

Supplementary Material:

Topological Superconductivity from Multi-fold Fermions in Chiral Crystal $\text{Li}_2\text{Pd}_3\text{B}$ and $\text{Li}_2\text{Pt}_3\text{B}$

CONTENTS

A. Pairing symmetry classification	1
B. Symmetry of the pairing function	2
C. Cubic dispersion Majorana bands on the (111) surface of DIII topological superconducting $\text{Li}_2\text{Pd}_3\text{B}$	5
D. Topological Invariants of the Gapless Superconductor $\text{Li}_2\text{Pt}_3\text{B}$	6
E. k·p model and explicit matrix representations of the little groups	8
1. Four-fold fermion at Γ	8
2. Three-fold fermion at R	9
F. Identification of unconventional fermions	10
G. First-principles calculation of band structures and surface states for $\text{Li}_2\text{Pd}_3\text{B}$ and $\text{Li}_2\text{Pt}_3\text{B}$	11
H. The first-principles band structure of other superconducting materials with multifold fermions	12
References	12

A. Pairing symmetry classification

To find the possible pairing states and analyze their quasi-particle spectrum, one first has to classify all the pairing channels according to the point group symmetry. For multi-dimensional representations, symmetry has to be further identified by finding the local minima (stationary points) of the corresponding Ginzburg-Landau free energy. Resulting symmetry is described by the isotropy group, which can then be used to find the possible quasi-particle gap structures [S1–S3]. For the normal state in the presence of SOC, the full symmetry group should be $G_{total} = G \times U(1) \times \mathcal{T}$, where G is the double space group of the lattice. In the vicinity of T_c , the symmetry group is spontaneously lowered into the subgroup G'_{total} of G_{total} . Explicitly speaking, $g \in G'_{total}$ should be an element of $H \subset G$, accompanied by a phase factor from $U(1)$ or a complex conjugate from $\mathcal{T}$. We list these in table S1 in the form of isotropy group $H(\Gamma_i)$. It can be understood that if a pairing is invariant under $H(\Gamma_i)$, it transforms as if it is the i -th irreducible representation (IR) Γ_i , of H .

The H reflects the symmetry of energetics $E_{\mathbf{k}}$, which can be probed in spectroscopic measurements. We did not consider any further mixing due to the symmetry breaking of the pairing potential [S2].

A₁ pairing— This pairing can be connected to the trivial s-wave pairing. Nodal structure is accidental. In this case, as argued in the main text, it is a possible DIII class topological superconductor, supporting chiral majorana fermions at its surface.

A₂ pairing— In this phase, $C_{2,xy}$ and $C_{4,z}$ are accompanied by an $e^{i\pi}$ phase. This forces nodes in pairing potential, which is discussed in the next section.

E pairing— In the E -pairing case, the homogeneous GL free energy density can be expressed as

$$f = \alpha|\boldsymbol{\eta}|^2 + \beta_1|\boldsymbol{\eta}|^4 + \beta_2(\eta_1^*\eta_2 - \eta_2^*\eta_1)^2 + \gamma_1|\boldsymbol{\eta}|^6 + \gamma_2|\boldsymbol{\eta}|^2|\eta_1^2 + \eta_2^2|^2 + \gamma_3|\eta_1^2||3\eta_2^2 - \eta_1^2|^2 \quad (\text{S1})$$

where $\boldsymbol{\eta} = (\eta_1, \eta_2)$ is the two component order parameter, and α, β, γ are material dependent parameters. The sixth order term has to be included to split accidental degeneracy. Local minima of the free energy can be found at $(1, 0)$, $(0, 1)$ and $(1, i)$. A multi-component order parameter allows a complex configuration $(1, i)$, spontaneously breaking TR symmetry.

T₁/T₂ pairing. — In both cases, the order parameter has three components $\boldsymbol{\eta} = (\eta_1, \eta_2, \eta_3)$, and the GL free energy density can be written as $f = \alpha|\boldsymbol{\eta}|^2 + \beta_1|\boldsymbol{\eta}|^4 + \beta_2|\boldsymbol{\eta} \cdot \boldsymbol{\eta}|^2 + \beta_3(|\eta_1|^2|\eta_2|^2 + |\eta_2|^2|\eta_3|^2 + |\eta_3|^2|\eta_1|^2)$. Now the distinct ground states are: $(1, 0, 0)$, $(1, 1, 1)$, $(1, \omega, \omega^2)$ and $(1, i, 0)$, with $\omega = e^{i2\pi/3}$. Again, the last two terms are related to the time-reversal symmetry breaking (TRSB) phase. According to Table S1, the saddle points of multi-dimensional IRs are either nematic or TRSB, and only $A_{1/2}$ preserves the full point group symmetry and TR.

B. Symmetry of the pairing function

Time-reversal symmetry can be written as $\mathcal{T} = C\mathcal{K}$ with $\mathcal{T}^2 = -1$ (spinful) so that

$$C_{\mathbf{k}}C_{\mathbf{k}}^\dagger = 1 \quad C_{\mathbf{k}} = -C_{-\mathbf{k}}^T, \quad \mathcal{K}a = a^*\mathcal{K}, \quad \text{for } a \in \mathbb{C}. \quad (\text{S2})$$

Then we have:

$$\mathcal{T}H\mathcal{T}^{-1} = H \quad \Rightarrow \quad C_{-\mathbf{k}}H_{-\mathbf{k}}^*C_{-\mathbf{k}}^\dagger = H_{\mathbf{k}}. \quad (\text{S3})$$

Also, TR symmetry has the properties that given a space group symmetry $g \in G$:

$$g\mathcal{T}|\psi_{\mathbf{p},\alpha}\rangle = \mathcal{T}g|\psi_{\mathbf{p},\alpha}\rangle \Rightarrow CD(g)^* = D(g)C. \quad (\text{S4})$$

This indicates that the C matrix can change a representation to its conjugate (adjoint) partner.

