + i \frac{i}{2} & 0 \end{pmatrix} \]
\[ p_{\pm}^0 = \frac{1}{\sqrt{3}} \begin{pmatrix} -1 & \frac{1}{2} + i \frac{i}{2} & 1 & i \frac{i}{2} & 1 & 1 & i \frac{i}{2} \end{pmatrix} \]
\[ p_{\pm}^{-2} = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & -1 - i \frac{i}{2} & 0 & 1 - i \frac{i}{2} & 0 & 1 - i \frac{i}{2} \end{pmatrix} \] (S-5)

It is worthwhile to note that they are related to each other by \( s_{2x} \) or \( T \).

Now we can project the eight-band \( \mathbf{k} \cdot \mathbf{p} \) Hamiltonian onto this basis \((p_z, p_{\pm}, p_{\pm}^0, p_{\pm}^{-2})\). It becomes a four-dimensional \( \mathbf{k} \cdot \mathbf{s} \) form. This can be understood since the Hamiltonian around \( \Gamma \) point is constraint by the Little group isomorphic to point group \( \mathbb{T} \). The Hamiltonian at \( \Gamma \) point \((\vec{k} = 0)\) has four-fold degenerate bands with the same mass \( m \) and it can be written into a four-dimensional linearized form around \( \Gamma \).

\[ H_{3/2} = m \mathbb{I} + a \delta \vec{k} \cdot \vec{S} + b \delta \vec{k}^\prime \cdot \vec{S}^\prime + c [S_z, (S_x S_x - S_y S_y)] \] (S-6)

where \( a, b \) and \( c \) are three independent real-valued parameters and \( \mathbb{I} \) is a four-dimensional matrices. \( \vec{S} = (S_x, S_y, S_z) \) and \( \vec{S}^\prime = (S_x^3, S_y^3, S_z^3) \), in which \( S_x, S_y, S_z \) and \( S_{2x} \) are spin-3/2 matrices:

\[ S_x = \frac{1}{2} \begin{pmatrix} \sqrt{3} & 0 & 0 & 0 \\ 0 & 2 & 0 & \sqrt{3} \\ 0 & 0 & 0 & \sqrt{3} \\ 0 & \sqrt{3} & 0 & 0 \end{pmatrix}, \quad S_y = \frac{1}{2i} \begin{pmatrix} 0 & \sqrt{3} & 0 & 0 \\ -\sqrt{3} & 0 & 2 & 0 \\ 0 & -2 & 0 & \sqrt{3} \\ 0 & 0 & -\sqrt{3} & 0 \end{pmatrix}, \quad S_z = \frac{1}{2} \begin{pmatrix} 3 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -3 \end{pmatrix} \] (S-7)

The two forms (Eqs. \((S-2)\) and \((S-6)\)) are related with \( m = -m_\Gamma + 3v_q + v_q - v_r - \mu_\Gamma, a = \frac{1}{12}(14v_{s1} - 9v_{s2} + 9v_{s3} + 4v_\Gamma), b = \frac{1}{3}(-2v_{s1} + v_{s2} - v_{s3}) \) and \( c = \frac{1}{6}(v_{s2} + v_{s3}) \).
Supplementary Figure S1. (Color online) (a) The bulk band structure for RhSi along high symmetry lines and (b) the surface states in the BdG spectrum with SC order parameter \( \Delta = 0.5 \). \( \nu_1 = \nu_2 = -\nu_3 = -0.76 \) and the other parameters are the same with Fig. 2(b).

It is easy to find the eigenstates at \( b = c = 0 \) and \( m = 0 \), by setting \( v_{s1} = v_{s2} = -v_{s3} \) and \( \mu_R = -m_R + 3v_q + v_1 - v_2 \). Note that although the parameters are changed to \( v_{s1} = v_{s2} = -v_{s3} = -v_p \), the energy degeneracy at \( \Gamma \) and \( R \) are kept, as shown in Fig.S1(a). And the existence of TSC for the new set of parameters is established by Fig. S1(b).

The two eigenvectors of of Equation (S-6) with positive eigenvalues \( \frac{3}{2} \) and \( \frac{1}{2} \) are

\[
\phi_{\Gamma,3/2} = \frac{e^{-3i\phi}}{2\sqrt{2}} \left\{ - \left( \cos \frac{\theta}{2} - \sin \frac{\theta}{2} \right) ^3, -\sqrt{3}e^{i\phi} (\sin \theta - 1) \left( \sin \frac{\theta}{2} + \cos \frac{\theta}{2} \right) ^3 \right\} \\
\phi_{\Gamma,1/2} = \frac{e^{-3i\phi}}{4} \left\{ - \sqrt{3} (\sin \theta - 1) \left( \sin \frac{\theta}{2} + \cos \frac{\theta}{2} \right) ^3, -e^{i\phi} (3 \sin \theta + 1) \left( \cos \frac{\theta}{2} - \sin \frac{\theta}{2} \right) ^3 \right\} \\
e^{2i\phi} (3 \sin \theta - 1) \left( \sin \frac{\theta}{2} + \cos \frac{\theta}{2} \right) ^3, e^{3i\phi} \frac{\sqrt{3} \cos^2 \theta}{\cos \frac{\theta}{2} - \sin \frac{\theta}{2}} \right\}.
\]

Accordingly, with \( v_{s1} = v_{s2} = -v_{s3} \) and \( \mu_R = -m_R + 3v_q + v_1 - v_2 \), the eigenstate of Eq. (S-2) can be easily obtained \( |\psi_{\Gamma,i}\rangle = |\phi_{\Gamma,i}\rangle |p_{\frac{3}{2}}^+ , p_{\frac{3}{2}}^- , p_{\frac{1}{2}} , p_{\frac{1}{2}}^- \rangle \).

