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Tri-Dirac surface modes in topological superconductors

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We propose a new type of topological surface modes having cubic dispersion in three-dimensional topological superconductors. Lower order dispersions are prohibited by the threefold rotational symmetry and time-reversal symmetry. Cooper pairing in the bulk changes sign under improper rotations, akin to $^3\text{He-B}$. The surface manifestations are a divergent surface density of states at the Fermi level and isospins that rotate three times as they circle the origin in momentum space. We propose that Heusler alloys with band inversion are candidate materials to harbor the novel topological superconductivity.

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I. INTRODUCTION

Topological superconductors (TSCs) are a novel class of superconductors where Fermi surface topology and unconventional Cooper pairing in the bulk lead to gapless Majorana surface excitations [1]—aptly named [2] as the particle-hole symmetry (PHS) renders their on-site creation and annihilation operators equal. The possibility of finding these new fermions, long sought in high energy physics, in condensed matter systems has excited a wave of interesting studies [3–16].

In three dimensions (3D), TSCs are predicted in doped semiconductors having conduction/valence bands inverted by spin-orbit coupling containing Cooper pairing that is odd under inversion and invariant under time-reversal symmetry (TRS) [7,8,17]. The surface Bogoliubov quasiparticle excitations of these TSCs form linear, spin-split Dirac cones as opposed to the spin-degenerate cones in graphene [3,5,18]. More recently, both theoretical and experimental studies show that crystalline symmetries protect new classes of topological phases. References [19–22] show that mirror reflection symmetry protects gapless excitations in several IV-VI semiconductors and superconductors possessing mirror-odd Cooper pairing. It then follows that a gap may only be opened in the system by spontaneously breaking TRS or by forming a surface topologically ordered state [23,24].

In this paper, we show that the threefold rotation symmetry and TRS can protect an exotic type of surface states in TSCs whose dispersion consists of two cubic-dispersing bands touching each other at $\bar{\Gamma}$ in the surface Brillouin zone (BZ). Lower order dispersions, i.e., linear and quadratic, are excluded by the symmetry group generated by $\{C_3, T\}$, if and only if the doublet at $\bar{\Gamma}$ of the surface BZ has angular momenta $\pm 3/2\hbar$ along the normal direction. The surface density of states (DOS) at the Fermi level diverges due to the cubic dispersion, and by deriving a generic kp model, we see that the spin polarization makes three full rotations as a wave packet traces an isoenergy contour. We then determine the requirement on the bulk superconductivity for these surface modes to appear.

We show that the Fermi level in the bulk must cross bands formed by the $j_z = \pm 3/2$ states ($\hbar \equiv 1$ hereafter), branching from a Γ_8 representation (denoting the four p states with total angular momentum $j = 3/2$ in a spin-orbit split system) on a cubic lattice. This requirement is met in a series of Heusler alloys that are zero gap semiconductors [25–28]. Furthermore, the Cooper pairs are required to transform nontrivially under the cubic symmetry group: they change sign under improper rotations but not under proper ones. We perform a concrete model study of a spin-3/2 Fermi liquid with full $O(3)$ symmetry and TRS, showing its leading instability towards this nontrivial singlet Cooper pairing, induced by screened Coulomb repulsion. The resultant superconductivity is a close analog of the superfluidity in the B phase of ^3He [29,30], but in a Fermi liquid whose constituent particle is spin-3/2. Finally, we discuss experimental signatures that characterize the new TSC.

II. TRI-DIRAC SURFACE STATES

We start by considering a two-band kp theory for the surface states of a TSC, in the Bogoliubov–de Gennes (BdG) form, around $\bar{\Gamma}$ where a doublet of Majorana modes are *assumed* to exist. The symmetries are the TRS (T), PHS (P), and the threefold rotation (C_3). They commute with each other, as they each act on different degrees of freedom: time, charge, and space, respectively. The spin-orbit coupling has broken the $SU(2)$ symmetry of spin rotation so C_3 simultaneously rotates the position and the spin of a particle. For odd-half-integer spins, $C_3^3 = -1$ due to the Berry phase brought by the spin. These constraints result in the following irreducible representations of the group generators (up to an arbitrary unitary transformation):

$$\begin{aligned} E_{1/2} : T &= K(i\sigma_y), & P &= K\sigma_x, & C_3 &= e^{i\sigma_z\pi/3}, \\ E_{3/2} : T &= K(i\sigma_y), & P &= K\sigma_x, & C_3 &= -I_{2\times 2}. \end{aligned} \quad (1)$$

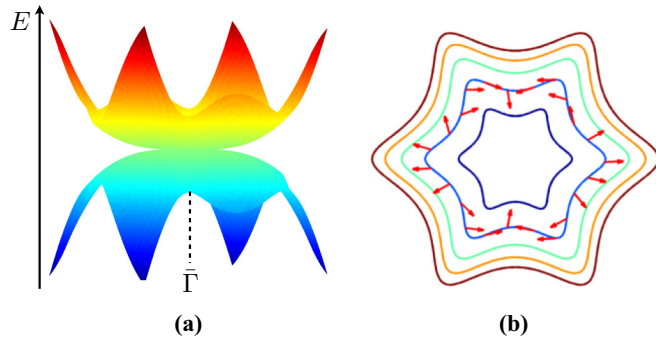


FIG. 1. (Color online) (a) The energy dispersion of the Bogoliubov excitations around a tri-Dirac point. (b) The isoenergy contours and the pseudospin structure of $h_{3/2}(\mathbf{k})$ along the contour taking $c_2 = 2c_3 = 1$.