IR	Stationary points	Time-Reversal	Isotropy group H	Node type	$\Delta_{\mathbf{k}}$
A_1	–	TR	$O(A_1) : \{C_{3,xyz}, C_{4,z}, C_{2,xy}\}$	–	$1, k_x^2 + k_y^2 + k_z^2$
A_2	–	TR	$O(A_2)\{C_{3,xyz}, -C_{4,z}, -C_{2,xy}\}$	L	$(k_x^2 - k_y^2)(k_y^2 - k_z^2)(k_z^2 - k_x^2)$
E	$(1, 0)$	TR	$D_4(B_1) : \{-C_{4,z}, -C_{2,xy}\}$	L	$\sqrt{3}(k_x^2 - k_y^2)$
	$(0, 1)$	TR	$D_4(A_1) : \{C_{4,z}, C_{2,xy}\}$	–	$2k_z^2 - k_x^2 - k_y^2$
	$(1, i)$	TRSB	$O(E) : \{\omega C_{3,xyz}, \omega^2 C_{4,z}, \omega^2 C_{2,xy}\mathcal{K}\}$	P	$k_x^2 + \omega k_y^2 + \omega^2 k_z^2$
T_1	$(1, 0, 0)$	TR	$D_4(A_2) : \{C_{4,x}, -C_{2,yz}\}$	L	$k_y k_z (k_y^2 - k_z^2)$
	$(1, 1, 1)$	TR	$D_3(A_2) : \{C_{3,xyz}, -C_{2,x\bar{y}}\}$	L	$k_y k_z (k_y^2 - k_z^2) + k_z k_x (k_z^2 - k_x^2) + k_x k_y (k_x^2 - k_y^2)$
	$(1, \omega, \omega^2)$	TRSB	$D_3(E) : \{\omega C_{3,xyz}, -\omega C_{2,x\bar{y}}\mathcal{K}\}$	P	$k_y k_z (k_y^2 - k_z^2) + \omega k_z k_x (k_z^2 - k_x^2) + \omega^2 k_x k_y (k_x^2 - k_y^2)$
	$(1, i, 0)$	TRSB	$D_4(E) : \{iC_{4,z}, -C_{2,y}\mathcal{K}\}$	L	$k_y k_z (k_y^2 - k_z^2) + i k_z k_x (k_z^2 - k_x^2)$
T_2	$(1, 0, 0)$	TR	$D_4(B_2) : \{-C_{4,x}, -C_{2,y}\}$	L	$k_y k_z$
	$(1, 1, 1)$	TR	$D_3(A_1) : \{C_{3,xyz}, C_{2,x\bar{y}}\}$	–	$k_y k_z + k_z k_x + k_x k_y$
	$(1, \omega, \omega^2)$	TRSB	$D_3(E) : \{\omega C_{3,xyz}, \omega C_{2,x\bar{y}}\mathcal{K}\}$	P	$k_y k_z + \omega k_z k_x + \omega^2 k_x k_y$
	$(1, i, 0)$	TRSB	$D_4(E) : \{iC_{4,z}, -C_{2,y}\mathcal{K}\}$	L	$k_y k_z + i k_z k_x$

TABLE S1. The local minima of various pairing states. TR and TRSB indicate time-reversal and time-reversal symmetry breaking phases, respectively. The isotropy group H describes the symmetry of the minima, which is isomorphic to the subgroup of the O . The explicit form of the generators is also given. For the node type in single band pairing, ‘ P ’ denotes symmetry protected point nodes, ‘ L ’ denotes line nodes, and ‘–’ denotes that there is possibility of finding accidental nodes. Examples of basis functions are given in the last column. These may have accidental nodes that will be eliminated when higher-order terms of $\mathbf{k}$ are included. Also note that when projected to a specific band, the pairing function should always be an even function of $\mathbf{k}$. Here $\omega = e^{i2\pi/3}$.

Now given a superconducting BdG Hamiltonian:

$$\mathcal{H}_{\text{BdG}}(\mathbf{k}) = \begin{pmatrix} H_{\mathbf{k}} & \Delta_{\mathbf{k}} \\ \Delta_{\mathbf{k}}^\dagger & -H_{-\mathbf{k}}^T \end{pmatrix}, \quad (\text{S5})$$

it is very helpful to define a TR basis when TR symmetry is present:

$$\Psi_{\mathbf{k}} = [\psi_{\mathbf{k}}, \mathcal{T}\psi_{\mathbf{k}}^\dagger \mathcal{T}^{-1}]^T = [\psi_{\mathbf{k}}, C_{\mathbf{k}}^T \psi_{-\mathbf{k}}^\dagger]^T. \quad (\text{S6})$$

In this basis, the BdG Hamiltonian now reads:

$$\begin{aligned} \tilde{\mathcal{H}}_{\text{BdG}}(\mathbf{k}) &= \begin{pmatrix} \mathbb{1} & \\ & C_{\mathbf{k}}^T \end{pmatrix} \begin{pmatrix} H_{\mathbf{k}} & \Delta_{\mathbf{k}} \\ \Delta_{\mathbf{k}}^\dagger & -H_{-\mathbf{k}}^T \end{pmatrix} \begin{pmatrix} \mathbb{1} & \\ & C_{\mathbf{k}}^* \end{pmatrix} \\ &= \begin{pmatrix} H_{\mathbf{k}} & \tilde{\Delta}_{\mathbf{k}} \\ \tilde{\Delta}_{\mathbf{k}} & -H_{\mathbf{k}} \end{pmatrix} = \tau_z \otimes H_{\mathbf{k}} + \tau_x \otimes \tilde{\Delta}_{\mathbf{k}}. \end{aligned} \quad (\text{S7})$$

Note that the last line only holds when TR symmetry is present. Now the new pairing function, $\tilde{\Delta}_{\mathbf{k}} = \Delta_{\mathbf{k}} C_{\mathbf{k}}^*$ has the following properties required by TR/space group symmetry and Fermi statistics:

$$\begin{aligned} \mathcal{T} : \quad & \tilde{\Delta}_{\mathbf{k}}^\dagger = \tilde{\Delta}_{\mathbf{k}}, \\ g : \quad & D(g) \tilde{\Delta}_{\mathbf{k}} D(g)^\dagger = \tilde{\Delta}_{g\mathbf{k}}, \\ \text{Fermi statistics :} \quad & \tilde{\Delta}_{\mathbf{k}} = C_{-\mathbf{k}} \tilde{\Delta}_{-\mathbf{k}}^T C_{-\mathbf{k}}^\dagger \end{aligned} \tag{S8}$$

Then we can expand this function $\tilde{\Delta}_{\mathbf{k}} = \sum_{i,\mu} \eta_{i\mu} \Gamma_{i\mu}(\mathbf{k})$ into IRs of the point group. $\eta_{i\mu}$ is the corresponding order parameter in Ginzburg-Landau (GL) free energy, which is real or complex when TR symmetry is present or absent, respectively.

