Classification of accidental band crossings and emergent semimetals in two-dimensional noncentrosymmetric systems

Sungjoon Park and Bohm-Jung Yang*
Department of Physics and Astronomy, Seoul National University, Seoul 08826, Korea; Center for Correlated Electron Systems, Institute for Basic Science (IBS), Seoul 08826, Korea; and Center for Theoretical Physics (CTP), Seoul National University, Seoul 08826, Korea
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We classify all possible gap-closing procedures which can be achieved in two-dimensional time-reversal invariant noncentrosymmetric systems. For exhaustive classification, we examine the space-group symmetries of all 49 layer groups lacking inversion, taking into account spin-orbit coupling. Although a direct transition between two insulators is generally predicted to occur when a band crossing happens at a general point in the Brillouin zone, we find that a variety of stable semimetal phases with point or line nodes can also arise due to the band crossing in the presence of additional crystalline symmetries. Through our theoretical study, we provide the complete list of nodal semimetals created by a band inversion in two-dimensional noncentrosymmetric systems with time-reversal invariance. The transition from an insulator to a nodal semimetal can be grouped into three classes depending on the crystalline symmetry. First, in systems with a twofold rotation about the \( z \) axis (normal to the system), a band inversion at a generic point generates a two-dimensional Weyl semimetal with point nodes. Second, when the band crossing happens on the line invariant under a twofold rotation (mirror) symmetry with the rotation (normal) axis lying in the two-dimensional plane, a Weyl semimetal with point nodes can also be obtained. Finally, when the system has a mirror symmetry about the plane embracing the whole system, a semimetal with nodal lines can be created. Applying our theoretical framework, we identify various two-dimensional materials as candidate systems in which stable nodal semimetal phases can be induced via doping, applying electric field, or strain engineering, etc.

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I. INTRODUCTION

Recent discovery of three-dimensional (3D) Dirac \([1–12]\) and Weyl \([13–21]\) fermions in condensed matter has triggered intensive research in semimetals with point or line nodes, dubbed nodal semimetals (NSM). Broadly, NSMs can be grouped into two classes. In the first class, the degeneracy at the band crossing point/line is enforced by the noncentrosymmetric space-group symmetry of the system. In this class of NSMs, a certain minimal number of bands are required to stick together. Thus the presence of nodal points/lines at the Fermi level can be guaranteed by the electron filling \([22]\). On the other hand, in the second class of NSMs, the gap-closing points/lines are created via a band inversion, that is, through a transition from an insulator to a semimetal via an accidental band crossing (ABC). In this class of NSMs, the location of nodal points/lines in the momentum space varies depending on external parameters such as pressure, chemical doping, etc. Here each nodal point/line carries a quantized topological charge, which guarantees the stability of NSMs \([6,8,23–25]\). In the case of semimetals with point nodes belonging to this class, a pair-creation/pair-annihilation of nodal points can even mediate topological quantum phase transitions between two insulators \([5,24,25]\).

In contrast to 3D, it is generally more difficult to have stable NSMs in two dimensions (2D) due to the lower dimensionality. For instance, even the well-known Dirac fermions in graphene become unstable, and thus gapped, once spin-orbit coupling (SOC) is included \([26,27]\). Recently, several interesting ideas have been proposed to stabilize 2D NSMs by using nonsymmorphic crystalline symmetries, thus leading to symmetry-enforced NSMs \([28,29]\). However, there has been no systematic study yet on the other class of 2D NSMs created via a band inversion. Considering that the band gap of 2D systems is easier to control than that of 3D systems via gating or strain engineering, it is essential to understand the outcome of a band inversion and the nature of resulting NSMs for future device application as well as for its fundamental physical aspect.

In this paper, we classify all possible ABC events in time-reversal invariant 2D noncentrosymmetric systems. For exhaustive investigation of ABCs and the resultant semimetals, we use a group theoretical approach by considering all possible layer groups (LGs) with broken inversion symmetry including SOC. We have found that there are three different types of ABC events as summarized in Fig. 1. In the first type, there is a direct transition between two insulators. In the second type, a band inversion creates a 2D Weyl semimetal with point nodes. We will call such twofold degenerate point nodes with linear dispersion “Weyl” points (WPs) instead of two-dimensional “Dirac” points, which we reserve for fourfold degenerate point nodes with linear dispersion. Finally, in the third type, a nodal line semimetal is created by a band inversion. At the critical point between an insulator and its neighboring phase, one can find characteristic fermionic excitations which lead to novel quantum critical behaviors. We propose various 2D materials in which our theory can be tested by engineering the electronic band structure.

The rest of this paper is organized as follows. In Sec. II we give a complete classification of a gap-closing pattern, which is summarized in Table I, and the \( \mathbf{k} \cdot \mathbf{p} \) Hamiltonian at the quantum
critical point. In Sec. III, we briefly discuss the topological charges that protect the nodal semimetallic phases in Sec. II. In Sec. IV, we explain how our classification scheme can be used, which is followed by discussion in Sec. V. In Appendix A, we give a detailed derivation of the $k\cdot p$ Hamiltonian presented in Sec. II. In Appendix B, we discuss how consideration of time-reversal symmetry affects degeneracy of bands, which must be known for the derivation of the classification scheme in Sec. II. In Appendix C, we discuss the topological phase transition that may be expected in black phosphorous in the perspective of our theory. Finally, in Appendix D, we explain the labels used for the high-symmetry points and lines in the two-dimensional Brillouin zones.

II. CLASSIFICATION OF ABC EVENTS IN LAYER GROUPS

Our strategy for classifying ABC events is as follows. In the absence of inversion symmetry, energy bands are generally nondegenerate at a generic momentum $k$. Thus, the relevant symmetry group at $k$, the $k$ group hereafter, would have a one-dimensional irreducible representation (1D irrep). In such cases, the ABC at $k_0$ between two nondegenerate bands can be described by a $2 \times 2$ Hamiltonian,

$$H(q, m) = f_0(q, m) + \sum_{i=1,2,3} f_i(q, m) \sigma_i,$$

(1)

where $\sigma_i$ are the Pauli matrices describing the two bands and $f_{0,1,2,3}$ are real functions of the momentum $q = k - k_0$ and an external parameter $m$ representing pressure, doping, etc. Here one can ignore $f_0$ as it does not contribute to the band gap. On the other hand, as discussed more fully in Appendix B, one may expect a band degeneracy associated with a higher dimensional irrep at some high-symmetry lines or points, such as a time-reversal invariant momentum (TRIM) [30]. However, since the bands degenerate at $k_0$ generally disperse linearly away from $k_0$, the band minimum or maximum is located away from $k_0$, which means that an ABC always happens away from $k_0$. Thus, we can limit ourselves to the case where the irrep of the conduction and the valence bands, $R_c$ and $R_v$, respectively, are one dimensional with the effective Hamiltonian in Eq. (1) [31].

Since the symmetry of a 2D crystal embedded in a 3D space is described by a layer group, one can exhaustively classify all possible ABC events in 2D by analyzing the 49 inversion asymmetric LGs in the presence of SOC.