In Eq. (1), the C_3 -rotation operator is $\exp(i\hat{j}_z \frac{2\pi}{3})$ with $\hat{j}_z = \sigma_z/2$ ($\hat{j}_z = 3\sigma_z/2$) for the $E_{1/2}$ ($E_{3/2}$). The kp Hamiltonian, $h(\mathbf{k})$, must satisfy the following symmetry constraints:

$$\begin{aligned} Th(\mathbf{k})T^{-1} &= h(-\mathbf{k}), \\ Ph(\mathbf{k})P^{-1} &= -h(-\mathbf{k}), \\ C_3h(k_+, k_-)C_3^{-1} &= h(k_+e^{i2\pi/3}, k_-e^{-i2\pi/3}), \end{aligned} \quad (2)$$

where $k_{\pm} = k_x \pm ik_y$. Using Eqs. (1) and (2), we obtain

$$\begin{aligned} h_{1/2}(\mathbf{k}) &= \text{Re}[c_1k_+] \sigma_x + \text{Im}[c_1k_+] \sigma_y, \\ h_{3/2}(\mathbf{k}) &= \text{Re}[c_2k_+^3 + c_3k_-^3] \sigma_x + \text{Im}[c_2k_+^3 + c_3k_-^3] \sigma_y, \end{aligned} \quad (3)$$

where $c_{1,2}$ are complex numbers that are material dependent. Hence, we find that while the dispersion of $h_{1/2}$ is linear around $\mathbf{k} = 0$, the dispersion of $h_{3/2}$ is cubic [see Fig. 1(a)], $E_{3/2}(\mathbf{k}) = |c_2k_+^3 + c_3k_-^3|$ without lower order terms. This can be understood by examining the continuum limit of C_{∞} symmetry: a hopping from a state of $j_z = \pm 3/2$ to $j_z = \mp 3/2$ changes the total angular momentum by ∓ 3 , so, in order to preserve rotation symmetry, this hopping should be ‘‘balanced’’ by an orbital contribution of k_{\pm}^3 .

The wave function of $h_{3/2}(\mathbf{k})$ in Eq. (3) is described by the pseudospin structure at each \mathbf{k} . The pseudospin up (down) states correspond to the first (second) basis vector in the kp model, i.e., the two degenerate states at $\mathbf{k} = 0$. The pseudospin at any \mathbf{k} is then given by a unit vector in the xy plane, as is guaranteed by PHS, whose two components are $(S_x, S_y) = (\text{Re}[c_2k_+^3 + c_3k_-^3]/|c_2k_+^3 + c_3k_-^3|, \text{Im}[c_2k_+^3 + c_3k_-^3]/|c_2k_+^3 + c_3k_-^3|)$. As the momentum makes a full clockwise (counterclockwise) rotation enclosing the origin, the pseudospin completes three full commensurate rotations if $|c_2| > |c_3|$ (counterclockwise if $|c_2| < |c_3|$) [see Fig. 1(b)]. We denote the degeneracy point at $h_{3/2}(\mathbf{k})$ in Eq. (3) at $\mathbf{k} = 0$ as the *tri-Dirac point* (TDP), as the evolution of the wave function around is topologically equivalent to that around three Dirac points, resulting in a total winding number of ± 3 . While a generic band crossing with linear dispersion (Dirac point) has vanishing DOS, the DOS at a TDP is divergent, given by $\rho(E) = \frac{1}{2} \int \delta[E_{3/2}(\mathbf{k}) - E] d\mathbf{k}^2 \propto E^{-1/3}$, where the prefactor $1/2$ results from each excitation close to the Fermi

level being roughly an equal weight linear superposition of electron and hole states.

One may naturally infer from the divergence of DOS at the band touching that the residual interaction between Bogoliubov excitations may be relevant and open a gap in the spectrum. As the surface states are of Majorana character, they contain two species of Bogoliubov excitations, namely, $\gamma_{1,2}(\mathbf{k})$, satisfying $\gamma_i(\mathbf{k}) = \gamma_i^\dagger(-\mathbf{k})$ in \mathbf{k} space, or $\gamma_i(\mathbf{r}) = \gamma_i^\dagger(\mathbf{r})$ as a real field in real space. The interaction hence must contain at least two spatial derivatives, such as $-g\gamma_1(\mathbf{r})\gamma_2(\mathbf{r})\nabla\gamma_1(\mathbf{r}) \cdot \nabla\gamma_2(\mathbf{r})$. Simple dimension counting shows that coupling constant g is irrelevant, meaning that it flows to zero under renormalization towards the long wavelength limit. Thus, the surface states of a tri-Dirac cone are robust against weak residual interactions between quasiparticles.

III. TOPOLOGICAL SUPERCONDUCTIVITY IN THE BULK

With the nature of the surface states understood, we now seek the form of the bulk superconductivity that gives rise to these surface states. As the TDP derives its protection from both C_3 symmetry and TRS, it may only appear on terminations that preserve both these symmetries, namely, the $\bar{\Gamma}$ point, in the surface BZ. Other C_3 -invariant points \bar{K} and \bar{K}' which are invariant under $C_2 * T$ do not have degeneracy because $(C_2 * T)^2 = +1$. Further, we need a pair of Majorana modes at $\bar{\Gamma}$, which depend on band structure along the line, parametrized by k_z , in the 3D BZ that projects onto $\bar{\Gamma}$. In the weak-coupling limit, the topology of this line depends on the signs of pairing amplitude at the Fermi points where the line crosses the Fermi surface: it is nontrivial/trivial if there are an odd/even number of Fermi points that have *negative* pairing signs in the region $k_z > 0$. Finally, the Majorana modes need to have angular momenta $\pm 3/2$. In the weak-coupling limit, the surface Bogoliubov excitations are linear combinations of particle and hole states on the Fermi surface in the bulk, so we need the Fermi level to cross bulk bands that have angular momenta $\pm 3/2$. In many Heusler alloys, the (111) terminations are C_3 symmetric; the Fermi level is at the Γ_8 representation, branching into two sets of doublet bands having angular momenta $\pm 3/2$ (the conduction band) and $\pm 1/2$ (the valence band) along ΓL from Γ , respectively [27]. In thin-film samples, chemical doping may be utilized [31] to tune the chemical potential into the $j_z = \pm 3/2$ bands in this system. The next question is, what interaction induces a Cooper pairing that changes sign between the two bands having $|j_z| = 3/2$? As the Fermi level is close to the Γ_8 representation, it is reasonable to consider a continuum model with TRS and a full $O(3)$ symmetry group, of which the point groups of half Heusler (T_d) and full Heusler alloys (O_h) are subgroups. The surface states obtained in this symmetry-enhanced model would certainly change as $O(3)$ breaks down to T_d or O_h , but the TDP on the surface would not be broken because only C_3 and TRS are needed for its protection. The normal-state Hamiltonian for a Fermi gas having $O(3)$ and TRS around Γ_8 representation is given by the following four-band kp model