At general points in chiral superconductors, strong asymmetric spin-orbit coupling lifts all degeneracy and superconductivity pairs electrons within a single band. This is also in line with the superconductivity fitness condition of [S5–S7], which states that pairing is most stable when $H_0(\mathbf{k})$ and $\tilde{\Delta}_0(\mathbf{k})$ are simultaneously diagonalized: $[H_0(\mathbf{k}), \tilde{\Delta}_0(\mathbf{k})] = 0$. In this eigen-band basis we can write the simple Bogoliubov-de Gennes Hamiltonian as

$$\tilde{\mathcal{H}}_{\text{BdG}}(\mathbf{k}) = \begin{pmatrix} \text{diag}[\xi_{\nu,\mathbf{k}}] & \text{diag}[\Delta_{\nu,\mathbf{k}}] \\ \text{diag}[\Delta_{\nu,\mathbf{k}}^*] & -\text{diag}[\xi_{\nu,\mathbf{k}}] \end{pmatrix}. \tag{S9}$$

TR matrix C is an odd function of $\mathbf{k}$, such that $t(\mathbf{k}) = -t(\mathbf{k})$ and $|t(\mathbf{k})| = 1$. For the pairing function $\tilde{\Delta}(\mathbf{k})$, it is an even function of $\mathbf{k}$. We discuss such pairing in the computations within the main text. For such single band pairing, symmetries with an additional $U(1)$ phase will stabilize nodes on the Fermi surface. For example, in an A_2 phase, there is a π phase accompanied with $C_{4,z}$ rotation. Then, there must be at least two line nodes traversing through the rotation axis, since the pairing potential is a real function of $\mathbf{k}$. For TRSB phase such as the $(1, i)$ for E , the C_3 has a $e^{i2\pi/3}$ phase. However, since the time-reversal symmetry is broken, we can only conclude that the pairing function is zero at the intersection between the rotation axis and Fermi surface, as the phase is not well defined only at this point. We list all the node types in Table S1.

On the Brillouin zone boundary, non-symmorphic symmetry combined with the time-reversal symmetry will force Kramers-type degeneracy. If a line node as classified in the last paragraph resides in this degenerate point, it is then necessary to ask whether this node is susceptible to inter-band pairing. Luckily, according to the results in Table S1, the line nodes in general are not located on the Brillouin zone boundary, thus inter-band pairing does not affect our result.

For the results of the superconducting case, we first adopted the basis defined in Eq. S7 to write the BdG Hamiltonian: $\mathcal{H}_{\mathbf{k}} = H_{\mathbf{k}} \otimes \tau_z + \tilde{\Delta}_{\mathbf{k}} \otimes \tau_x$. For the A_1 case, the pairing takes the form

$$\begin{aligned} \tilde{\Delta}_{\mathbf{k}} = & \{d_0 + d_1 [6 - 2 \cos(k_x) - 2 \cos(k_y) \\ & - 2 \cos(k_z)]\} \mathbb{1}_{8 \times 8}. \end{aligned} \tag{S10}$$

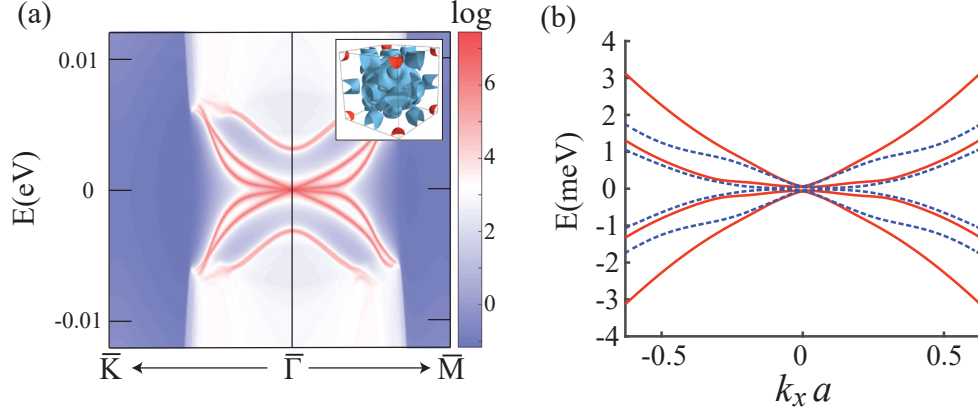


FIG. S1. The spectral function on the (111) left surface of DIII topologically superconducting $\text{Li}_2\text{Pd}_3\text{B}$ is shown in (a), where a linear Majorana cone and a cubic Majorana cone at $\bar{\Gamma}$ can be clearly identified. The inset in (a) indicates that the sign of projected pairing potential is positive (red) on the R pocket and negative (blue) on the rest. In (b), we present the Majorana spectrum of the surface projected 8-by-8 Hamiltonian, and the blue (red) curves represent the bands on the left (right) side surface. The different dispersion of the Majorana bands on the two surfaces is due to the broken inversion symmetry, but it is the same for the two surfaces that upon each of them there is one linear Majorana cone and one cubic Majorana cone.

And the parameters for DIII topological phases ($N = 4$) in Fig. 3 in the main text are $(d_0, d_1) = (-0.05, 0.005)$ (in units of eV). For A_2 pairing, it is taken as

$$\begin{aligned} \tilde{\Delta}_{\mathbf{k}} = & d_0 (\cos k_x a - \cos k_y a) \\ & \times (\cos k_y a - \cos k_z a) (\cos k_z a - \cos k_x a) \mathbb{1}_{8 \times 8}, \end{aligned} \quad (\text{S11})$$

where the size of d_0 doesn't affect the physics and is set to be 0.02 eV.

