Symmetry enforced line nodes in unconventional superconductors

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We classify line nodes in superconductors with strong spin-orbit interactions and time-reversal symmetry, where the latter may include non-primitive translations in the magnetic Brillouin zone to account for coexistence with antiferromagnetic order. We find four possible combinations of irreducible representations of the order parameter on high symmetry planes, two of which allow for line nodes in pseudo-spin triplet pairs and two that exclude conventional fully gapped pseudo-spin singlet pairs. We show that the former can only be realized in the presence of band-sticking degeneracies, and verify their topological stability using arguments based on Clifford algebra extensions. Our classification exhausts all possible symmetry protected line nodes in the presence of spin-orbit coupling and a (generalized) time-reversal symmetry. Implications for existing non-symmorphic and antiferromagnetic superconductors are discussed.

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Introduction:—The possibility of line-nodal odd-parity superconductivity in the presence of spin-orbit interactions has attracted recent attention \cite{1,2,3}. Blount \cite{5} has argued that odd-parity superconductivity should be free of nodal lines. Indeed, the vanishing of all three pseudo-spin triplet components is improbable for general points in the Brillouin zone, and line nodes may only occur on high symmetry planes intersecting the Fermi surface. The pseudo-spin components of the odd-parity wave function form, however, an axial vector, and in symmorphic lattices their components parallel and perpendicular to the symmetry plane transform according to different representations. This excludes a symmetry enforced vanishing of all three pseudo-spin components on the entire symmetry plane and only allows for point nodes.

The situation changes in the presence of non-symmorphic space group symmetries. Non-trivial phase factors, due to non-primitive translations, can conspire in a way to exclude representations on high symmetry planes and opens the possibility of nodal-line odd-parity superconductors \cite{4,6}. A similar situation arises in superconducting materials coexisting with antiferromagnetic (AF) order, where time-reversal symmetry only exists in conjunction with non-primitive translations in the magnetic zone. In recent work Nomoto and Ikeda \cite{7} studied one example of coexisting order which does not allow for nodal-line odd-parity superconductivity but also excludes conventional, fully gapped even-parity order parameters. A systematic understanding of the symmetry constraints which may lead to unconventional nodal properties is, however, missing. This calls for a general classification of nodal-line superconductors in the presence of spin-orbit that takes into account general non-symmorphic crystal structures and coexistence with antiferromagnetic order.

Here, we give a full classification of possible representations of the superconducting order parameter: (1) symmorphic (cases that obey Blount’s theorem), (2) non-symmorphic in space (allowing for odd-parity line nodes), (3) non-symmetric in both space and time (allowing for even-parity line nodes in antiferromagnets), and (4) non-symmetric in time (allowing for odd-parity and even-parity line nodes). That is, two of them allow for line nodes in odd-parity superconductors and two exclude conventional fully gapped even-parity pairing. The most interesting scenario, with exotic behavior in even- and odd-parity components protected by a mirror or glide plane symmetry, appears in coexistence with antiferromagnetic order, and has not been discussed previously. We derive the conditions under which each of the representations apply, verify topological stability of the line nodes, and discuss implications for existing materials.

Symmetries:—In systems with time-reversal ($\theta$) and inversion ($I$) symmetries, Kramer’s degeneracy of single-particle states survives the presence of spin-orbit interaction. The notion of spin-singlet and spin-triplet superconductivity then generalizes to corresponding pseudo-spin pairs formed out of the degenerate states $\psi$, $\theta I \psi$, $I \psi$, and $\theta \psi$. Pseudo spin-singlet and spin-triplet pairs correspond to the even, respectively odd, parity combinations. On high symmetry points in the Brillouin zone, even and odd parity pairs can be further characterized according to their transformation behavior under additional crystal symmetries. Line nodes may be symmetry-enforced on high-symmetry planes intersecting the Fermi surface. For a classification of nodal-line superconductors, it therefore suffices to concentrate on mirror symmetries $\sigma_z$ which may, however, be realized in combination with non-primitive translations.

\begin{equation}
\Sigma_z' \equiv (\sigma_z, t_z'), \quad t_z' = \begin{cases} 0 & \text{(mirror-plane)} \\ t_\parallel & \text{(mirror-plane$^*$)} \\ t_\perp & \text{(glide-plane)} \end{cases}
\end{equation}
Magnetism generally lifts the Kramer’s degeneracy of single-particle states. In the presence of antiferromagnetic order, a generalized time-reversal symmetry operates on symmetry planes $k_{\perp}$ with $[10–13]$, as referred to this symmetry as mirror* in the following. For a non-primitive translation $t_0$ within the symmetry plane, Eq. (1) is a (non-symmorphic) glide-plane operation. The absence of some of the possible representations realized on the symmetry planes.