$$H_0(\mathbf{k}) = (\lambda_1 + \frac{5}{2}\lambda_2)k^2 - 2\lambda_2(\mathbf{k} \cdot \mathbf{S})^2 - \mu, \quad (4)$$

where $\lambda_{1,2}$ are Luttinger parameters [e.g., $(\lambda_1, \lambda_2) \sim (-2.5, -3.8)2m_e/\hbar^2$ in ScPtBi [27]] and $\mathbf{S} = (S_x, S_y, S_z)$ are the spin operators of a spin-3/2 fermion, physically realized by spin-orbit splitting of the p orbitals. The isotropic dispersion of $H_0(\mathbf{k})$ is given by $\epsilon_{1/2,3/2}(\mathbf{k}) = (\lambda_1 \pm 2\lambda_2)k^2 - \mu$, where both bands are doubly degenerate. The general form of short-range density interaction is $\hat{V} = \sum_{\mathbf{q}} V(|\mathbf{q}|)n(\mathbf{q})n(-\mathbf{q})$, where $n(\mathbf{q})$ is the Fourier transform of local density operator and $V(|\mathbf{q}|) = V_0 - V_2q^2 + O(q^4)$ is the Fourier transform of the interaction in the long wavelength limit ($k_F \ll 1$). For a screened Coulomb repulsion $V(r) = \frac{e^2}{r}e^{-r/r_0}$, $V_0 = e^2r_0^2$, and $V_2 = e^2r_0^4$, where r_0 is the screening length. Decomposing the interaction into various channels of instability, we have (modulo nonsuperconducting channels)

$$\hat{V} = V_0 \left| \sum_{\mathbf{k}, m, m'} \left(1 - \frac{V_2}{V_0}k^2\right) b_{mm'}(\mathbf{k}) \right|^2 - 2V_2 \sum_{\mathbf{k}_1, \mathbf{k}_2, m, m'} \mathbf{k}_1 \cdot \mathbf{k}_2 b_{mm'}^\dagger(\mathbf{k}_1) b_{mm'}(\mathbf{k}_2), \quad (5)$$

where $b_{mm'}(\mathbf{k}) = c_m(\mathbf{k})c_{m'}(-\mathbf{k})$ is the electron pair operator and the spin index m runs in $(-3/2, -1/2, 1/2, 3/2)$. All pairing channels decompose into squares of irreducible representations of SO(3), a process which we briefly sketch before providing detailed derivation. Generally, a Cooper pair of zero momentum is determined by the total spin of the constituent electrons, \mathbf{S} , and the angular momentum describing the relative motion between them, \mathbf{L} . In the presence of spin-orbit coupling (SOC), the conserved quantities are S^2 , L^2 , J^2 , and J_z , where \mathbf{J} is the total angular momentum of the pair, or, $\mathbf{J} = \mathbf{L} + \mathbf{S}$. The order parameters are denoted by three quantum numbers (L, S, J) , and the ground state is $(2J + 1)$ -fold degenerate.

Formally, a general pairing operator of zero total momentum is represented by

$$\hat{\Delta}^{mm'} = \sum_{\mathbf{k}} f(\mathbf{k})c_m(\mathbf{k})c_{m'}(-\mathbf{k}). \quad (6)$$

In a system with symmetry, it is necessary to decompose $\hat{\Delta}^{mm'}$ into irreducible representations of the symmetry group. For SO(3), the procedure goes as follows: (i) The orbital part, $f(\mathbf{k})$, can be expanded in terms of irreducible representations in the function space:

$$f(\mathbf{k}) = \sum_{L, M} f_{LM}(k^2)Y_L^M(\hat{\mathbf{k}}), \quad (7)$$

where $Y_L^M(\hat{\mathbf{k}})$'s are spherical harmonics and $f_{LM}(k^2)$ is a complex function depending only on the radius of \mathbf{k} . (ii) The spin part $b_{mm'}(\mathbf{k}) = c_m(\mathbf{k})c_{m'}(-\mathbf{k})$ decomposes into irreducible representations in the spin space:

$$b_{mm'}(\mathbf{k}) = \sum_{S, S_z} \langle s, s; S, S_z | s, s; m, m' \rangle \hat{\delta}_{SS}^{S_z}(\mathbf{k}), \quad (8)$$

where $\hat{\delta}_{SS}^{S_z}$ is a pair operator annihilating a pair of electrons of total spin S and total spin along z axis S_z , at $\pm\mathbf{k}$. $\hat{\delta}_{SS}^{S_z}(\mathbf{k})$ is even/odd in \mathbf{k} if and only if $S = \text{even/odd}$, due to Fermi statistics. (In our case, there is $s = 3/2$, $m, m' = -3/2, -1/2, 1/2, 3/2$, $S = 0, 1, 2, 3$, and $S_z = -S, -S + 1, \dots, S$) (iii) Then we decompose the product of two irreducible

representations in the orbital part and the spin part into irreducible representations of fixed total angular momentum and total angular momentum along the z axis:

$$\begin{aligned} \sum_{\hat{\mathbf{k}}} Y_L^M(\hat{\mathbf{k}}) \hat{\delta}_{SS}^{S_z}(\mathbf{k}) \\ = \sum_{J=|L-S|, \dots, L+S, J_z=-J, \dots, +J} \langle L, S; J, J_z | L, S; M, S_z \rangle \\ \times \delta(J_z - M - S_z) \hat{\Delta}_{LSJ}^{J_z}(k^2), \end{aligned} \quad (9)$$