Suppose that the band gap of a system which can be tuned by varying $m$ stays finite for $m < m_c$ but closes at $m = m_c$. We are interested in the nature of this system when $m > m_c$. To describe an ABC at a generic momentum $k$, three equations $f_{1,2,3} = 0$ must be satisfied. Since we have three parameters $(k_x, k_y, m)$, we expect a unique solution near the critical point. Such a solution describes the critical point between two insulators, as illustrated in Fig. 1(b). However, when the $k$ group at the gap-closing point $k_0$ has certain crystalline symmetries that impose constraints on $f_{1,2,3}$, the gap-closing condition can be modified, leading to NSM when $m > m_c$. Below, we list all symmetries in a $k$ group that give nontrivial solutions to the problem at hand. We work out the nonsymmetric symmetry explicitly only in case [b] below, since a similar idea can be applied to the other cases.
[a] No symmetry: There is no constraint on \( f_{1,2,3} \), thus one can find a unique gap-closing solution \((k_0, m_e)\). In this case, an ABC occurs only through fine tuning. We label this process by \( \text{f} \), representing fine tuning.

[b] Twofold rotation \( C_{2z} \) (similarly for \( C_{2x} \) or mirror \( M_{1z}, M_{1y} \)): (i) If \( R_x = R_y \), we may take \( C_{2z} = c\sigma_0 \) where \( \sigma_0 \) is the \( 2 \times 2 \) identity matrix and \( |c| = 1 \). Here \( c \) may be a function of \( k \) if we consider a nonsymorphic counterpart of this symmetry. On a symmetry line, the Hamiltonian is as in Eq. (1), since \( C_{2z} \) does not give any further constraint. Thus, the gap-closing condition gives three equations whereas there are only two variables, that is, \( m \) and the momentum on the symmetry line. Thus, in general, the band gap cannot be closed on the symmetry line. (ii) If \( R_x = -R_y \), we can write \( C_{2z} = c\sigma_3 \) so \( H = f_3\gamma_3 \) on the symmetry line. In this case, the gap-closing problem has two variables and one equation so the solution is one dimensional in the parameter space. We label this as \( \text{II} \), where \( \text{I} \) denotes the number of WP pairs created and \( \text{II} \) indicates the WPs are on the symmetry line [see Fig. 2(d)].

[c] \( C_{2z} ; C_{2z} \Theta \) is a local symmetry in the 2D momentum space. Since \( C_{2z} \Theta \) is antummuty, its general form is \( C_{2z} \Theta = UK \), where \( K \) denotes complex conjugation and \( U \) indicates a unitary matrix. After a suitable unitary transformation, one can always have \( C_{2z} \Theta = K \) as shown in Appendix B. Since \( C_{2z} \Theta \) requires the Hamiltonian \( H(k) \) to be real, \( f_3 = 0 \). Then the gap-closing condition gives two equations whereas there are three parameters. This means that the solution is one-dimensional, and this describes a creation of a WP pair and their evolution in the momentum space. We label this by \( \text{1p} \), where \( \text{p} \) stands for the plane where WPs are located and \( \text{1} \) indicates the number of WP pairs. Let us note that we count the number of WP pairs locally. In fact, \( C_{2z} \) implies that there is another WP pair created at \(-k_0\) [see Fig. 2(b)]. Let us also note that in systems with \( C_{2z} \Theta \), the Weyl semimetal is stable irrespective of the eigenvalues of the bands, since each WP carries a quantized \( \pi \) Berry phase [32,33].

[d] \( M_{1z} ; M_{1y} \) is also a local symmetry in the 2D momentum space. (i) If \( R_y = R_x \), only fine tuning gives 2D WPs since there are three equations and three variables. (ii) If \( R_y = -R_x \), one can choose \( M_z = \sigma_3 \), which gives \( H = f_3\gamma_3 \). The gap-closing condition gives one equation while we have three parameters, so ABC occurs in a 2D manifold in the parameter space, which translates to the creation of a line node and its evolution. Since the gap-closing points, in general, form a loop in the momentum space, we label it by \( \text{loop} \) [see Fig. 2(a)].

[e] \( C_{2z} \) and \( C_{2z} \Theta \) (similarly for \( C_{2x} \) and \( C_{2x} \Theta \) or \( M_{1z} ; M_{1y} \) and \( M_{1y} \Theta \)): Since \( C_{2z}, C_{2z} \Theta \propto C_{2x} \Theta (M_z M_y \propto C_{2z} \Theta) \), a WP is stable even when it is away from high-symmetry axes. (i) Considering \( C_{2z} \Theta \) eigenvalues, if \( R_y = R_x, C_{2z} = i\sigma_3 \) and the Hamiltonian is not constrained by \( C_{2z} \Theta \) on its invariant axis. However, due to \( C_{2z} \Theta \), the Hamiltonian should be real. Then on the \( C_{2z} \Theta \) invariant axis, the gap-closing condition gives two equations with two parameters, including the momentum along the invariant axis and \( m \), which leads to case \( \text{f} \) on the invariant axis. However, a more detailed analysis shows that the gap closing on the \( C_{2z} \Theta \) invariant axis creates a pair of WP that move symmetrically away from the invariant axis. We label this case as \( \text{3s} \) where \( s \) means symmetrical [see Fig. 2(e)]. (ii) If \( R_y = -R_x \), one can choose \( C_{2z} = i\sigma_3 \). Then the Hamiltonian on the invariant axis depends only on \( f_3 \), and the gap-closing condition gives one equation with two parameters, which describes the creation of a WP pair following the pattern \( \text{III} \).

[f] \( C_{2z} \) and \( M_{1z} \): Since \( C_{2z}, M_y \propto M_{1z} \), a nodal line can appear after a band inversion. Let us note that \( C_{2z} \) and \( M_{1z} \) share the same invariant line. (i) If \( \{ C_{2z}, M_{1z} \} = 0 \) on the invariant line (recall that these can be nonsymmetric), two bands with different \( C_{2z} \) (or \( M_{1z} \)) eigenvalues are doubly degenerate. In this case, a band inversion does not happen on the invariant line. (ii) If \( \{ C_{2z}, M_{1z} \} = 0 \) on the invariant line, each band on the invariant line carries \( C_{2z} \) and \( M_{1z} \) eigenvalues simultaneously. When a band inversion happens between two bands with different \( C_{2z} \) (or \( M_{1z} \)) eigenvalues while sharing the same \( M_{1z} \) (or \( C_{2z} \)) eigenvalues, a nodal line is created after the band inversion corresponding to a \( \text{loop} \). If both \( C_{2z} \) and \( M_{1z} \) eigenvalues are different between two bands, the band inversion creates a WP pair on the invariant line corresponding to \( \text{III} \).

[g] \( C_{3z} \) plus \( M_{1z} \): This happens at the \( K \) or \( KA \) point of the hexagonal Brillouin zone. Since two bands with \( C_{3z} \) eigenvalues \( e^{i\pi/3} \) and \( e^{-i\pi/3} \), respectively, are degenerate at \( K \) or \( KA \), a band inversion can happen only between two bands with \( C_{3z} \) eigenvalue \(-1 \). When these two bands carry different \( C_{3z} \) or \( M_{1z} \) eigenvalues, a band inversion can happen and create three pairs of WPs, which are located on the lines invariant under \( C_{2z} \) or \( M_{1z} \). We label it \( \text{3l} \), as shown in Fig. 2(e).