Throughout this work, we denote space group elements by $(g, t)$ with $g$ a point group operation and $t$ a possible non-primitive translation, and we set the lattice constants to unity. Eq. (1) is a mirror reflection for vanishing translation vector. In centrosymmetric crystals, a non-primitive translation perpendicular to the symmetry plane, $t_{\perp} \equiv e_z/2$, implies the presence of a two-fold screw axis $\Sigma_{z}^{\perp}$. Despite its non-primitive translation, $\Sigma_{z}^{\perp}$ is a symmorphic operation as the translation can be removed by redefinition of the origin. Therefore, we refer to this symmetry as mirror* in the following. For a non-primitive translation $t_0$ within the symmetry plane, Eq. (1) is a (non-symmorphic) glide-plane operation. The absence of some of the possible representations for the order parameter on the basal plane ($k_z = 0$) and/or the Brillouin zone face ($k_z = \pi$) then opens the possibility of nodal-line superconductivity.

Table I: Left: Character table for representations $P^+$ of anti-symmetrized Kronecker deltas induced by single-particle representations. Here $c_d = 0, 1$ corresponds to a Kramer’s (0) and band-sticking (1) degeneracy on the symmetry plane. Right: Character table for irreducible representations of the Cooper-pair wave function on high symmetry planes.

| $\rho$ | $\mathcal{E}$ | $\Sigma_\perp$ | $\mathcal{I}$ | $\Sigma_{\perp}^{\perp}$ |
|-------|--------------|----------------|-------------|----------------|
| $+$   | $-4 \Sigma_\perp$ | $2$            | $-2$        | $2$            |
| $-$   | $-4 \Sigma_\perp$ | $2$            | $-2$        | $2$            |

Table II: Decompositions of Cooper-pair representations ($\Pi^e_k$) into irreducible components summarized in Table I (right). Here Kramer’s degeneracy and band-sticking refer to $c_d = 0$ and $c_d = 1$, respectively.

| $\rho$ | Kramer’s deg. | $\rho$ | band sticking |
|-------|---------------|-------|---------------|
| $+$   | $A_g + 2A_u + B_u$ | $-$   | $B_g + 3A_u$ |
| $-$   | $B_g + A_u + 2B_u$ | $-$   | $A_g + 3B_u$ |

wave functions with vanishing total momentum. For pair representations one thus has to separate out the anti-symmetric parts $P^-$ of the corresponding (Kronecker) products of single particle representations. $P^-$ are deduced from their characters which can be calculated from characters of the single particle representations $[11, 13]$. Applying the general recipe to our case we are left with $[12, 13]$

$$\chi(P^-(m)) = \chi(\Gamma_k(m)) \chi(\Gamma_k(Im\mathcal{I})), \quad (3)$$
$$\chi(P^-(Im)) = - \chi(\Gamma_k(Im\mathcal{I})), \quad (4)$$

where $m \in G_k$ and the left hand side defines the characters of $P^-$ for the symmetry group of Cooper pairs. For our purposes the single-particle representations $\Gamma_k$ are double-valued co-representations of the magnetic group $G_k = G_k + \Theta I G_k$, which take into account spin-orbit coupling and degeneracies due to a (generalized) time-reversal symmetry. Following this procedure we find four possible representations realized on the symmetry planes. These are summarized in Table II (left) where the values for $\rho$ and $c_d$ depend on the translations $t_\theta, t_i, t_s$. We note that the first and third characters in this table formalize the Brillouin zone face of a mirror* symmetry. On the basal plane, on the other hand, $\Pi^+$ always applies. Finally, the second character in Table II fixes the mirror eigenvalues of the induced representations. For reasons discussed below, we refer to cases $c_d = 0, 1$ as Kramer’s and band-sticking degeneracies, respectively. If $c_d = 1$ all four pairs share the same mirror eigenvalue, while $c_d = 0$ implies that two out of the four pairs have opposite mirror eigenvalues. To determine the conditions under which either of the two values $c_d$ applies, one needs to specify the single-particle co-representations $\Gamma_k$. Before doing so we first comment on implications of the four representations.