where

$$\hat{\Delta}_{LSJ}^{J_z}(k^2) \equiv \sum_{M', S'_z} \sum_{\hat{\mathbf{k}}} \langle L, S; M', S'_z | L, S; J, J_z \rangle Y_L^{M'}(\hat{\mathbf{k}}) \hat{\delta}_{SS}^{S'_z}(\mathbf{k}) \quad (10)$$

is the Cooper pair operator with total angular momentum J and total angular momentum along z axis J_z . The δ function in Eq. (9) is written down explicitly only to show the conservation of total angular momentum—it is already in the definition of the Clebsch-Gordan coefficients. Using Eqs. (8)–(10), we obtain

$$\begin{aligned} \sum_{\hat{\mathbf{k}}} Y_L^M(\hat{\mathbf{k}}) b_{mm'}(\mathbf{k}) = \sum_{S, J, J_z, S_z} \langle L, S; J, J_z | L, S; M, S_z \rangle \\ \times \langle s, s; S, S_z | s, s; m, m' \rangle \hat{\Delta}_{LSJ}^{J_z}(k^2). \end{aligned} \quad (11)$$

Since $Y_L^M(\hat{\mathbf{k}})$ is odd/even in \mathbf{k} when $L = \text{odd/even}$, and $\hat{\delta}_{SS}^{S_z}(\mathbf{k})$ is odd/even in \mathbf{k} when $S = \text{odd/even}$, L and S must have the same parity, or $\hat{\Delta}_{LSJ}$ vanishes.

In this system where electrons are spin-3/2, the total spin is $S = 0, 1, 2, 3$ and the orbital angular momentum $L = 0, 1$ as a pairing order parameter for $L \geq 2$ is at least quadratic in k from decoupling a quartic term in the expansion of $V(q)$. As a result, the possible pairings are $(L, S, J) = (0, 0, 0)$, $(1, 1, 0)$, $(1, 1, 1)$, $(0, 2, 2)$, $(1, 1, 2)$, $(1, 3, 2)$, $(1, 3, 3)$, and $(1, 3, 4)$. $(L, S, J) = (0, 0, 0)$ corresponds to the normal s -wave pairing and is invariant under all symmetry operations; $(L, S, J) = (1, 1, 0)$ pairing is analogous to the pairing in the B phase of ^3He , invariant under all proper rotations but changes sign under improper ones (parity odd) [8, 32]. While we cannot determine the complete phase diagram with all types of instabilities, we note that all pairings with $J > 0$ are nodal (assuming that the FS encloses Γ) and are generally less energetically favorable than full gaps, if they are induced from the same channel of instability. We note that it is purely due to SOC that a pairing with nonzero orbital angular momentum ($L \neq 0$) is consistent with a full gap. In a non-SOC system, any two-electron bound state with $L \neq 0$ must be degenerate, while SOC allows two electrons to form a unique bound state with $L = 1$, by aligning the total spin and the orbital angular momentum oppositely. Thus, we restrict the discussion to the two singlet pairings:

$$\hat{V} \approx \frac{|\hat{\Delta}_{000}|^2}{V_0} - \frac{2|\hat{\Delta}_{110}|^2}{3V_2}, \quad (12)$$

in which

$$\begin{aligned} \frac{\hat{\Delta}_{000}}{V_0} &\equiv \sum_{\mathbf{k}, m, m'} \left(1 - \frac{V_0}{V_2} k^2\right) \\ &\times \langle 3/2, 3/2; m, m' | 3/2, 3/2; 0, 0 \rangle b_{mm'}(\mathbf{k}), \\ \frac{\hat{\Delta}_{110}}{V_2} &\equiv \sum_{\mathbf{k}, M, S_z, m, m'} k^{(M)} \langle 1, 1; M, S_z | 1, 1; 0, 0 \rangle \\ &\times \langle 3/2, 3/2; m, m' | 3/2, 3/2; 1, S_z \rangle b_{mm'}(\mathbf{k}), \end{aligned} \quad (13)$$

where $k^{(\pm 1)} \equiv \mp \sqrt{3/2} k_{\pm}$, $k^{(0)} \equiv \sqrt{3} k_z$, and $\langle j_1, j_2; m_1, m_2 | j_1, j_2; J, M \rangle$'s are the Clebsch-Gordan coefficients, expanding the eigenstate of total angular momentum $|J, M\rangle$ in the product basis of $|j_1, m_1\rangle \otimes |j_2, m_2\rangle$. The derivation of Eq. (12) is given in Appendix A. The relative sign between the two terms in Eq. (12) is because the attraction (repulsion) favors the parity even (odd) pairs where the wave functions of the two electrons have greater (smaller) overlap in real space. The interaction leads to spontaneous superconducting ordering of $\hat{\Delta}_{000}$ and $\hat{\Delta}_{110}$ if $V_0 < 0$ (e.g., BCS attraction) and $V_2 > 0$ (e.g., screened Coulomb repulsion), respectively.

A standard mean-field calculation (see Appendix B) shows that when $V_0 < 0$, $T_e > T_o$, where $T_{e/o}$ are transition temperatures for even/odd parity superconductivity, meaning that as long as V_0 is attractive, the conventional s -wave pairing is energetically favored. The odd parity pairing is energetically favored if $V_0, V_2 > 0$; in other words, the interaction is repulsive. Here the Δ_{000} channel becomes attractive for $k > V_0/V_2$, as we did not keep higher order terms in the expansion of $V(|\mathbf{q}|)$. Generally, a repulsive screened Coulomb potential disfavors pairs of zero angular momentum. Additionally, we remark that while our truncation of $V(|\mathbf{q}|)$ cannot be rigorously justified, this is a simple way to obtain an attractive channel with $L > 0$, and a more serious treatment requires re-deriving the Kohn-Luttinger theorem for a Fermi surface with strong SOC near Γ_8 .