A. Classification table

We summarize all possible gap-closing patterns in Table I for 49 LGIs lacking inversion symmetry. We list LG numbers in the first column and the corresponding space-group numbers in the second column. Note that for each LG \( L \), there is a space group \( G \) such that if \( T(1) \) is a one-dimensional translation subgroup, \( L \approx G/T(1) \) [34,35]. In the third column, we list the possible gap-closing patterns. Here we use the notation \( ii \) to mean \( R_z = R_y \), and \( ij \) to mean \( R_z \neq R_y \). We also use the notation \( ii : ii \) to mean \( ii \) leads to \( 1s \) and \( ij \) leads to \( 1l \). \( \langle 4 \rangle : \text{loop} \rangle \text{II} \) is used for case \( \text{f} \) above, where there are four possible 1D irreps. In this case, different \( M_z \) eigenvalues lead to \( \text{looc} \) while different \( C_{2z} \) or \( M_y \) eigenvalues lead to \( \text{II} \).
FIG. 3. Evolution of the band structure across an ABC. (a) Bands before the gap closing with \( m < m_c \). (b–f) Bands at the critical point with \( m = m_c \). (g–k) Bands after the gap closing with \( m > m_c \). (b, g) For an insulator-to-insulator transition. (c, h) For a transition to a Weyl semimetal protected by \( C_{2z},z \) or \( M_{x,y} \). (d, i) For a transition to a Weyl semimetal protected by \( C_z \) together with \( C_{2z},z \) or \( M_{x,y} \). (e, j) For a transition to a Weyl semimetal protected by \( M_z \). (f, k) For a transition to a nodal line semimetal protected by \( M_z \).

The other is at the critical point between an insulator in which the bands disperse quadratically in two directions. Finally, there are two cases the case of \( \mathbf{1p} \), we do not specify \( R_c \) and \( R_e \) since WPs are stable independent of eigenvalue spectra. Here the labels on the Brillouin zone follow the conventions used in Ref. [35], which is illustrated in Appendix D [36].

### B. Effective Hamiltonian at the quantum critical point

To describe the effective Hamiltonian at the quantum critical point with \( m = m_c \), we redefine the coordinates so that the gap closes at \( \mathbf{k} = \mathbf{k}_0 = 0 \) and \( m = m_c = 0 \). As described below, the effective Hamiltonian at the critical point falls into three categories.

First, when there is an insulator-to-insulator transition, the bands disperse linearly in two directions at the critical point, as shown in Fig. 3(b). The relevant effective Hamiltonian is \( H = a_1 k_1^2 \sigma_1 + a_2 k_2^2 \sigma_2 \), where we use \( k_1, k_2 \) since they are not along \( k_x \) and \( k_y \) in general. Second, at the critical point where a pair of WPs is created, the bands disperse linearly in one direction but quadratically in the other direction. In particular, if the WPs are protected by \( C_{2z},z \) or \( M_{x,y} \), the relevant Hamiltonian is \( H = a_1 k_1^2 \sigma_1 + a_3 k_3^2 \sigma_3 \) [Fig. 3(c)], whereas in the case with \( C_z \), it is \( H = a_1 k_1^2 \sigma_1 + (a_2 k_2^2 + a_3 k_3^2) \sigma_3 \) [Fig. 3(d)]. Note that the presence of \( k_3^2 \) in the coefficient of \( \sigma_3 \) breaks \( k_2 \to -k_2 \) symmetry of the energy dispersion. Finally, there are two cases in which the bands disperse quadratically in two directions. One is at the critical point where three pairs of WPs are created [Fig. 3(e)]. The other is at the critical point between an insulator and a nodal line semimetal with the Hamiltonian \( H = (a_1 k_1^2 + a_3 k_3^2) \sigma_3 \), where we require \( a_1 a_3 > 0 \) [Fig. 3(f)]. The relevant Hamiltonian is \( H = u_1 k_1^2 \sin \theta \sigma_1 + u_3 k_3^2 \sigma_3 \), where \( u_1, u_3 \) are constants and \( k_x + i k_y = k e^{i \phi} \). (See Appendix A for the detailed form of the effective Hamiltonian covering \( m < m_c \) and \( m > m_c \) cases as well.)

### III. TOPOLOGICAL CHARGE

In this section, we show that the emergence of stable band degeneracy is always accompanied by a (quantized) topological charge. We define topological charge for each of the three classes of symmetry.

(i) \( C_{2z}, \theta \): Under time-reversal symmetry, the Berry curvature satisfies \( \Omega(\mathbf{k}) = \Omega(\mathbf{k}) \) while under the rotation symmetry, \( \Omega(\mathbf{-k}) = -\Omega(\mathbf{k}) \). Thus, \( \Omega(\mathbf{k}) = -\Omega(\mathbf{k}) \) under \( C_{2z}, \theta \), and the Berry curvature vanishes everywhere except for singularities realized by Weyl points [32]. This quantizes the Berry phase in units of \( \pi \).

(ii) \( \{M_v, t\} \): First, note that eigenvalues are \( \pm c \). Define \( \mathbf{k}_1 \) “inside” the loop and another point \( \mathbf{k}_2 \) “outside” the loop. Define \( N_{\pm}(\mathbf{k}) = N^e_{\pm}(\mathbf{k}) - N^o_{\pm}(\mathbf{k}) \). Here, \( N^o_{\pm}(\mathbf{k}) \) is the number of conduction (valence) bands with eigenvalues \( \pm c \) at \( \mathbf{k} \). The charge is defined to be (see Fig. 4)

\[
Q = \frac{\pi}{4} \sum_{\mathbf{k}} \left[ N_{\pm}(\mathbf{k}_1) - N_{\pm}(\mathbf{k}_2) - N_{\pm}(\mathbf{k}_3) + N_{\pm}(\mathbf{k}_4) \right].
\]  

(iii) \( \{C_{2z}, t\} \) or \( \{M_v, t\} \): The charge is defined exactly as in (2) but with \( \mathbf{k}_1 \) and \( \mathbf{k}_2 \) along the symmetry axis with \( \mathbf{k}_1 \) to the left and \( \mathbf{k}_2 \) to the right of the gap-closing point. We note that the topological charge can also be defined by integrating along a curve symmetric with respect to the symmetry line. In

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this case, $C_2$ (or $M_z$) implies that $Ω(k_x, k_y) = −Ω(k_x, −k_y)$ so the integral vanishes unless there is a singularity.

**IV. APPLICATION TO 2D MATERIALS**

Our theory can be applied to various 2D materials whose band gap is widely tunable by gating, doping, or strain engineering. Let us first focus on the variants of the 2D planar honeycomb lattice, since many 2D materials fall into this category. Because we have organized our results according to LG, it suffices to identify the LG of the lattice structure. The planar honeycomb lattice has the structure of the LG 80. By distorting the lattice, it is possible to obtain a puckered structure belonging to the LG 42 and a buckled structure with the LG 69 [33,38–42]. Although the planar and the puckered structures contain inversion symmetry, 2D materials are usually fabricated on a substrate, and this breaks inversion symmetry. (One could instead apply electric field normal to the plane of the material.) Then, the symmetry of the planar and the puckered structure is lowered to LG 77 and LG 24, respectively. Another variant of the honeycomb lattice structure is the dumbbell structure, whose symmetry group, like the planar structure, is also LG 80 [39,40]. Of course, there are also 2D materials whose structure is not based on the honeycomb lattice. For instance, Bi$_4$Br$_4$ has the structure belonging to LG 42, which lowers to LG 13 upon breaking inversion symmetry [43]. HgTe in a HgTe/CdTe quantum well belongs to LG 57 [33]. We summarize the candidate systems and their LGs in Table II. Once the LG for the given material is determined, all possible gap-closing patterns can be read off from Table I.