C. Cubic dispersion Majorana bands on the (111) surface of DIII topological superconducting $\text{Li}_2\text{Pd}_3\text{B}$

As described in the main text, for the case of $\text{Li}_2\text{Pd}_3\text{B}$ with the A_1 representation, the superconducting properties of the system depend on η_1 and η_2 of the order parameter $\Delta_{\nu, \mathbf{k}} = \eta_1 + \eta_2 (3 - \cos k_x a - \cos k_y a - \cos k_z a)$. We shall here study the dispersion of Majorana fermions on the (111) surface under symmetry constraint. Numerically we first set $\eta_1/\eta_2 = -5$, and obtain the eight eigen-states nearest to the zero energy at $\bar{\Gamma}$ and projected the complicated slab Wannier Hamiltonian to them to get the 8-by-8 surface Hamiltonian. The energy spectrum of this projected surface Hamiltonian is shown in Fig. 3d in main text, and the linear as well as the cubic dispersion were verified by suitable fitting. It should be noted that the band difference between the two surfaces is due to the lack of inversion symmetry.

It is pointed out in [S10] that the cubic Majorana cone can result from spin-3/2 fermions and is protected by time-reversal $\hat{\mathcal{T}}$, particle-hole $\hat{\mathcal{P}}$ and $\hat{C}_3$ rotation symmetry, which is exactly the case for the (111) surface of $\text{Li}_2\text{Pd}_3\text{B}$. The argument is as follows. Assuming that the Majorana surface states are formed from spin-3/2 fermions, the symmetry operators mentioned above and their restrictions on the surface Hamiltonian can be written as

$$\begin{aligned}\hat{\mathcal{T}} &= i\sigma_y\hat{\mathcal{K}}, \quad \hat{\mathcal{T}}^{-1}H(\mathbf{k})\hat{\mathcal{T}} = H(-\mathbf{k}), \\ \hat{\mathcal{P}} &= \sigma_x\hat{\mathcal{K}}, \quad \hat{\mathcal{P}}^{-1}H(\mathbf{k})\hat{\mathcal{P}} = -H(-\mathbf{k}), \\ \hat{C}_3 &= -\sigma_0, \quad \hat{C}_3^{-1}H(\hat{C}_3\mathbf{k})\hat{C}_3 = H(\mathbf{k}).\end{aligned}\tag{S12}$$

Simple calculation tells us that $\hat{\mathcal{T}}$ together with $\hat{\mathcal{P}}$ requires that the surface Hamiltonian should only contain $k^{(odd)}\sigma_{x,y}$ terms while $\hat{C}_3$ requires that $H(k_+, k_-) = H(k_+e^{i\frac{2}{3}\pi}, k_-e^{-i\frac{2}{3}\pi})$ with $k_{\pm} = k_x \pm ik_y$. Thus, to the lowest-allowed k terms, the surface Majorana Hamiltonian is

$$H(k_+, k_-) = c_1(k_+^3\sigma_+ + k_-^3\sigma_-) + c_2(k_+^3\sigma_- + k_-^3\sigma_+),\tag{S13}$$

where $\sigma_{\pm} = \sigma_x \pm i\sigma_y$. In the contrast, for spin-1/2 fermions, the lowest-allowed terms are linear in k . In the weak pairing limit, the surface Majorana states are just linear combinations of particle and hole states near the Fermi level of bulk $\text{Li}_2\text{Pd}_3\text{B}$. In this sense, the existence of cubic Majorana bands is the direct result of the spin-3/2 unconventional fermions on the Fermi surfaces of $\text{Li}_2\text{Pd}_3\text{B}$.

D. Topological Invariants of the Gapless Superconductor $\text{Li}_2\text{Pt}_3\text{B}$

Throughout this work, we study the superconducting system with particle-hole symmetry $\hat{\mathcal{P}}$, time-reversal symmetry $\hat{\mathcal{T}}$ and their combination the chiral symmetry $\hat{\mathcal{C}} = i\hat{\mathcal{P}}\hat{\mathcal{T}}$, which makes the fully-gapped superconducting $\text{Li}_2\text{Pd}_3\text{B}$ classified into the 3-d DIII topological class with a $\mathbb{Z}$ topological invariant [S8]. In comparison, for the gapless superconducting $\text{Li}_2\text{Pt}_3\text{B}$ with nodal lines, to define an overall topological invariant upon the 3-d first BZ is not possible. However, it is still possible to define a $\mathbb{Z}$ topological invariant for any 1-d loop that do not intersect with any nodal line, because with the preserved chiral symmetry $\hat{\mathcal{C}}$ this loop the system can be classified into the 1-d AIII topological class. We have provided a way to define this $\mathbb{Z}$ topological invariant in Eq.2 in the main text. Here, we further justify it.

In Sec. B, we have written the BdG Hamiltonian in the TR basis as

$$\begin{aligned}
\tilde{\mathcal{H}}_{\text{BdG}}(\mathbf{k}) &= V \mathcal{H}_{\text{BdG}}(\mathbf{k}) V^\dagger \\
&= \begin{pmatrix} \mathbb{1} & \\ & C_{\mathbf{k}}^T \end{pmatrix} \begin{pmatrix} H_{\mathbf{k}} & \Delta_{\mathbf{k}} \\ \Delta_{\mathbf{k}}^\dagger & -H_{\mathbf{k}}^T \end{pmatrix} \begin{pmatrix} \mathbb{1} & \\ & C_{\mathbf{k}}^* \end{pmatrix} . \\
&= \begin{pmatrix} H_{\mathbf{k}} & \tilde{\Delta}_{\mathbf{k}} \\ \tilde{\Delta}_{\mathbf{k}} & -H_{\mathbf{k}} \end{pmatrix} = \tau_z \otimes H_{\mathbf{k}} + \tau_x \otimes \tilde{\Delta}_{\mathbf{k}} .
\end{aligned} \tag{S14}$$