IV. THREE TOPOLOGICAL SUPERCONDUCTING PHASES

When the $(L, S, J) = (1, 1, 0)$ phase is favored, there are three possible scenarios (see Fig. 2), in which the Fermi level crosses: (i) the $E_{1/2}$ bands, (ii) the $E_{3/2}$ bands, and (iii) all four Γ_8 bands. In case (i), there is a Dirac point at the $\bar{\Gamma}$ with linear dispersion at its vicinity; in case (ii), the Dirac point is replaced by a TDP, having cubic dispersion and divergent DOS; in case (iii), there are two doublets at Γ , having angular momentum $j_z = \pm 1/2$ and $j_z = \pm 3/2$, respectively. This is the first example where two surface Dirac cones are pinned to the same point in a superconductor, thus deserving additional discussion. The two doublets are forbidden to hybridize and open a gap at $\bar{\Gamma}$ due to the rotation symmetry. We choose the basis such that

$$j_z = \begin{pmatrix} \frac{1}{2} & 0 & 0 & 0 \\ 0 & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & \frac{3}{2} & 0 \\ 0 & 0 & 0 & -\frac{3}{2} \end{pmatrix}, \quad (14)$$

$$T = K \sigma_y \oplus \sigma_y. \quad (15)$$

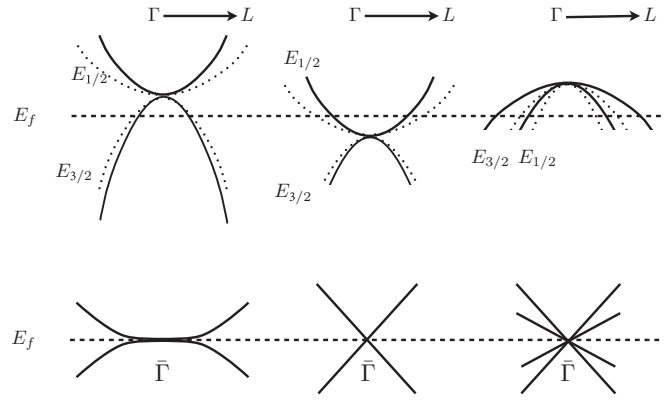


FIG. 2. Three possible scenarios for the Fermi level crossing the bulk Γ_8 bands and the schematic dispersions of the surface states [from left to right: case (ii), (i), and (iii)]. Solid and dotted lines mean that the corresponding band has positive and negative pairing amplitude, respectively, in the nontrivial superconducting phase. See Ref. [41] for a discussion of the case of degenerate bands in the presence of inversion.

Note that this choice is valid since $\sigma_y \oplus \sigma_y$ is antisymmetric so $T^2 = -1$ as required for fermions. Symmetry requires that

$$\begin{aligned} e^{ij_z \theta} H_{\text{eff}}(k_+, k_-) e^{-ij_z \theta} &= H_{\text{eff}}(k_+ e^{i\theta}, k_- e^{-i\theta}), \\ T H_{\text{eff}}(\mathbf{k}) T^{-1} &= H_{\text{eff}}(-\mathbf{k}). \end{aligned} \quad (16)$$

To the first order in \mathbf{k} , the Hamiltonian is in the following general form:

$$H_{\text{eff}}(\mathbf{k}) = \begin{pmatrix} 0 & c_1 k_- & c_2 k_+ & 0 \\ c_1^* k_+ & 0 & 0 & -c_2^* k_- \\ c_2^* k_- & 0 & 0 & 0 \\ 0 & -c_2 k_+ & 0 & 0 \end{pmatrix}, \quad (17)$$

whose dispersion can be solved as

$$E = \pm \sqrt{|c_1|^2 + 2|c_2|^2 \pm |c_1| \sqrt{|c_1|^2 + 4|c_2|^2} k} / \sqrt{2}. \quad (18)$$

All four bands are linear in \mathbf{k} . As we claim above, on the surface there are two Dirac cones pinned to the same time-reversal invariant momentum.

It is interesting to consider the Z index of the class DIII superconductors for these cases and one obtains ± 1 , ± 3 , and ± 2 . In the first two cases the Chern numbers of the Fermi surface (FS) associated with the $E_{1/2, 3/2}$ bands are ± 1 and ± 3 . Therefore if the sign of pairing changes between its two pieces, we have $z = \pm 1$, ± 3 , respectively [9]. For case (iii), there are a pair of sign-changing $E_{1/2}$ -FS and another of sign-changing $E_{3/2}$ -FS, thus we can have either ± 2 or ± 4 . An expansion of $\hat{\Delta}_{110}$ in Eq. (13) shows a relative minus sign between the pairing on $E_{1/2}$ and $E_{3/2}$ bands, leaving ± 2 the only possibility. Therefore, only in case (ii) does the phase exhibit protected tri-Dirac surface states with cubic dispersion. To realize this scenario, the conduction and the valence bands, which touch at Γ due to the point group symmetry, must bend oppositely, making the normal state a doped zero gap semiconductor. Heusler alloys offer a wide spectrum of zero gap semiconductors, where SOC

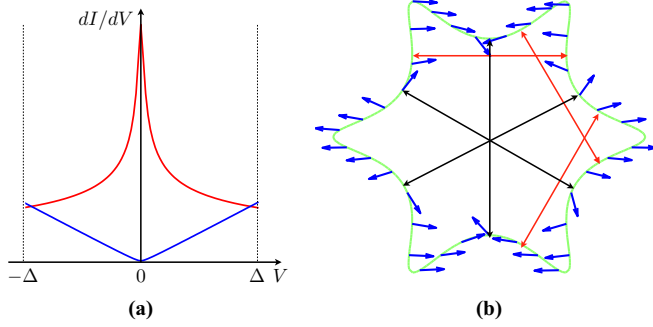


FIG. 3. (Color online) (a) Schematic plot of the differential conductance on the surface of TSCs with Dirac (blue) and tri-Dirac surface states inside the bulk superconducting gap. (b) Typical symmetry-forbidden scattering vectors on the isoenergy contour of the tri-Dirac surface states. Black arrows indicate scattering vectors forbidden by TRS, and red arrows are vectors strongly suppressed due to the special pseudospin structure of tri-Dirac surface states, also plotted on the contour.

is stronger than hybridization [27,33,34]. When hole doped, these materials have Fermi level in the $E_{3/2}$ bands. As we adopt the most general form of short-range electron interaction in the long wavelength limit (small $|\mathbf{q}|$), our results suggest that superconducting Heusler alloys such as YPtBi [28] and LaPtBi [25] be candidate materials.