**TABLE II.** List of candidate 2D materials. The first column lists the lattice structure. The second column lists the layer group (LG) number for the structure, considering the inversion symmetry breaking effect. The third column lists specific materials that fall under the category.

| Structure                  | LG  | Material examples                                      |
|----------------------------|-----|-------------------------------------------------------|
| Planar honeycomb           | 77  | Graphene                                              |
| Puckered honeycomb         | 24  | Arsenene [38], antimony [39], bismuth [40], black phosphorus [33] |
| Buckled honeycomb          | 69  | Arsenene [38], blue phosphorous [41], silicon, germanium [42], antimony [39], bismuth [40] |
| Dumbbell                   | 77  | Stanene [47], Sn$_6$Ge$_4$, Sn$_6$Ge$_4$H$_4$ [48] |
| Bi$_4$Br$_4$               | 13  | Bi$_4$Br$_4$ [43]                                     |
| HgTe                       | 57  | HgTe/CdTe heterostructure [33]                        |

**V. DISCUSSION**

One important application of our classification table is to use it for engineering topological band structure. For instance, recent theoretical and experimental studies on few-layer black phosphorus have shown that it is possible to achieve a transition from an insulator to a Weyl semimetal by doping potassium [33,44,45]. Due to its puckered structure, few-layer black phosphorus under a vertical electric field belongs to LG 24. Since the gap closing happens on the $k_z$ axis invariant under $M_z$, $C_2$, $Θ$, and the $M_łl$ eigenvalues of the conduction and valence bands are identical (see Appendix C), the gap-closing pattern should be $1s$, which is confirmed by theoretical studies. Interestingly, a recent theory has shown that such an emergent 2D Weyl semimetal phase can even mediate a transition between a normal insulator and a quantum spin Hall insulator [33]. Moreover, at the critical point for an ABC, unusual fermion dispersion develops, which can generate unconventional quantum critical phenomena. As presented in Sec. II and derived in Appendix A, at the critical point for an insulator-insulator transition, the bands disperse linearly in two directions so that the density of states $D(E) ∝ E$. On the other hand, at the critical point where a pair of WP is created, bands disperse linearly in one direction but quadratically in the other direction so that $D(E) ∝ \sqrt{E}$. Finally, at the critical point where either a line node or three pairs of WPs are created, bands disperse quadratically in two directions, and therefore, the density of states at the Fermi energy becomes finite. In fact, previous theoretical studies on 2D semimetals with quadratic band crossing have shown the short-range Coulomb interaction is marginally relevant due to the enhanced low energy density of states. Thus, it can induce various insulating phases with broken symmetries [46]. Since such a quadratic dispersion is expected at the critical point in our problem, it is natural to expect novel quantum critical behavior associated with an ABC, which we leave for future study.

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APPENDIX A: GENERAL k-p HAMILTONIAN

As explained in the main text, we may write

\[ H = \sum_{i=1}^{3} a_i \sigma_i, \quad \text{(A1)} \]

which we will use throughout this section. (We have ignored a term proportional to the 2 × 2 identity matrix because it does not contribute to the band gap.) Hermiticity of the Hamiltonian requires that and \( a = (a_1, a_2, a_3) \) be real functions of \( k_1, k_2, m \).

Let us redefine the coordinates so that the gap closes at \( m = 0, k = (k_1, k_2) = 0 \). Also define \( q = (q_1, q_2, q_3) = (k_1, k_2, m) \).

With this notation, the gap closes at \( q = 0 \). We will sometimes also use \( k_1, k_2 \) instead of \( k_1, k_2 \) when it is more convenient to fix the direction of the coordinates. We will also frequently make use the following property of Pauli matrices.

Suppose that \( \sigma'_j = \sum_{j=1}^{3} O_{ij} \sigma_i \) is a set of matrices obtained from the Pauli matrices by an orthogonal transformation \( O \). Then, if \( H' = \sum_{i,j=1}^{3} b_{ij} \sigma_i \sigma_j \), the eigenvalues are \( E'_\pm = \pm \sqrt{b_{11}^2 + b_{22}^2 + b_{33}^2} \). To show this, note first that the eigenvalues of a Hamiltonian of the form \( (A1) \) are \( E_\pm = \pm \sqrt{a_1^2 + a_2^2 + a_3^2} \).

To see this, use the fact that Pauli matrices transform like a vector under SU(2). Thus, there is always an SU(2) transformation that takes the Hamiltonian to \( H = \pm \sqrt{a_1^2 + a_2^2 + a_3^2} \), from which the statement follows. Now, using the fact that \( O \) is an orthogonal matrix, \( \sigma'_j = \sum_{j=1}^{3} O_{ij} \sigma_i \) and \( \sigma'_j = \sum_{j=1}^{3} O_{ij} \sigma_j \). Then, it follows that \( E'_\pm = \pm \sqrt{b_{11}^2 + b_{22}^2 + b_{33}^2} \).

Thus, \( \sigma'_j \) obtained from orthogonal transformation of the Pauli matrices are just as good for expanding the Hamiltonian.

1. No symmetry

In this section, we explore in more detail how the gap closes for the case labeled by \( \Gamma \) in the main text. Expanding \( a \) to first order in \( q \) around the gap-closing point, we have \( a = MQ \).

Here, the matrix \( M \) has components \( M_{ij} = \frac{\partial a_i}{\partial q_j} \), \( i, j = 1, 2, 3 \).

We first examine what happens when \( M \) is not invertible. If the matrix has rank 2, the solution is one dimensional in the parameter space, while if the matrix has rank 1, it is two dimensional [49]. Thus, for these cases, a gap-closing solution exists for arbitrary value of \( m \). Since we are assuming that the gap is open when \( m < 0 \), these cases can be excluded from our consideration. Note that the case \( M = 0 \) is unlikely. To see this, carry out the singular value decomposition of \( M = A^TDB \), where \( A \) and \( B \) are orthogonal matrices while \( D \) is diagonal. If \( M \) is not invertible, one or more of the entries of \( D \) is zero, which should not happen without special reason.

The conditions we impose on the Hamiltonian, that the gap closes at \( m = 0 \) but that the gap does not close for \( m < 0 \), do not give such a constraint. Therefore, we expect \( M \) to be invertible, and in particular, \( M \neq 0 \).

Thus, \( M \) is in general invertible, and there is only one solution to the gap-closing condition in the neighborhood of \( q = 0 \). This gives a Hamiltonian with linearly dispersing bands which are degenerate at \( k = 0 \) when \( m = 0 \) but quadratically dispersing with a gap when \( m \neq 0 \). To see this, first write the Hamiltonian as

\[ H = \sum_{i,j=1}^{3} M_{ij} q_i q_j \sigma_i. \quad \text{(A2)} \]

Carry out the QR decomposition on the matrix \( M = QR \). Here, \( Q \) is an orthogonal matrix and \( R \) is an upper triangular matrix. Redefine \( \sigma'_j = \sigma_j Q_{jj} \) and \( q'_j = R_{jj} q_j \), so that \( \sum_{j=1}^{3} M_{ij} q'_i \sigma'_j = \sum_{j=1}^{3} q'_i \sigma'_j \). Notice that we may carry out the decomposition such that the diagonal components of \( R \) are positive. This follows because \( \text{det}(R) = R_{11} R_{22} R_{33} \neq 0 \), and whenever any one of \( R_{ij} \) (\( i = 1, 2, 3 \)) is negative, the sign may be absorbed into the matrix \( Q \). For example, if \( R_{11} \) is negative, define \( D = \text{diag}(-1, 1, 1) \). Then, \( QR = QDQ \).

The QR decomposition can be carried out with \( Q = QDQ \) and \( R = D \) instead, in which case \( R_{11}' \) is positive. The \( \sigma'_j \) are orthogonal transformations of the Pauli matrices and \( q'_j = (k'_1, k'_2, m') \), where \( k'_1 \) and \( k'_2 \) are linear transformations of \( k_1 \) and \( k_2 \), while \( m' = cm \) for a positive constant \( c \). The Hamiltonian is then

\[ H = k'_1 \sigma'_1 + k'_2 \sigma'_2 + m' \sigma'_3. \quad \text{(A3)} \]

Now, it is easier to see that the dispersion is linear when \( m = cm \) while the dispersion is quadratic when \( m' \neq 0 \). Note, however, that this transformation comes with a price that \( k'_1 \) and \( k'_2 \) no longer form an orthogonal coordinate system.