Under this basis, the chiral symmetry can be simply formulated as

$$\tilde{U}_C = \tau_y, \tag{S15}$$

with $(\tilde{U}_C)^2 = \mathbb{1}$ and $\{\tilde{\mathcal{H}}_{\text{BdG}}(\mathbf{k}), \tilde{U}_C\} = 0$. We further rewrite the BdG Hamiltonian in the eigen-basis of the chiral symmetry as

$$\begin{aligned}
\tilde{\mathcal{H}}'_{\text{BdG}}(\mathbf{k}) &= V' \tilde{\mathcal{H}}_{\text{BdG}}(\mathbf{k}) V'^\dagger \\
&= \frac{1}{\sqrt{2}} \begin{pmatrix} \mathbb{1} & -i \\ & i \end{pmatrix} \begin{pmatrix} H_{\mathbf{k}} & \tilde{\Delta}_{\mathbf{k}} \\ \tilde{\Delta}_{\mathbf{k}} & -H_{\mathbf{k}} \end{pmatrix} \frac{1}{\sqrt{2}} \begin{pmatrix} \mathbb{1} & \mathbb{1} \\ i & -i \end{pmatrix} \\
&= \begin{pmatrix} & Q_{\mathbf{k}} \\ Q_{\mathbf{k}}^\dagger & \end{pmatrix}
\end{aligned} \tag{S16}$$

with $Q_{\mathbf{k}} = H_{\mathbf{k}} - i\tilde{\Delta}_{\mathbf{k}}$.

With these preliminary matrix transformations, we now justify that the quantity

$$N_C = \frac{1}{2\pi} \text{Im} \int_C d\mathbf{k} \text{Tr}[\partial_{\mathbf{k}} \ln Q_{\mathbf{k}}] \tag{S17}$$

is indeed a quantized topological invariant. Here $\mathcal{C}$ is a closed loop that do not intersect with any nodes. As we are only concerned about the weak pairing limit, $H_0(\mathbf{k})$ and $\tilde{\Delta}_0(\mathbf{k})$ can be simultaneously diagonalized as

$$H_{\mathbf{k}} = \text{diag}[\xi_{\nu,\mathbf{k}}], \quad \tilde{\Delta}_{\mathbf{k}} = \text{diag}[\Delta_{\nu,\mathbf{k}}], \tag{S18}$$

with real numbers $\xi_{\nu,\mathbf{k}}$ and $\Delta_{\nu,\mathbf{k}}$ for each band ν . Then we have

$$N_{\text{AIII},C} = \frac{1}{2\pi} \int_C d\mathbf{k} \partial_{\mathbf{k}} [\text{Im} \text{Tr} \ln Q_{\mathbf{k}}] = \frac{1}{2\pi} \sum_{\nu} \int_C d\mathbf{k} \partial_{\mathbf{k}} [\arg(q_{\nu,\mathbf{k}})] \tag{S19}$$

with $q_{\nu,\mathbf{k}} = \xi_{\nu,\mathbf{k}} - i\Delta_{\nu,\mathbf{k}}$. Now we can easily see that $N_{\text{AIII},C}$ is the summation of the winding numbers of $q_{\nu,\mathbf{k}}$ around the origin on the complex plane, which is a $\mathbb{Z}$ topological invariant.

Moreover, when studying the surface states, this 1-d loop can be chosen to be any straight line, which goes across the 1st BZ along the normal direction of the surface and also do not intersect with any nodal lines. Now the topological invariant $N_{\text{AIII},C}$

we just defined has a physical meaning – the number of Majorana zero modes at each end of this quasi-1d system. At one end, all the Majorana zero modes have the same chiral eigen-value C_n and this condition protects them from coupling to each other and being lifted to a finite energy as

$$\begin{aligned}\langle \psi_n | \hat{\mathcal{H}}_{BdG} | \psi_{n'} \rangle &= \langle \psi_n | \hat{C} \hat{C} \hat{\mathcal{H}}_{BdG} | \psi_{n'} \rangle \\ &= -\langle \psi_n | \hat{C} \hat{\mathcal{H}}_{BdG} \hat{C} | \psi_{n'} \rangle \\ &= -C_n C_{n'} \langle \psi_n | \hat{\mathcal{H}}_{BdG} | \psi_{n'} \rangle,\end{aligned}\tag{S20}$$

$$(1 + C_n C_{n'}) \langle \psi_n | \hat{\mathcal{H}}_{BdG} | \psi_{n'} \rangle = 0.\tag{S21}$$

In short, $\langle \psi_n | \hat{\mathcal{H}}_{BdG} | \psi_{n'} \rangle$ is forced to be zero when $C_n C_{n'} = 1$.

E. $\mathbf{k} \cdot \mathbf{p}$ model and explicit matrix representations of the little groups

To analyze the low energy effect model of multi-fold fermions, it is ideal to construct a $\mathbf{k} \cdot \mathbf{p}$ model. We focus on the linear terms of $\mathbf{k}$, so that the Hamiltonian can be written in the form:

$$H(\delta \mathbf{k}) = \sum_{i=1,2,3} M^i \delta \mathbf{k}_i,\tag{S22}$$

with $\delta \mathbf{k} = \mathbf{k} - \mathbf{K}_{\Gamma/R}$. The induced representation would be $(\bar{E}_1 \uparrow G) \downarrow G_\Gamma \approx \bar{\Gamma}_6(2) \oplus \bar{\Gamma}_7(2) \oplus \bar{\Gamma}_8(4)$ at the Γ point and $(\bar{E}_1 \uparrow G) \downarrow G_R \approx \bar{R}_6(2) \oplus \bar{R}_7 \bar{R}_8(6)$ at the R point, which can be found at *Bilbao Crystallographic server* [S15]. The numbers in the parentheses indicate the numbers of degeneracy, and $\bar{R}_7$ and $\bar{R}_8$ are related by TR symmetry. Here, $G_{\Gamma/R}$ denotes the little group of point Γ/R . This means that the four-fold fermion is subject to $\bar{\Gamma}_8(4)$, and the two three-fold fermions are subject to $\bar{R}_7(3)$, $\bar{R}_8(3)$, respectively. Then, to find the $\mathbf{k} \cdot \mathbf{p}$ Hamiltonian, for example, of the four-fold fermion at Γ , one just needs to find one set of matrix representations $D(g)$ of $\bar{\Gamma}_8(4)$ for $g \in G_\Gamma$ explicitly and then construct a 4-band $\mathbf{k} \cdot \mathbf{p}$ Hamiltonian $H_{\mathbf{k}}$ that is invariant, such that $D(g)H_{g^{-1}\mathbf{k}}D(g)^\dagger = H_{\mathbf{k}}$. Then, all the allowed terms can be derived from this relation.