\( (|\psi_{\Gamma,3/2}\rangle \text{ and } |\psi_{\Gamma,1/2}\rangle) \) are the time-reversal partners of each other after fixing the phase.

Similarly, we can expand the Hamiltonian near \( R \) point \( (H|_{k_x=k_y=k_z=\pi} - \delta k_x \partial H / \partial k_x |_{k_x=k_y=k_z=\pi} \text{ and } \delta k_y \partial H / \partial k_y |_{k_x=0,k_y=0,k_z=\pi} \text{ and } \delta k_z \partial H / \partial k_z |_{k_x=0,k_y=0,k_z=\pi} \rangle \) and obtain

\[
H_R = +v_p (\tau_y \mu_z k_x + \tau_y \mu_z k_y + \mu_y k_z) \\
+ v_{s3} (\tau_y \mu_z \sigma_x + \tau_y \mu_z \sigma_y + \mu_y \sigma_z) \\
+ v_{s1} (\mu_x \sigma_z k_x + \tau_x \mu_z \sigma_z k_y + \tau_y \mu_z \sigma_y k_z) \\
+ v_{s2} (\tau_x \sigma_y k_x + \tau_x \mu_z \sigma_z k_y + \mu_x \sigma_x k_z) \\
+ v_{s3} (\tau_x \mu_z \sigma_z k_x - \tau_y \mu_z \sigma_y k_y - \tau_z \mu_z \sigma_y k_z) \\
- 3v_2 - \mu_R.
\]

At \( R \), the Hamiltonian is six-fold degenerate and a three-dimensional irreducible representation can be given by the three generators

\[
s_{2x}^R = \{ C_{2x} | 1 \ 3 0 \} , \quad s_{2y}^R = \{ C_{2y} | 0 \ 3 2 \} , \quad \text{and} \quad s_3 = \{ C_{3,111}^{-1} | 0 1 0 \}.
\]

They satisfy \( \{ C_{3,111}^{-1} | 0 1 0 \} ^3 = \{ R | 111 \} , \{ C_{2x} | 1 \ 3 0 \} ^2 = \{ R | 100 \} , \{ C_{2y} | 0 \ 3 2 \} ^2 = \{ R | 030 \} \), and thus are different from the generators at \( \Gamma \).
Similar to the matrices at \( \Gamma \) without SOC, the representation at \( R \) is \([s_{2xR}, s_{2zR}] = 0\) and can be form a 3d irreducible representation. We take one of the \( p' \)'s in the 3d irreducible basis \( p_R \) and its \( C_3 \) rotation partner \( |p_R\rangle, G_3|p_R\rangle \) and \( G_3^2|p_R\rangle \) form a 3d representation, while their time-reversal partners \( (\mathcal{T}|p_R\rangle, G_3\mathcal{T}|p_R\rangle \) and \( G_3^2\mathcal{T}|p_R\rangle \)) consist another 3d representation. In combination, a six-dimensional (6d) basis is formed

\[
\{ |p_R\rangle, G_3|p_R\rangle, G_3^2|p_R\rangle, \mathcal{T}|p_R\rangle, G_3\mathcal{T}|p_R\rangle, G_3^2\mathcal{T}|p_R\rangle \}. \tag{S-10}
\]

which gives a 6d representation of the Hamiltonian in a \( \delta \mathbf{k} \cdot \mathbf{S} \) form.

To construct this 6D representation for SG \( P2_13 \) at \( R \), we note that the unitary subgroup of the little group is isomorphic to the little group of SG \( 199 \) and satisfies

\[
H_{198}(\delta \mathbf{k}) = \begin{pmatrix}
H_{199}(a, \delta \mathbf{k}) & bH_{199}(1, \delta \mathbf{k}) \\
b^*H_{199}(1, \delta \mathbf{k}) & -H_{199}^*(a, \delta \mathbf{k})
\end{pmatrix} \tag{S-11}
\]

where the Hamiltonian for SG \( 199 \) is given by Gell-Mann matrices as

\[
H_{199} = \begin{pmatrix}
0 & a\delta k_x & a^*\delta k_y \\
a^*\delta k_x & 0 & a k_z \\
 a k_y & a^*k_z & 0
\end{pmatrix} \tag{S-12}
\]

with \( a = |a|e^{i \eta} \) is a complex parameter.

When \( \eta = \frac{\pi}{6} \), we note that Eq. (S-11) can be exactly solvable. The eigenvector above the fermi surfaces is

\[
\phi_{R,-1} = \left\{ 0, 0, 0, \frac{(1 - i)(3 + \sqrt{3}) \cos \theta}{(3 + (2 + i)\sqrt{3})(\sin \theta \cos(\phi) + i \sin(\phi))}, \frac{(\sqrt{3} - i)(\cos(\phi) + i \sin \theta \sin(\phi))}{2 \sin \theta \cos(\phi) + 2i \sin(\phi)}, 1 \right\}
\]

When the eigenvectors projected onto \( p \) orbitals basis, they are written into eight-dimensional vectors \( |\psi_{R,-1}\rangle = |\phi_{R,-1}\rangle p_1, p_0, p_{-1} \). While \( |\psi_{R,1}\rangle \) can be utilized to project the Hamiltonian to one of the Fermi surfaces with \( C = -2 \) around \( R \), its time-reversal partner \( \mathcal{T}|\psi_{R,1}\rangle \) project to the other Fermi surface.