The gap-closing process is illustrated in Figs. 3(a), 3(b) and 3(g).

When \( m = 0 \), we can write \( a = Lk \), where \( L \) is a real matrix with components \( L_{ij} = \frac{\partial a_i}{\partial k_j} \) \( (i, j = 1, 2, 3) \). Use the singular value decomposition on \( L \) to write \( a = U^T \Sigma V k \), where \( U \) and \( V \) are orthogonal matrices and \( \Sigma \) is a \( 3 \times 2 \) rectangular diagonal matrix with the only nonzero entries \( \Sigma_{11} = v_1, \Sigma_{22} = v_2 \). Defining \( a = Ua \) and \( k' = V k \), the Hamiltonian can be written as

\[ H = v_1 k'_1 \sigma'_1 + v_2 k'_2 \sigma'_2. \quad \text{(A4)} \]

where \( \sigma'_i \) is orthogonal transformation of the Pauli matrices.

2. C_\pi or M_\pi symmetry

In this section, we carry out a similar analysis for the case labeled \( \Pi \) in the main text. As explained in the main text, the requirement for stable band crossing is that \( R_c \neq R_v \), where \( R_c \) and \( R_v \) are the 1D irreducible representations of the symmetry for the conduction and the valence band along the high-symmetry line. This restricts the Hamiltonian to \( H = \alpha_3 \delta_3 \) on the symmetry lines \( k_x = 0, \pi \). Furthermore, off the symmetry axis, \( a_{1,2,3} = k_1 b_2(k_1^2, k_2^2) \) and \( a_{3} = a_3 \delta_3 k_2^2 \) due to the constraint that \( H(k_x, k_y) = C_{2\pi} H(k_x, k_y) C_{-2\pi}^{-1} \).

We can approximate \( a_1 = a_{33} k_x + a_{33} k_x^3 + a_{33} k_x^5 + a_{33} m \). The number of solutions is determined by the discriminant, \( D = a_{33}^2 - 4 a_{33} a_{33} a_{33} m \). Thus, we must have \( a_{33} = 0 \) while \( a_{33} a_{33} < 0 \). Now, make the following expansions: \( a_{1,2} = k_1 a_{1,2}, a_3 = a_{33} k_x^3 + a_{33} k_x^5 + a_{33} m \). We do not include \( k_x \) because there is a term linear in \( k_x \), that will overwhelm \( k_x \) when \( k_x \neq 0 \), while when \( k_x = 0 \), it is zero. \( m \) was ignored for similar reasons.) Thus, the effective Hamiltonian

\[ H = \sum_{i,j=1}^{3} M_{ij} q_i q_j. \quad \text{(A5)} \]
This describes the gap closing and the subsequent evolution of Weyl points as shown in Figs. 3(a), 3(c) and 3(h). When \( m = 0 \), we have \( H = k_x a_1 + k_y a_2 + k_z a_3 \). Carrying out a rotation in the \( \sigma_i \) space, we find

\[
H = a_1' k_x \sigma_1' + a_2' k_y \sigma_2' + a_3' k_z \sigma_3'.
\]

(A6)

Here, the set \( (\sigma_1', \sigma_2', \sigma_3') \) is an orthogonal transformation of the Pauli matrices and \( a_i' \) is the rotation in the \( i \) direction. However, this case is slightly different in that there is no \( k_2 \rightarrow -k_2 \) symmetry. The Weyl points move in the quadratically dispersing direction in this case as well. This can be seen from the gap-closing conditions, which are \( (u_{11})_1 k_1^3 + N_1 m = 0 \) and \( (u_{11})_3 k_3^2 + u_3 k_2 + N_2 m = 0 \). The former shows that for \( m \) slightly greater than 0, \( k_2 \approx \sqrt{m} \) and the latter shows that \( k_2 \approx m \). Thus, for small \( m \), the Weyl points move predominantly in the quadratically dispersing direction.

4. \( C_{2z}, C_{2z} \theta \)

We expand on the discussion in the main text in a similar manner with the symmetries \( C_{2z} \) and \( C_{2z} \theta \), which give rise to either pattern \( \mathbf{H} \) or pattern \( \mathbf{I} \). Since the case for \( \mathbf{H} \) was discussed in Appendix A 2, we discuss only the case \( \mathbf{I} \). For this case, we may take \( C_{2z} = \pi \sigma_0 \) and \( C_{2z} \theta = K \). (We assumed that the conduction and the valence bands both have eigenvalues \( -i \) since the case for eigenvalues \( +i \) is similar.) These symmetries restrict the Hamiltonian to \( H = a_1 \sigma_1 + a_3 \sigma_3 \), where \( C_{2z} \) requires that \( a_1, a_3 \) be even in \( k_y \). Then, to lowest order, \( a_{13} = M_{13} k_x + M_{31} k_z + N_{13} m \). Explicitly,

\[
\begin{bmatrix} a_1 \\ a_3 \end{bmatrix} = \begin{bmatrix} M_{1x} & M_{1z} \\ M_{3x} & M_{3z} \end{bmatrix} \begin{bmatrix} k_x \\ k_z \end{bmatrix} + \begin{bmatrix} N_1 \\ N_3 \end{bmatrix}
\]

(\( A11 \))

Note that we have defined \( \tilde{k} = (k_x, k_y) \). Using the QR decomposition, we can write \( M = QR \), where \( Q \) is orthogonal and \( R \) is upper triangular. Rewrite the Hamiltonian as

\[
H = \sum_{i=1,2} \sigma_i a_i = \sum_{i,j,k=1,2} \sigma_j Q_{ji} (Q^T)_{ik} a_k
\]

(\( A12 \))

where we have defined \( \sum_{j=1,2} \sigma_j Q_{ji} = a_j' \) and \( \sum_{k=1,2} (Q^T)_{ik} a_k = a_i' \). Noting that \( a' = Q^T a = RK + m Q^T N \), the Hamiltonian takes the form

\[
H = \begin{bmatrix} R_{11} k_x + R_{13} k_y^2 + m N_1 \sigma_1' + (R_{21} k_y + m N_2 \sigma_3', \;
\]

(\( A13 \))

If we make the correspondence \( k_1 \approx k_x, k_2 \approx k_y \), this has the form of Eq. (A9). Setting \( m = 0 \) takes us to (A10). Then, we see that this describes the evolution of a pair of Weyl points symmetrically with respect to the high-symmetry lines \( k_y = 0, \pi \).
5. C3 and C2x or M1

In this section, we similarly discuss the case labeled 3l in the main text. The groups 68, 70, 76, and 78 contain threefold rotation about the z axis and twofold rotation or mirror about the in-plane axis as symmetries at the K point. As shown in Appendix B 3, it is possible to create three pairs of Weyl points that evolve from K (KA) point. When this occurs, the representation for C3 is –σ0 and the representation for C2x (M1) is ±σ3.