1. Four-fold fermion at Γ

For $\bar{\Gamma}_8$ of G_Γ , we use the following form [S15]:

$$\begin{aligned}\{1|0\} &= \mathbb{1}_{4 \times 4}, & \{2_{001}|\frac{1}{2}0\frac{1}{2}\} &= \begin{pmatrix} -i & & & \\ & i & & \\ & & i & \\ & & & -i \end{pmatrix}, & \{2_{010}|0\frac{1}{2}\frac{1}{2}\} &= \begin{pmatrix} & -1 & & \\ 1 & & & \\ & & -i & \\ & & & -i \end{pmatrix}, \\ \{1^d|0\} &= -\mathbb{1}_{4 \times 4}, & \{3_{111}^+|0\} &= \frac{\sqrt{2}}{2} \begin{pmatrix} e^{i5\pi/12} & e^{-i\pi/12} & & \\ e^{i5\pi/12} & e^{i11\pi/12} & & \\ & e^{-i5\pi/12} & e^{i7\pi/12} & \\ & e^{-i11\pi/12} & e^{-i11\pi/12} & \end{pmatrix}, & \{2_{110}|\frac{1}{4}\frac{3}{4}\frac{1}{4}\} &= \begin{pmatrix} & -1 & & \\ 1 & & & \\ & & 1 & \\ & & & -1 \end{pmatrix}.\end{aligned}\tag{S23}$$

Here $\{1^d|0\}$ denotes the 2π rotation. We first get two sets of matrices so that $M^i = v_1 F_1^i + v_2 F_2^i$:

$$\begin{aligned} F_1^1 &= \begin{pmatrix} \sigma_x & \\ & \sigma_y \end{pmatrix}, F_1^2 = \begin{pmatrix} \sigma_y & \\ & \sigma_x \end{pmatrix}, F_1^3 = \begin{pmatrix} \sigma_z & \\ & -\sigma_z \end{pmatrix}, \\ F_2^1 &= \begin{pmatrix} 0 & 0 & e^{i\pi/12} & 0 \\ 0 & 0 & 0 & -ie^{i\pi/12} \\ e^{-i\pi/12} & 0 & 0 & 0 \\ 0 & ie^{-i\pi/12} & 0 & 0 \end{pmatrix}, F_2^2 = \begin{pmatrix} 0 & 0 & -e^{-i\pi/12} & 0 \\ 0 & 0 & 0 & -ie^{-i\pi/12} \\ -e^{i\pi/12} & 0 & 0 & 0 \\ 0 & ie^{-i\pi/12} & 0 & 0 \end{pmatrix}, \\ F_2^3 &= \begin{pmatrix} 0 & 0 & 0 & e^{i\pi/4} \\ 0 & 0 & e^{-i\pi/4} & 0 \\ 0 & e^{i\pi/4} & 0 & 0 \\ e^{-i\pi/4} & 0 & 0 & 0 \end{pmatrix}. \end{aligned} \quad (\text{S24})$$

The four-fold fermion at the Γ point of a cubic lattice was previously identified as a spin-3/2 fermion [S1, S17–S21]. To better connect this effective Hamiltonian to the spin-3/2 fermion, we recombine the two sets of F matrices to find the required form: $J^i = -\frac{1}{2}F_1^i + F_2^i$, and $T^i = F_1^i + \frac{1}{2}F_2^i$, so that $H = \mathbf{k} \cdot (v_1' \mathbf{J} + v_2' \mathbf{T})$. In this way, the J^i matrices form a 4-dimensional, spin-3/2 representation of $SO(3)$: $[J^i, J^j] = i\epsilon^{ijk} J^k$ and $\sum J^2 = \sqrt{\frac{1}{2}l(l+1)}\mathbb{1}$ with $l = 3/2$. And the remaining T matrices introduce the effect of a cubic crystalline field.

2. Three-fold fermion at R

At the R point, the 6-fold degeneracy is composed of an $\bar{R}_7 \bar{R}_8$ representation, where $\bar{R}_7$ and $\bar{R}_8$ are connected by TR symmetry. They are interpreted as two spin-1 fermions. We can first write one of the spin-1 fermion as $H_{\mathbf{k}} = \mathbf{k} \cdot \Gamma$. We project the Γ matrices to the $\bar{R}_7$ representation, whose explicit form is

$$\begin{aligned} \{1|0\} &= \mathbb{1}_{3 \times 3}, & \{2_{001}|\frac{1}{2}0\frac{1}{2}\} &= \begin{pmatrix} 1 & & \\ & 1 & \\ & & -1 \end{pmatrix}, & \{2_{010}|0\frac{1}{2}\frac{1}{2}\} &= \begin{pmatrix} 1 & & \\ & -1 & \\ & & 1 \end{pmatrix}, \\ \{1^d|0\} &= -\mathbb{1}_{3 \times 3}, & \{3_{111}^+|0\} &= \begin{pmatrix} & & \\ 1 & & \\ & & -1 \end{pmatrix}, & \{2_{110}|\frac{1}{4}\frac{3}{4}\frac{1}{4}\} &= \begin{pmatrix} & & \\ & -i & \\ -i & & \end{pmatrix}. \end{aligned} \quad (\text{S25})$$

The same can be done for $\bar{R}_8$, whose matrices are the complex conjugate of those of $\bar{R}_7$ since $\bar{R}_8 = \bar{R}_7^*$. The full Hamiltonian can be written as:

$$H_{\delta\mathbf{k}} = \begin{pmatrix} a\delta\mathbf{k} \cdot \Gamma & be^{i\theta}\delta\mathbf{k} \cdot \Omega \\ be^{-i\theta}\delta\mathbf{k} \cdot \Omega & a\delta\mathbf{k} \cdot \Gamma \end{pmatrix}, \quad (\text{S26})$$

with a, b, θ being real parameters. The resulting Γ^i and Ω^i matrices are:

$$\begin{aligned}\Gamma^1 &= \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -i \\ 0 & i & 0 \end{pmatrix}, \Gamma^2 = \begin{pmatrix} 0 & 0 & -i \\ 0 & 0 & 0 \\ i & 0 & 0 \end{pmatrix}, \Gamma^3 = \begin{pmatrix} 0 & -i & 0 \\ i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \\ \Omega^1 &= \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \Omega^2 = \begin{pmatrix} 0 & 0 & -1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{pmatrix}, \Omega^3 = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}.\end{aligned}\tag{S27}$$