V. EXPERIMENTAL PREDICTIONS

Experimentally, the new TSCs can be identified by measuring its surface DOS using scanning tunneling microscopy [35]. The dI/dV curve diverges as $dI/dV \propto V^{-1/3}$ in the vicinity, as opposed to $dI/dV \propto V$ in TSCs with simple Dirac surface states [see Fig. 3(a)]. Quasiparticle interference on the surface can be used to verify the pseudospin structure [36,37]. The

isoenergy contour is generically a hexagram even at low energy, similar to the contour in the surface states of the Bi_2Te_3 topological insulator away from the linear Dirac regime. In the latter, the strongest peaks in quasiparticle interference result from scattering between states having opposite velocity and not related by TRS. On a hexagram contour, the two momenta of the interfering states make an angle of $\sim 60^\circ$. However, for the tri-Dirac surface states, these scattering channels are strongly suppressed, because the pseudospins are exactly opposite to each other between states related by a 60° rotation, a signature of the new topological surface states.

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APPENDIX A: DECOMPOSITION OF THE INTERACTION

With the technique developed in the text, we can now decompose the pairing channels in the interaction into pairings that are irreducible representations of $\text{SO}(3)$. Here we only consider an isotropic interaction expanded to the second order in the momentum space as shown in Eq. (12).

1. The first term in Eq. (5)

Following the procedure, we rewrite $\sum_{\mathbf{k}} b_{mm'}(\mathbf{k})$ as

$$\begin{aligned} & \sum_{\mathbf{k}} \sum_{S, S_z} Y_0^0(\hat{\mathbf{k}}) \langle 3/2, 3/2; S, S_z | 3/2, 3/2; m, m' \rangle \hat{\delta}_{\frac{3}{2}, \frac{3}{2}}^{S_z}(\mathbf{k}) \\ &= \sum_{\mathbf{k}} Y_0^0(\hat{\mathbf{k}}) \left[\langle 3/2, 3/2; 0, 0 | 3/2, 3/2; m, m' \rangle \hat{\delta}_{\frac{3}{2}, \frac{3}{2}}^0(\mathbf{k}) + \sum_{S_z=-2, \dots, +2} \langle 3/2, 3/2; 2, S_z | 3/2, 3/2; m, m' \rangle \hat{\delta}_{\frac{3}{2}, \frac{3}{2}}^{S_z}(\mathbf{k}) \right] \\ &= \langle 3/2, 3/2; 0, 0 | 3/2, 3/2; m, m' \rangle \hat{\Delta}_{000}^0(k^2) + \sum_{J_z=-2, \dots, +2} \langle 3/2, 3/2; 2, S_z | 3/2, 3/2; m, m' \rangle \hat{\Delta}_{022}^{J_z}(k^2), \end{aligned} \quad (\text{A1})$$

where only $J = \text{even}$ terms are included as $J = \text{odd}$ terms vanish by Fermi statistics.

The first term in Eq. (5) can thus be put in the form

$$\sum_{m, m'} \left| \sum_{\mathbf{k}} \left(1 - \frac{V_2 k^2}{V_0} \right) b_{mm'}(\mathbf{k}) \right|^2 = V_0 \sum_{S=0, 2; J_z=-S, \dots, S} \left| \sum_{\mathbf{k}} \left(1 - \frac{V_2 k^2}{V_0} \right) \hat{\Delta}_{0SS}^{J_z}(k^2) \right|^2. \quad (\text{A2})$$

Then after defining

$$\hat{\Delta}_{000} = \sum_{\mathbf{k}} \left(1 - \frac{V_2 k^2}{V_0} \right) \hat{\Delta}_{000}^0(k^2) / V_0, \quad \hat{\Delta}_{022}^{J_z} = \sum_{\mathbf{k}} \left(1 - \frac{V_2 k^2}{V_0} \right) \hat{\Delta}_{022}^{J_z}(k^2) / V_0, \quad (\text{A3})$$

we have decomposed the first term in Eq. (5) into irreducible representations of SO(3):

$$\sum_{mm'} \left| \sum_{\mathbf{k}} b_{mm'}(\mathbf{k}) \right|^2 = \left(|\hat{\Delta}_{000}|^2 + \sum_{J_z=-2,\dots,2} |\hat{\Delta}_{022}^{J_z}|^2 \right) / V_0. \quad (\text{A4})$$

2. The second term in Eq. (5)

The second term in Eq. (5) can be rewritten as

$$-2V_2 \sum_{\mathbf{k}_1, \mathbf{k}_2, m, m'} \mathbf{k}_1 \cdot \mathbf{k}_2 b_{mm'}(\mathbf{k}_1) b_{mm'}^\dagger(\mathbf{k}_2) = -\frac{2V_2}{3} \sum_{M, m, m'} \left| \sum_{\mathbf{k}} k Y_1^M(\hat{\mathbf{k}}) b_{mm'}(\mathbf{k}) \right|^2. \quad (\text{A5})$$

From Eq. (11), we have

$$\sum_{\hat{\mathbf{k}}} Y_1^M(\hat{\mathbf{k}}) b_{mm'}(\mathbf{k}) = \sum_{S, S_z, J, J_z, M} \langle 1, S; J, J_z | 1, S; M, S_z \rangle \langle 3/2, 3/2; S, S_z | 3/2, 3/2; m, m' \rangle \hat{\Delta}_{1S J}^{J_z}(k^2). \quad (\text{A6})$$