To describe this gap-closing process, it is convenient to use polar coordinates (r, θ) with the K point at r = 0. We may also orient our axis so that θ = 0 corresponds to one of the high-symmetry lines. As before, we demand that the gap closes at m = 0 while it stays open for m < 0. The symmetries of the system imply that H(r, θ) = H(r, θ = 2π/3) and H(r, −θ) = −a1(r, θ)σ1 − a2(r, θ)σ2 + a3(r, θ)σ3. The former shows that we cannot Fourier expand in θ while the latter shows that a1, a2 are odd and a3 is even in θ. Expanding the Hamiltonian to lowest order, H = ur3 sin 3θσ1 + u′r3 sin 3θσ2 + (um + m + u3r2)σ3. Note that the analyticity of the Hamiltonian demands that sin 3θ should appear with r3. After performing a rotation in the σ1, σ2 space, we may simplify the Hamiltonian as follows:

$$H = ur^3 \sin 3\theta \sigma_1 + (um + u_3r^2)\sigma_3.$$  
(A14)

Finally, imposing the constraint that there is no gap closing for m < 0, we get the constraint u3m + u3 < 0. This describes closing of the gap and formation of three pairs of Weyl points as shown in Figs. 3(a), 3(e) and 3(j). When m = 0, the Hamiltonian is

$$H = ur^3 \sin 3\theta \sigma_1 + u_3r^2 \sigma_3.$$  
(A15)

The dispersion is quadratic in all directions, as can be seen in Fig. 3(j).

6. Mz

Finally, we discuss the case labeled by loop in the main text. This corresponds to the case when the eigenvalues of $M_z$ for the conduction and the valence bands are different, which restricts the Hamiltonian to $H = a_3\sigma_3$. Expanding to first order, $a_3 = b_1k_1 + b_2k_2 + a_3m$. The solution space of the gap-closing condition is a plane in the parameter space, which is incompatible with the constraint that there is no solution for m < 0. Thus, we include second-order terms, $a_3 = b_1k_1 + b_2k_2 + a_1k_1^2 + 2a_2k_1k_2 + a_3k_2^2 + a_3m$. The extremum for $a_3$ when m = 0 must be 0 at $k_1 = k_2 = 0$. This condition for extremum gives $b_1 = b_2 = 0$. If we now vary m, there should be a solution for m > 0, and it must be a closed loop as we is shown below. Assuming this for now, the solution must be an ellipse for small m. The condition for an ellipse is that det(A) > 0, where A is the matrix with components $a_{ij}, i, j = 1, 2$. Notice that we may diagonalize this matrix through an orthogonal matrix $P$. Defining $K = PK$, $a_3 = \lambda_1k_1^2 + \lambda_2k_2^2 + a_3m$. The condition for ellipse now reads $\lambda_1, \lambda_2 > 0$, while the condition for solution coming into existence for m ≥ 0 becomes $\lambda_1, \lambda_2 > 0$.

Now, we explain why the solution should be an ellipse. This is because a parabola requires $\lambda_1'$ or $\lambda_2'$ to be zero, which is not likely. On the other hand, a hyperbola would be in contradiction with our assumption because there would exist a solution to the gap-closing equation for arbitrary m. Thus, the Hamiltonian is

$$H = (\lambda_1k_1^2 + \lambda_2k_2^2 + a_3m)\sigma_3.$$  
(A16)

This describes the gap closing and the formation of a line node as illustrated in Figs. 3(a), 3(f) and 3(k). When m = 0, the Hamiltonian becomes

$$H = (\lambda_1k_1^2 + \lambda_2k_2^2)\sigma_3.$$  
(A17)

Thus, the dispersion is quadratic in both directions.

APPENDIX B: CONSIDERATION OF TIME-REVERSAL SYMMETRY

Although time-reversal symmetry fixes only points in the Brillouin zone by itself, it may combine with other crystal symmetries to fix lines or planes. The former occurs when it combines with twofold rotation or mirror symmetry with an in-plane axis, while the latter occurs when it combines with twofold rotation with the axis normal to the plane. We analyze the latter case first, then the former case, and finally, analyze high-symmetry points that are not TRIM. Our goal will be to determine whether consideration of time-reversal symmetry will induce extra double degeneracy, and if not, to determine whether there is any other possible emergent semimetallic phases which were not discussed in detail in the main text. In particular, we discuss the case 3l in the main text.

1. High-symmetry plane with time-reversal symmetry

In this section, we prove that $C_{2z}\theta = IST$ can be represented by $K$, where $K$ is the complex conjugation operator. Because $C_{2z}$ is unitary and $\theta$ is antiunitary, $IST$ must be antiunitary. Thus, $IST = UK$, where U is an $N \times N$ unitary matrix:

$$U^\dagger = 1.$$  
(B1)

Also, the condition $I_{ST}^2 = 1$ implies that

$$U^* = 1.$$  
(B2)

These two conditions imply that $U^{-1} = U^\dagger = U^*$. Thus, $U$ is symmetric and unitary and we may write $U = e^{iM}$, where $M$ is symmetric and Hermitian. In other words, $M$ is a real symmetric matrix, and such matrices can be diagonalized by a real orthogonal matrix. Since $U$ transforms under real orthogonal change of basis by matrix $O$ as $U \rightarrow OUO^T$, we see that $M$ can be diagonalized to a matrix $\phi$ with diagonal entries $\phi_n, n = 1, ..., N$. Another transformation with matrix $D = diag(e^{-i\phi_1/2}, ..., e^{-i\phi_N/2})$ gets rid of the phase factors: $e^{i\phi}K \rightarrow D e^{i\phi}KD^\dagger = K$. Thus, for any set of bands, $IST$ can be diagonalized, and we may discuss $IST$ acting on a single energy band (i.e., it does not introduce degeneracy). This means that we may talk about $IST$ acting on an arbitrary pair of bands as complex conjugation.

2. High-symmetry line with time-reversal symmetry

The analysis for $IST$ can be applied whenever time reversal is combined with a unitary operator that commutes with it and squares to −1. It is then clear that $C_{2z}\theta$ and $M_z\theta$ also do not enforce double degeneracy. The same comment applies
when \( C_2 \) is replaced by \( \{C_2|ab\} \), because \( \{C_2|ab\}^2 = 1 \).

The analysis becomes more complicated for \( \{C_2|ab\theta\} \) and \( \{M_1|ab\theta\} \), where \( a, b = 0 \) or \( \frac{1}{2} \). If we denote either of the operators by \( R, R^2 = -e^{2\pi i} \), and \( (R\theta)^2 = e^{2\pi i} \). Writing \( \{C_2|ab\theta\} = UK \), we have, in addition to (B1),

\[
UU^* = e^{2\pi i}.
\]

If \( a = 0 \), the previous analysis applies and there is no degeneracy along the symmetry lines for \( \{C_2|ab\theta\} \), namely, the lines \( k_i = 0, \pi \). In addition, because the basis can be chosen so that \( R\theta = K \), a gap-closing event is not protected along the symmetry line. (\( H = a_1\sigma_1 + a_3\sigma_3 \), so two equations need to be satisfied for the gap to close while there are two parameters, \( m \) and the momentum along the symmetry line.) Since gap closing is not protected off the symmetry line, this does not lead to stable semimetalline phase. On the other hand, if \( a = 1/2 \), \( (R\theta)^2 = -1 \), so there is a double degeneracy along the line \( k_i = \pi \), but not along the line \( k_i = 0 \) \([50]\).