TR operator here reads $\mathcal{T} = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \mathcal{K}$, with $\mathcal{K}$ the conjugate operator. Here, we still have $\mathcal{T}^2 = -1$, despite it being a ‘spin-1’ fermion, as the fundamental block is a spin-1/2 electron. Again, to make the feature of the spin-1 fermion more explicit, we have

$$J^i = \begin{pmatrix} \Gamma^i & \\ & \Gamma^i \end{pmatrix}, \quad T^i = \begin{pmatrix} & e^{i\theta} \Omega^i \\ e^{-i\theta} \Omega^i & \end{pmatrix}.\tag{S28}$$

Here $\sum J^2 = 4\mathbb{1}$, as it represents two copies of a spin-1 fermion. These double spin-1 fermions are also found in previous literature about chiral cubic crystals [S17–S19].

F. Identification of unconventional fermions

The origin of these various types of fermions in lattice systems is from particle physics. Given a relativistic fermion with spin- N , we have a Hamiltonian $H_{\mathbf{k}} = v(\mathbf{k} \cdot \mathbf{J})_{(2N+1) \times (2N+1)}$, with a real coefficient v , and $\mathbf{J} = \{J_x, J_y, J_z\}$ is the $(2N+1)$ dimensional (or spin- N) IR of rotation group $SO(3)$. The energies of the bands are $E_{\mathbf{k}} = vnk$, with $n = -N, -N+1, \dots, N-1, N$. For the n -th band $|n_{\mathbf{k}}\rangle$, the berry curvature can be calculated as

$$\begin{aligned}\mathcal{F}^n(\mathbf{k}) &= -i\epsilon^{ijk} \sum_{m \neq n} \left[\langle \partial_j n_{\mathbf{k}} | m \rangle \langle m | \partial_j n_{\mathbf{k}} \rangle \right] \\ &= -i\epsilon^{ijk} \sum_{m \neq n} \left[\frac{\langle n | \partial_i H | m \rangle \langle m | \partial_j H | n \rangle}{(E_n - E_m)^2} \right],\end{aligned}\tag{S29}$$

whose result can be found by

$$\mathcal{F}^n(\mathbf{k}) = n \frac{\hat{k}}{k^2}.\tag{S30}$$

Then, after integration over the enclosing surface, the Chern number of the n -th band can be found to be $C_n = 2n$, and the monopole charge can be identified as

$$\begin{aligned}
 C_{\text{monopole}} &= \sum_{E_n > 0} C_n \\
 &= \begin{cases} \text{sgn}(v)(N^2 + N) & \text{(integer spin)} \\ \text{sgn}(v)(N + 1/2)^2 & \text{(half integer spin)} \end{cases} \quad (\text{S31})
 \end{aligned}$$

Due to the crystalline symmetry in these solids, the dispersions of these fermions are distorted. However, the Chern numbers of a given band and degeneracy at high symmetry points are unaffected and can be used to identify such fermions. For example, for the 4-fold fermion No. 14 of Table I in the main text, we numerically computed the Chern numbers of the four bands at a tiny sphere around Γ , and we found them to be 3, 1, -1 and -3 (from lower to the higher band). This indicates that the fermion has spin-3/2 with monopole charge -4 . Numerical computation was done with the *WannierTools* package [S27].

G. First-principles calculation of band structures and surface states for $\text{Li}_2\text{Pd}_3\text{B}$ and $\text{Li}_2\text{Pt}_3\text{B}$

All the density functional theory (DFT) [S22] calculations were performed with the *Vienna Ab initio Simulation Package* (VASP) [S23] with the projector-augmented wave method [S24] and the exchange-correlation functional of the Perdew-Berke-Ernzerhof (PBE) form [S25] in the generalized-gradient approximation [S26]. Before we calculated the band structures, the atomic structures of Li_2BPd_3 and Li_2BPt_3 were fully relaxed with the maximum residual force $10^{-4} \text{ eV}\cdot\text{\AA}^{-1}$. The Monkhorst-Pack k-point sampling of $9 \times 9 \times 9$ was adopted for the Brillouin zone integration in the relaxation as well as for the self-consistent calculation. The Wannier tight-binding Hamiltonian was obtained with the *Wannier90* package by projecting the DFT wave functions to the d orbital of Pd(Pt) atoms. We then developed a novel method to get the BdG Hamiltonian by adding the pairing term directly to the Wannier tight binding model under the band basis. For the sake of simplicity, we set the pairing term in the same form for all bands, however, our method could be used in more generalized pairing configurations. With such obtained Wannier tight-binding and BdG Hamiltonians, we were then able to calculate surface spectral functions and topological invariants with the *WannierTools* package [S27].