Using the normalization conditions

$$\begin{aligned} \sum_{m, m'} \langle 3/2, 3/2; S, S_z | 3/2, 3/2; m, m' \rangle \langle 3/2, 3/2; m, m' | 3/2, 3/2; S', S'_z \rangle &= \delta_{SS'} \delta_{S_z S'_z}, \\ \sum_{M, S_z} \langle 1, S; J, J_z | 1, S; M, S_z \rangle \langle 1, S; M, S_z | 1, S; J', J'_z \rangle &= \delta_{JJ'} \delta_{J_z J'_z}, \end{aligned} \quad (\text{A7})$$

we obtain

$$\sum_{M, m, m'} \left| \sum_{\mathbf{k}} k_1 k_2 Y_1^M(\hat{\mathbf{k}}) b_{mm'}(\mathbf{k}) \right|^2 = \sum_{S, J, J_z} \sum_{k_1, k_2} k_1 k_2 \hat{\Delta}_{1S J}^{J_z}(k_1) \hat{\Delta}_{1S J}^{J_z \dagger}(k_2) = \sum_{S, J, J_z} \left| \sum_k k \hat{\Delta}_{1S J}^{J_z}(k) \right|^2. \quad (\text{A8})$$

Defining

$$\Delta_{1S J}^{J_z} = \sum_k k \hat{\Delta}_{1S J}^{J_z}(k) / V_2, \quad (\text{A9})$$

we have

$$-2V_2 \sum_{\mathbf{k}_1, \mathbf{k}_2, m, m'} \mathbf{k}_1 \cdot \mathbf{k}_2 b_{mm'}(\mathbf{k}_1) b_{mm'}^\dagger(\mathbf{k}_2) = -\frac{2}{3V_2} \sum_{S=1,3, J=|S-1|, \dots, |S+1|, J_z} |\Delta_{1S J}^{J_z}|^2. \quad (\text{A10})$$

APPENDIX B: PHASE DIAGRAM OF THE SUPERCONDUCTING PHASES

We use mean-field approximation to obtain the BdG Hamiltonian, and use that to calculate the free energy and hence the phase diagram. The interaction in Eq. (12) is mean-field decoupled as

$$\begin{aligned} \frac{|\hat{\Delta}_{000}|^2}{V_0} - \frac{2|\hat{\Delta}_{110}|^2}{3V_2} &= \frac{\hat{\Delta}_{000}^\dagger \langle \hat{\Delta}_{000} \rangle + \text{H.c.}}{V_0} - \frac{2(\hat{\Delta}_{110}^\dagger \langle \hat{\Delta}_{110} \rangle + \text{H.c.})}{3V_2} + \frac{2|\langle \hat{\Delta}_{000} \rangle|^2}{3V_2} - \frac{|\langle \hat{\Delta}_{110} \rangle|^2}{V_0} \\ &+ \frac{|\hat{\Delta}_{000} - \langle \hat{\Delta}_{000} \rangle|^2}{V_0} - \frac{2|\hat{\Delta}_{110} - \langle \hat{\Delta}_{110} \rangle|^2}{3V_2}. \end{aligned} \quad (\text{B1})$$

The mean-field decoupled BdG Hamiltonian is obtained by ignoring the last term of fluctuation:

$$\hat{H}_{\text{BdG}} = \sum_{\mathbf{k} \in \text{BZ}} c^\dagger(\mathbf{k}) H_0(\mathbf{k}) c(\mathbf{k}) - \frac{2\Delta_o \hat{\Delta}_{110}^\dagger}{3V_2} + \frac{\Delta_e \hat{\Delta}_{000}^\dagger}{V_0} + \text{H.c.} + \frac{2|\Delta_o|^2}{3V_2} + \frac{|\Delta_e|^2}{-V_0},$$

where we have defined $\Delta_e \equiv \langle \hat{\Delta}_{000} \rangle$ and $\Delta_o \equiv \langle \hat{\Delta}_{110} \rangle$. The dispersion of the BdG Hamiltonian is very easy to solve by utilizing SO(3) symmetry. Due to the symmetry, the dispersion must be isotropic, and we hence only need to solve it at $\mathbf{k} = (0, 0, k)$. Writing \hat{H}_{BdG} in Nambu basis

$$\psi(\mathbf{k}) \equiv [c_{3/2}(\mathbf{k}), c_{1/2}(\mathbf{k}), c_{-1/2}(\mathbf{k}), c_{-3/2}(\mathbf{k}), c_{3/2}^\dagger(-\mathbf{k}), c_{1/2}^\dagger(-\mathbf{k}), c_{-1/2}^\dagger(-\mathbf{k}), c_{-3/2}^\dagger(-\mathbf{k})]^T, \quad (\text{B2})$$

we have

$$\begin{aligned}
 H_{\text{BdG}}^o[\mathbf{k} = (0,0,k)] &= \psi^\dagger(\mathbf{k}) \begin{pmatrix} \epsilon_{3/2}(k) & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{\Delta_o k}{\sqrt{5}} \\ 0 & \epsilon_{1/2}(k) & 0 & 0 & 0 & 0 & \frac{\Delta_o k}{\sqrt{45}} & 0 \\ 0 & 0 & \epsilon_{1/2}(k) & 0 & 0 & \frac{\Delta_o k}{\sqrt{45}} & 0 & 0 \\ 0 & 0 & 0 & \epsilon_{3/2}(k) & -\frac{\Delta_o k}{\sqrt{5}} & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{\Delta_o k}{\sqrt{5}} & -\epsilon_{3/2}(k) & 0 & 0 & 0 \\ 0 & 0 & \frac{\Delta_o k}{\sqrt{45}} & 0 & 0 & -\epsilon_{1/2}(k) & 0 & 0 \\ 0 & \frac{\Delta_o k}{\sqrt{45}} & 0 & 0 & 0 & 0 & -\epsilon_{1/2}(k) & 0 \\ -\frac{\Delta_o k}{\sqrt{5}} & 0 & 0 & 0 & 0 & 0 & 0 & -\epsilon_{3/2}(k) \end{pmatrix} \psi(\mathbf{k}), \\
 H_{\text{BdG}}^e[\mathbf{k} = (0,0,k)] &= \psi^\dagger(\mathbf{k}) \begin{pmatrix} \epsilon_{3/2}(k) & 0 & 0 & 0 & 0 & 0 & 0 & \frac{\Delta_e(1-\frac{v_2 k^2}{V_0})}{2} \\ 0 & \epsilon_{1/2}(k) & 0 & 0 & 0 & 0 & -\frac{\Delta_e(1-\frac{v_2 k^2}{V_0})}{2} & 0 \\ 0 & 0 & \epsilon_{1/2}(k) & 0 & 0 & \frac{\Delta_e(1-\frac{v_2 k^2}{V_0})}{2} & 0 & 0 \\ 0 & 0 & 0 & \epsilon_{3/2}(k) & -\frac{\Delta_e(1-\frac{v_2 k^2}{V_0})}{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{\Delta_e(1-\frac{v_2 k^2}{V_0})}{2} & -\epsilon_{3/2}(k) & 0 & 0 & 0 \\ 0 & 0 & \frac{\Delta_e(1-\frac{v_2 k^2}{V_0})}{2} & 0 & 0 & -\epsilon_{1/2}(k) & 0 & 0 \\ 0 & -\frac{\Delta_e(1-\frac{v_2 k^2}{V_0})}{2} & 0 & 0 & 0 & 0 & -\epsilon_{1/2}(k) & 0 \\ \frac{\Delta_e(1-\frac{v_2 k^2}{V_0})}{2} & 0 & 0 & 0 & 0 & 0 & 0 & -\epsilon_{3/2}(k) \end{pmatrix} \psi(\mathbf{k}). \tag{B3}
 \end{aligned}$$