Next, consider the possibility of multiple antiunitary symmetry along a line. This happens when there is a simultaneous presence of \( C = \{C_2|ab\theta\} \) and \( M = \{M_1|ab\theta\} \) along the lines \( k_i = 0 \) or \( \pi \). If \( a \) or \( a' \) is 1/2, there will be a double degeneracy along the lines as we have shown above. If we exclude these cases, they can be diagonalized individually but it is not clear if they can be simultaneously diagonalized. If we set \( a = a' = 0 \), \( CM : (x, y, z, t) \rightarrow (x, y + b - b', -z, t) \) and \( MC : (x, y, z, t) \rightarrow (x, -y + b + b', z, t) \). Writing \( C = U_1K \) and \( M = U_2K \), with symmetric and unitary \( U_1 \) and \( U_2 \), this condition becomes

\[
U_1U_2^* = \pm U_2U_1^*.
\]

Now, we showed above that \( U_1 = 1 \) with a suitable choice of basis, so \( (B4) \) implies that in this basis, \( U_2 \) is either real or purely imaginary. Because \( U_2 \) is symmetric and either \( U_2 \) or \( iU_2 \) is real, it can be diagonalized by real orthogonal transformation, under which \( U_1 \) will remain invariant. Thus, \( C \) and \( M \) can be simultaneously diagonalized. This analysis could have been carried out by considering the eigenvalues of \( M_1 \), since \( MC \approx M_1 \), but this clarifies how the two antiunitary operators can be simultaneously diagonalized. Note that a stable semimetalline phase arises only when \( R \neq R_\tau \) for the \( M_1 \) eigenvalues, which leads to a nodal line, as we already have seen.

We next consider the case when \( IST = C_2\theta \) is present with a nonsymmetric rotation or mirror with in-plane axis where the translational part is nonzero for the direction normal to the line preserved by the rotation or mirror. In other words, the nonsymmetric symmetries are of the form \( \{C_2|ab\} \) and \( \{M_1|ab\} \), where \( a = 0 \) or \( 1/2 \) and \( b = 1/2 \). We first note the action of \( IST \) and \( \{C_2|ab\} \), where \( a = 0 \) or \( 1/2 \) and \( b = 1/2 \). We first note the action of \( IST \) and \( \{C_2|ab\} \) on real space and spin space:

\[
\text{\( IST : (x,y,z,t) \otimes \sigma_0 \rightarrow (-x,-y,z,-t) \otimes \sigma_0 \) and \( \{C_2|ab\} : (x,y,z,t) \otimes \sigma_0 \rightarrow (x+a,-y+b,-z,t) \otimes \sigma_0 \).}
\]

Thus, \( \{C_2|ab\}IST : (x,y,z,t) \otimes \sigma_0 \rightarrow (-x+y+b,-z,-t) \otimes (-K) \) and \( IST\{C_2|ab\} : (x,y,z,t) \otimes \sigma_0 \rightarrow (-x+a,-y-b,-z,-t) \otimes K \). Thus,

\[
\text{\( \{C_2|ab\}IST = -T_{2\alpha,2\beta} IST\{C_2|ab\} \approx -e^{(2\pi i)(2\alpha/2\beta)} IST\{C_2|ab\}. \) (B5)}
\]

Here, \( T_{2\alpha,2\beta} \) is the translation operator with translation in \( x \) and \( y \) direction by \( 2\alpha \) and \( 2\beta \), respectively.

Now, we examine if \( IST \) doubles the dimension of the representation by examining the eigenvalue of the nonsymmetric operator. Since \( \{C_2|ab\}^2 = -e^{2\pi i} \), the eigenvectors are \( \pm \) with eigenvalues \( \pm e^{\pi i} \). The question is whether \( IST \{\pm\} \) has the same \( \{C_2|ab\} \) eigenvalues. Using \( (B5) \), \( \{C_2|ab\}IST \{\pm\} = \pm e^{(2\pi i)(2\alpha/2\beta)} IST \{\pm\} \). Now, it is easy to see that the eigenvalues switch if and only if \( b = 1/2 \) and \( k_i = \pi \) mod \( 2\pi \). The analysis for mirror symmetry is similar. See, for example, groups \( 20, 21, 24, 25 \). In hindsight, we see that this double degeneracy is actually due to \( \{C_2|ab\} \) and \( \{M_1|ab\} \), where \( a, b = 1/2 \) along \( k_i = \pi \), but the proof of the double degeneracy is simpler here due to the presence of unitary symmetry whose eigenvalues switch under the action of an antiunitary symmetry. Finally, note that when there is no double degeneracy, the stable semimetalline phase that may arise corresponds to the pattern ii:ij:is,iII discussed in the main text. This concludes the analysis of all sublattices that may arise along symmetry lines due to time-reversal symmetry.

3. High-symmetry points that are not TRIM

It is well known that time-reversal forces double degeneracy at TRIM and we may exclude these points from our analysis. This leaves us with only \( K \) and \( KA \) points in the hexagonal Brillouin zone in Fig. 5. There are two questions that need to be addressed. Are there cases where there is no 1D representation at \( K \) or \( KA \)? If not, can there be the creation of a stable band degeneracy starting from the \( K \) or \( KA \) point by tuning an external parameter? The answer to the first question is no, as analysis of the inversion asymmetric groups show. The answer to the second question is yes.

We tackle the second question first because this will answer much of the first question. To determine whether stable band degeneracy can evolve from the \( K \) point, it helps to notice that protection of Weyl points is due to either \( IST \) or \( C_2, \{M_1\} \) type of symmetries when the Weyl points move off the symmetry point.

a. K point in the presence of IST

This requires the presence of sixfold rotational symmetry in the crystal because there is both \( C_2 \) and \( C_3 \) symmetry. We present the analysis for group 73, which contains only sixfold rotation in addition to translations. The expectation that the gap closes at \( K \) and that \( IST \) will protect the subsequent creation of three pairs of Weyl points is not met.

We showed previously that \( IST \) may be represented by the complex conjugation operator \( K \). On the other hand, the presence of additional symmetry such as \( C_3 \) can complicate matters because in the representation where \( IST = K, C_3 \) is not in general a diagonal matrix despite the fact that \( C_3 \) and \( C_2, \theta \) commute (because \( IST \) is antiunitary). In fact, operation of \( C_3 \) may mix states between different bands, so it may not even be possible to talk about \( C_3 \) with an arbitrary pair of bands (because the action of \( C_3 \) will take states in one of these two bands into a state from a different band).

To make this clear, begin by finding the eigenvalues of the operator \( C_3 \). Since \( (C_3)^3 = -1 \), the eigenvalues are \( e^{i(n\pi/3 + 2\pi n/3)} \) where \( n \) is an integer. If it were to be possible to
We have shown that it is possible to choose $I_{ST} = K$. However, we can speak of $C_3$ symmetry acting on these two bands depends on the eigenvalues of $C_3$ at the $K$ point. If it is possible to speak of $C_3$, the eigenvalues of the two bands must be paired as $\{-1, -1\}$ or $\{e^{i\pi/3}, e^{-i\pi/3}\}$. Otherwise, we must add two additional energy bands to get a four-band model to speak of the $C_3$ operator.

We note that this can be seen in a different way by examining how the $C_3$ eigenvalue of a state changes under the operation of $I_{ST}$. Denote a state having $C_3$ eigenvalue $e^{i(\pi/3+2n\pi/3)}$ by $|n\rangle$. Then $I_{ST}|n\rangle$ has eigenvalue $e^{-i(\pi/3+2n\pi/3)}$. This means that unless the eigenvalue is $-1$, $I_{ST}$ imposes double degeneracy. Also, if we want to talk about $C_3$ and $I_{ST}$ simultaneously on a two-band model, the eigenvalues must be paired as $\{-1, -1\}$ or $\{e^{i\pi/3}, e^{-i\pi/3}\}$, in agreement with the previous analysis.

b. $K$ point in the presence of $C_{2s}$ or $M_1$ type of symmetry

The simplest case is when there is only the threefold rotation and $C_{2s}$ or $M_1$ (twofold rotation or mirror) whose symmetry axis passes through the $K$ point, as in groups 68 and 70, respectively. The 1D representation for $C_3$ is $-1$, while those for twofold rotation or mirror is $\pm 1$. This is due to the relation $C_3P = PC_3^{-1}$, where $P$ is either $C_{2s}$ or $M_1$, which implies that unless a state has eigenvalue $-1$ for $C_3$, the representation cannot be one-dimensional.