Decomposition into their irreducible components (Table II (right)) one arrives at Table III which is a central result. The four representations in this table give an exhaustive classification of nodal-line superconductors in the presence of spin-orbit, and (generalized) time-
reversal, inversion and mirror symmetries (2). Blount’s theorem on the absence of nodal-line odd-parity pairing holds whenever the Cooper pair belongs to one of the two Kramer’s degenerate representations $c_d = 0$, but may be violated in the two cases of band sticking $c_d = 1$. Moreover, out of the two representations belonging to each type of degeneracy, one excludes conventional singlet pairing with a fully gapped order parameter from $\mathcal{A}_g$.

Kramer’s degeneracies and band sticking:—The second character in Table II (left) can be expressed in terms of the single-particle co-representation (2) $\chi(P^- (\Sigma_z)) = e^{-ik(2t_e + \sigma t_y - t_i)} \chi^2 (\Gamma_k (\Sigma_z))$, and to specify $\Gamma_k$ one needs to account for degeneracies induced by $\Theta$. The latter are detected by Herring’s criterion, and for centrosymmetric crystals with (generalized) time-reversal symmetry, one either encounters Kramer’s or band-sticking degeneracies [15,17,18]. In the absence of spin-orbit, the latter occur for each spin component, and it is this fourfold degeneracy the name alludes to [11,17,18]. Both types of degeneracies are accounted for by passing from double-valued representations $\gamma_k$ of the little group to corresponding co-representations of the magnetic group $\mathcal{G}_k$. That is, $\gamma_k \rightarrow \Gamma_k \equiv (\gamma_k^m)^{-1} m \Gamma \Theta$ for Kramer’s and $\gamma_k (m) = \gamma_k (m)$ for band-sticking degeneracies [14]. One readily verifies that co-representations of the former come in pairs of opposite sign, i.e. $\chi (\Gamma_k (\Sigma_z)) = 0$ independent of translations $t_0, t_1, t_2$. Representations of band-sticking degeneracies, on the other hand, come in identical pairs, i.e. $\chi (\Gamma_k (\Sigma_z)) = \pm 2 e^{ik(2t_e + \sigma t_y - t_i)}$ and $\chi (P^- (\Sigma_z)) = -4 \rho$, as summarized in Table II [14]. Finally, inspection of Herring’s criterion gives $c_d$ as a function of the translations. For the convenience of the reader we here summarize the two equations fixing representations $\Pi^a_2$ [13],

$$(-1)^{c_d} = e^{2ik_\parallel e_z \cdot (t_0 + t_y - t_z)} ,$$

$$\rho = e^{2ik_\parallel e_z \cdot (t_0 - t_y)} .$$

Eqs. (5), (6) are a central result and allow to identify the pair representation from the translation vectors defining the basic symmetries Eq. (2). Band sticking occurs for vanishing $t_0$ on the Brillouin zone face of a mirror symmetry in the absence of magnetic order, or a mirror symmetry with coexistent antiferromagnetic order $t_0 = t_\perp$. We also notice that glide and mirror symmetries have identical implications for the nodal structure. We next verify topological protection of the encountered line nodes [3], which allows to extend the above results to more general conditions such as pairing of non-degenerate states in multi-band systems.

Topological stability of line nodes:—We recall that a line node is topologically stable if the space of Dirac Hamiltonians describing its vicinity, and accounting for all symmetries leaving it invariant, has a non-trivial topology [2]. The topology of this “classifying space” $\mathcal{Q}$ is encoded in a Clifford algebra extension problem [20], which counts how many topologically distinct ways a “mass term” $H^I = \psi_i k_i \gamma_0$ can be added to $H = \psi_\parallel (k_z - \pi) \gamma_1$ without violating symmetry constraints [21]. Here $k_i$ is the momentum parallel to the mirror-invariant zone face, $\gamma_0, \gamma_1$ are positive generators [22] of a Clifford algebra, and “counting ways” refers to the number of (path-)connected components as encoded in the zeroth homotopy group $\pi_0 (\mathcal{Q})$. In practical terms, we need to identify the Clifford algebra spanned by $\gamma_0, \gamma_1$, a generator $\gamma_2$ representing the complex unit $J$, and three further generators $\gamma_3, \gamma_4, \gamma_5$ representing the symmetries of the line node, $\mathcal{IC}$, $\mathcal{I} \Theta$, and $\Sigma_z$ with $\mathcal{C}$ the particle-hole symmetry [23]. The algebra is determined by the (anti-)commutation relations between the symmetry elements once the reflection and mirror eigenvalues of the order parameter have been specified. Referring for details to Ref. [13] we notice that in our context only those conditions Eq. (6) which indicate band sticking lead to a topologically nontrivial classifying space, $\pi_0 (\mathcal{Q}) = \mathbb{Z}$. That is, the topological protection of a nodal-line superconductor should be related to the band sticking.