The mean-field transition temperatures are determined by the following gap equations:

$$\frac{1}{-V_0} = \sum_{n=1/2,3/2} \int_0^\Lambda \frac{k^2 dk}{2\pi^2} \tanh \frac{|\epsilon_n(k)|}{2T_e} \frac{\partial^2 E_n^e(k)}{\partial \Delta_e^2} \Big|_{\Delta_e=0}, \quad \frac{1}{3V_2/2} = \sum_{n=1/2,3/2} \int_0^\Lambda \frac{k^2 dk}{2\pi^2} \tanh \frac{|\epsilon_n(k)|}{2T_o} \frac{\partial^2 E_n^o(k)}{\partial \Delta_o^2} \Big|_{\Delta_o=0}, \tag{B4}$$

where

$$E_n^e(k) = \sqrt{\epsilon_n^2(k) + \Delta_e^2 \left(1 - \frac{V_2 k^2}{V_0}\right)^2} / 4, \quad E_{1/2}^o(k) = \sqrt{\epsilon_{1/2}^2(k) + \frac{\Delta_o^2}{45} k^2}, \quad E_{3/2}^o(k) = \sqrt{\epsilon_{3/2}^2(k) + \frac{\Delta_o^2}{5} k^2} \tag{B5}$$

are the quasiparticle dispersions of \hat{H}_{BdG} .

We now provide a simple proof that as long as $V_0 < 0$, the system always energetically favors the conventional even parity pairing. The free energy of the two phases is given by

$$\begin{aligned}
 F_o(\Delta_o, T) &= -\frac{2T}{(2\pi)^3} \sum_{n=1/2,3/2} \int dk^3 \ln \cosh [E_n^o(k)/2T] + \frac{2|\Delta_o|^2}{3V_2}, \\
 F_e(\Delta_e, T) &= -\frac{2T}{(2\pi)^3} \sum_{n=1/2,3/2} \int dk^3 \ln \cosh [E_n^e(k)/2T] + \frac{|\Delta_e|^2}{-V_0}. \tag{B6}
 \end{aligned}$$

Assume $V_0 < 0$ and define $\Delta_1 = \Delta_e/\sqrt{-V_0}$ and $\Delta_2 = \sqrt{2}\Delta_o/\sqrt{3V_2}$ to make the two terms $2\Delta_o^2/(3V_2)$ and $\Delta_e^2/(-V_0)$ have the same functional dependence. Then we have

$$\begin{aligned}
 E_n^e(k, \Delta_1) &= \sqrt{\epsilon_n^2(k) + \Delta_1^2 |V_0| \left(1 - \frac{V_2 k^2}{V_0}\right)^2} / 4 = \sqrt{\epsilon_n^2(k) + \Delta_1^2 \left(|V_0| + \frac{V_2 k^2}{2} + \frac{V_2^2 k^4}{4|V_0|}\right)}, \\
 E_{1/2}^e(k, \Delta_2) &= \sqrt{\epsilon_{1/2}^2 + \frac{V_2 \Delta_2^2}{30} k^2}, \quad E_{3/2}^e(k, \Delta_2) = \sqrt{\epsilon_{3/2}^2 + \frac{3V_2 \Delta_2^2}{10} k^2}. \tag{B7}
 \end{aligned}$$

Obviously we have

$$E_n^e(k, \Delta) > E_n^o(k, \Delta) \tag{B8}$$

for $n = 1/2, 3/2$. This means that

$$F_o(\Delta, T) > F_e(\Delta, T) \quad (\text{B9})$$

for any Δ and T . Therefore the transition corresponding to Δ_e must happen at a higher temperature.

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- [41] Each band is doubly degenerate. At \mathbf{k} on the Fermi surface, we pick one eigenstate $|\psi_1(\mathbf{k})\rangle$, and the other state is chosen to be $|\psi_2(\mathbf{k})\rangle \equiv \hat{P} * \hat{T} |\psi_1(\mathbf{k})\rangle$, where \hat{P} is the inversion operator. The gauge at $-\mathbf{k}$ is fixed to be $|\psi_{1,2}(-\mathbf{k})\rangle \equiv \hat{T} |\psi_{1,2}(\mathbf{k})\rangle$. Therefore the generic pairing is expressed by a two-by-two matrix D_{ij} . Time reversal requires that D is a linear combination of $\sigma_{0,x,y,z}$ matrices with real coefficients. If $D \propto \sigma_0$, the pairing operator is invariant under inversion; and if $\text{Tr}(D) = 0$, the pairing operator changes sign under inversion. The latter case is topologically nontrivial. One can redefine $|\psi_{1,2}(\mathbf{k})\rangle$ such that D is diagonal; in other words, either σ_0 or σ_z , meaning the two states have same or opposite pairings. This is the accurate meaning of “two Fermi surfaces having same/opposite pairing” in the presence of inversion.