For two pairs of energy bands whose $C_3$ eigenvalue is $-1$ at the $K$ point, it is the eigenvalues of $P$ that determine whether bands may close at the high-symmetry point. If $R_v = R_v$ for $P$, the gap does not close at the $K$ point in general because $P \propto \sigma_0$, but it may close if $R_v \neq R_v$ because $P \propto \sigma_3$. After the gap closes, there will be evolution of three pairs of Weyl points along the three high-symmetry lines that cross at the $K$ point because $R_v \neq R_v$ along these lines and the problem reduces to 11 discussed in the main text. This pattern of gap closing is labeled 31. Note that the mechanism for protection of Weyl points in this case is the same as that for $C_{2s}$ or $M_1$. 

FIG. 5. The schematic figure describing the first Brillouin zone and the relevant high symmetry points and lines for the layer groups. (a) Primitive oblique, (b) primitive rectangular, (c) centered rectangular, (d) primitive square, and (e) primitive hexagonal.
Next, we discuss the case with $C_3$ replaced by $C_6$ symmetry, which is equivalent to considering an additional $I_{ST}$ symmetry at the $K$ point. This occurs for 76 and 77, which contain $C_{2z}$ or $M_1$, respectively, in addition to $C_3$ and $I_{ST}$ at the $K$ point. From the above analysis, the only 1D representation possible is $C_3 = -1$ and $P = \pm i$, where $P = C_{2z}$ or $M_1$. The claim is that $I_{ST}$ does not force degeneracy. This is easy to see because we have already shown in Appendix B 2 that the group relation between $I_{ST}$ and $P$ is consistent with the representation, and we have shown in the previous section that the group relation between $I_{ST}$ and $C_3$ is consistent with the representation, and finally, we have shown in this section that the group relation between $C_3$ and $P$ is consistent with the representation. The conclusion follows by observing that $C_3$, $P$, and $I_{ST}$ generate the group.

Now, 76 contains 68 as a subgroup, and 77 contains 70 as a subgroup. Restricting the representation for 76 and 77 to these subgroups, we obtain the representation for 68 and 70 that was found previously. Thus we see then that if $R_c = R_c$ for $P$, the gap does not close at $K$, while if $R_c \neq R_c$, it is possible to obtain 71.

c. Possibility of additional double degeneracy at the K point

Now, we come back to the question of whether consideration of time-reversal symmetry can forbid a one-dimensional representation at the $K$ point. We begin by listing all of the possible symmetries:

$$C_3,M_2,C_{2z},M_1,M_1,\theta,C_{2zθ},I_{ST}. \quad (B8)$$

Here, $M_2$ and $C_{2z}$ is a mirror symmetry or twofold rotation symmetry that leaves invariant one of the high-symmetry lines passing through the $K$ point. They fix the line LE passing through the $KA$ point in Fig. 5(e). Note that we have not listed symmetries that can be formed by combining one of the symmetries we have listed with $C_3$, which will always be present for the hexagonal Brillouin zone. For example, $M_1$ and $M_3$, which are also mirror symmetries that leave invariant one of the high-symmetry lines passing through the $K$ point, are not listed because they can be obtained by a suitable combination of $M_2$ and $C_3$. Note also that $C_{2z}$ is a twofold rotation symmetry and $M_1$ is a mirror symmetry fixing the line $SN$ in Fig. 5(e). It can be shown by going through all of the combinations that it suffices to consider only the following symmetries in addition to $C_3$ at the $K$ point:

$$(M_1,\theta),(C_{2zθ},(I_{ST}),(M_1, I_{ST}),(C_{2z}, I_{ST}),(C_{2zθ}, M_1, \theta). \quad (B9)$$

Note that the combination is such that there is no inversion symmetry, and time-reversal symmetry appears in combination with some spatial symmetry. Before moving on, we note that there does exist one case where there is no 1D irrep because of the simultaneous presence of $M_2$ and $C_{2z}$, which has been discussed in the main text (see group 79).

We have actually carried out most of the calculations needed to determine that addition of time-reversal symmetry to the system does not prohibit 1D representation at the $K$ point. The presence of $C_{2zθ}$ or $M_1,\theta$ in addition to $C_3$ appears as a subgroup of 76 and 77, respectively. This leaves us with the case with $C_{2zθ},M_1,\theta$. However, we have already shown that it is possible to simultaneously diagonalize these symmetries, which means it is possible to talk about these symmetries acting on one band. In general, we may take $C_{2zθ} = K, M_1,\theta = \pm iK$ to satisfy (B4). A candidate representation for $C_3$ is $-1$. We have shown that this representation is consistent with the group relation between $C_{2zθ}$ and $C_3$. If $M_1,\theta = K$, our previous calculation would show that this is also consistent with $C_3 = -1$. However, the phase factor in front of $K$ is irrelevant for the group relation between $M_1,\theta$ and $C_3$. This concludes the proof.

APPENDIX C: BLACK PHOSPHOROUS

In this section, we present a simple application to the k-p model of black phosphorous. As shown in Ref. [33], the k-p Hamiltonian near the $\Gamma$ point takes the form

$$H(k_x,k_y) = A k_x \sigma_z + (M - B_1 k_x^2 - B_2 k_y^2) \sigma_z + \lambda_1 s_z \sigma_y + \lambda_2 k_y s_x. \quad (C1)$$

Here, $s_i$ and $\sigma_i$ are the Pauli matrices for spin and orbital degrees of freedom, respectively, $M$ is a tunable parameter, and $A,B_1,B_2,\lambda_1,\lambda_2$ are constants. Black phosphorous has a puckered structure, and when the symmetry is lowered by breaking the inversion symmetry, it belongs to layer group 24, which contains $M_1$ and $M_5$ symmetries (note that $M_1 M_5 \approx C_{2z}$). Although the mirror symmetries are nonisomorphic, this is irrelevant for k-p theory near the $\Gamma$ point. Taking this into account, the symmetries take the following representations:

$$M_5 = is_z \sigma_z, M_5 = is_y \theta = is_y K. \quad (C2)$$

Here, $\theta$ is the usual time-reversal symmetry. As we tune the parameter $M$, the gap may close or open along $k_x = 0$ or $k_y = 0$. Our claim is that this gap closing follows the pattern 1s.

As an example, we verify this along $k_x = 0$, along which $M_5$ is a symmetry. In particular, we show that the $M_5$ eigenvalues for the gap-closing bands are equal. To do this, set $k_y = 0$ in the Hamiltonian to get

$$H(k_x,k_y) = A k_x \sigma_z + (M - B_1 k_x^2) \sigma_z + \lambda_1 s_z \sigma_y. \quad (C3)$$
Notice that we have changed the basis in the spin sector so that $s_x \rightarrow s_z$. In this basis, $M_y = i s_z$. Now, it is easy to see that the gap closes between bands in the sector with the same $s_z$ eigenvalues, which means that the $M_y$ eigenvalues are equal for the bands that cross.

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[50] It can be shown [52] that if an antiunitary operator A satisfies A² = e⁻φ, it can be diagonalized if e⁻φ = 1, while it can only be block diagonalized with 2 × 2 matrices of the form cos φ/2σ₁ − sin φ/2σ₂ along the diagonal if e⁻φ ≠ 1.

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