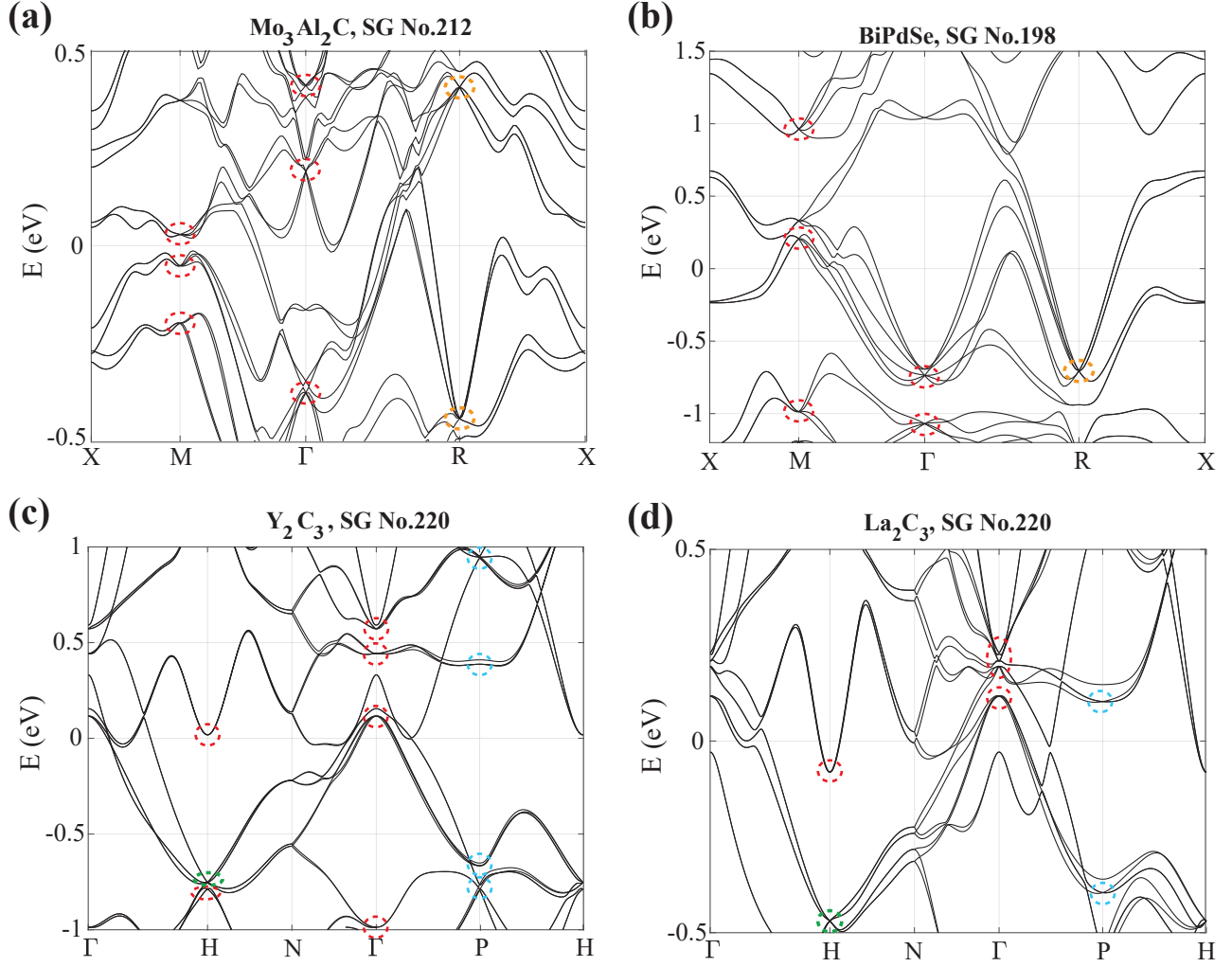


FIG. S2. The first-principles band structure of other multifold fermion superconductors, $\text{Mo}_3\text{Al}_2\text{C}$, BiPdSe , Y_2C_3 and La_2C_3 . The blue, red, orange and green dashed circles highlight the 3-, 4-, 6- and 8-fold fermions, respectively.

H. The first-principles band structure of other superconducting materials with multifold fermions

As mentioned in the main text, we calculated the band structures of superconducting $\text{Mo}_3\text{Al}_2\text{C}$, BiPdSe , Y_2C_3 and La_2C_3 . The results are shown in Fig. S2.

[S1] J. W. F. Venderbos, L. Savary, J. Ruhman, P. A. Lee, and L. Fu, Phys. Rev. X **8**, 11029 (2018).

[S2] M. Sigrist and K. Ueda, Rev. Mod. Phys. **63**, 239 (1991).

[S3] G. E. Volovik, L. P. Gor'kov, Zh. Eksp. Teor. Fiz, 1985, **88**: 1412-1428.

- [S4] K.-W. Lee, and W. E. Pickett, Phys. Rev. B **72**, 174505 (2005).
- [S5] A. Ramires and M. Sigrist, Phys. Rev. B **94**, 104501 (2016)
- [S6] A. Ramires, D. F. Agterberg, M. Sigrist, Phys. Rev. B, **98**, 024501 (2018).
- [S7] P. A. Frigeri, et al, Phys. Rev. Lett. **92**, 097001. (2004)
- [S8] A. P. Schnyder, S. Ryu, A. Furusaki and A.W.W. Ludwig, Phys. Rev. B **78**, 195125 (2008).
- [S9] X.-L. Qi, T. L. Hughes, and S.-C. Zhang, Phys. Rev. B **81**, 134508 (2010).
- [S10] C. Fang, B. A. Bernevig and M. J. Gilbert, Phys. Rev. B, **91**, 165421 (2015).
- [S11] W. Yang, Y. Li, and C. Wu, Phys. Rev. Lett. **117**, 075301 (2016).
- [S12] M. I. Aroyo et al., Bulg. Chem. Commun. **43**(2) 183-197 (2011).
- [S13] M. I. Aroyo et al., Z. Krist. **221**, 1, 15-27 (2006).
- [S14] M. I. Aroyo et al., **A62**, 115-128 (2006).
- [S15] L. Elcoro et al., J. of Appl. Cryst. **50**, 1457-1477 (2017).
- [S16] B. Bradlyn et al., Nature **547**, 298-305 (2017).
- [S17] B. Bradlyn et al., Science **353**, 6299 (2016).
- [S18] P. Tang, Q. Zhou and S. C. Zhang, Phys. Rev. Lett. **119**, 206402 (2017).
- [S19] G. Chang et al., Phys. Rev. Lett. **119**, 206401 (2017).
- [S20] H. Kim et al., Sci. Adv. **4**, 1 (2018).
- [S21] P. M. R. Brydon, L. Wang, M. Weinert and D. F. Agterberg, Phys. Rev. Lett. **116**, 1 (2016).
- [S22] P. Hohenberg, W. Kohn, Phys. Rev. B **136** (3B), B864-B871 (1964).
- [S23] G. Kresse, J. Furthmuller, Comput. Mater. Sci. **6**, 15-50 (1996).
- [S24] P. E. Blöchl, Phys. Rev. B **50**, 17953-17979 (1994).
- [S25] J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. **77**, 3865-3868 (1996).
- [S26] D. C. Langreth, M. J. Mehl, Phys. Rev. B **28**, 1809-1834 (1983).
- [S27] Q. Wu, S. Zhang, H. Song, M. Troyer and Alexey A. Soluyanov, Comp. Phys. Comm. **224**, 405-416 (2018).