Applications:—Our results are summarized in Table III. On the basal plane the absence of non-trivial phase factors associated with non-primitive translations implies symmorphic behavior of representation $\Pi^z_\parallel$ (first entry in Table III). The latter is characterized by the validity of Blount’s theorem, i.e. the absence of odd-parity nodal-line superconductors, and possibility of conventional fully gapped singlet pairing. Interesting behavior can be expected on the Brillouin zone face where, depending on the symmetries encoded in the translations $t_\theta, t_\perp, t_\sigma$, all four cases can be realized. The second entry in Table III, representation $\Pi^z_\perp$, has been previously discussed in Refs. [4,7] and is here generalized to include glide plane symmetries [24], and coexistence with antiferromagnetic order. A scenario summarized by representation $\Pi^z_0$, third entry in the table, has recently been studied by Nomoto and Ikeda [4]. Finally, representation $\Pi^z_1$, given in the fourth entry, has to our knowledge not been discussed before.

Table IV lists a number of non-symmorphic and antiferromagnetic superconductors with their space group symmetry, non-symmorphic group operations (GO), the experimentally indicated nodal structure (Node) and pair representation (Rep) obtained from our analysis. As we discuss next, for several of these examples the observed non-symmorphic behavior is in agreement with the indicated pair representations [13].

As pointed out in several recent works [1, 2, 6, 7], the pair representation $\Pi^z_\parallel$ may be realized in UPt$_3$ where the Fermi surface intersects the symmetry plane $k_z = \pi$ of a mirror* symmetry $\Sigma_z = (\sigma_y, e_z/2)$. As discussed in Ref. [13] the same may occur for Na$_2$CoO$_2$, Li$_2$Pt$_3$B, and CrAs. This is readily verified from Eqs. (5), (6) noting that $t_\theta, t_\perp = 0$ and $t_\sigma = e_z/2.$ Our above analysis fur-
Indeed, translation vectors defining pair symmetries on the Brillouin zone face is $t = t_r = t_a$ and $t_x = t_z = t_0$. Inserting these vectors into Eqs. (5), (6) one readily verifies that the representation $\Pi_1$ also applies in the presence of the antiferromagnetic order. Moreover, symmetry planes $\Sigma_x = \{0, x, t_x, t_0\}$ and $\Sigma_y = \{y, t_y, t_0\}$ lead to interesting behavior on the AF Brillouin zone faces $k_x = \pi/\sqrt{3}$ and $k_y = \pi$. With $t_0 = t_r = t_a$ and $t_x = t_z + t_a$, respectively, one identifies with the help of Eqs. (9), (10) replacing as well $k_x$ by $k_y$ and $k_y$, respectively, the pair representation $\Pi_1$ on both zone faces. Since Fermi surfaces intersect both of these two zone faces, this opens up the possibility for $B_u$ line nodes for AF UPt3 and also implies the absence of conventional fully gapped even-parity pairing.

UPd$_2$Al$_3$ provides a further interesting example, as recently discussed in Ref. [4]. The Fermi surface intersects the symmetry plane $k_x = \pi$ of a mirror $\sigma_y$ symmetry. For antiferromagnetic order along the $c$-axis and orientation of the moments within the basal plane, the translations are $t_0 = e_z/2$, $t_y = e_z/2$ and $t_0 = 0$. From Eqs. (9), (10) one readily finds the pair representation $\Pi_1^\perp$, implying the absence of conventional fully gapped $s$-wave superconductivity and consistency with Blount’s theorem [4]. For magnetic moments oriented along the $c$-axis, on the other hand, $t_x = 0$ while the other translations are unchanged. A brief glance at Eqs. (3), (4) then shows that the pair representation on the Brillouin zone face is $\Pi_1^\perp$ in this case. The latter allows for odd parity line nodes, while the conclusion on the absence of conventional fully gapped $s$-wave superconductivity is unaltered. The same considerations apply for UNi$_2$Al$_3$ for the $c$-axis zone face, since the AF wave vector along $c$ is the same as UPd$_2$Al$_3$.

**Summary and discussion:** We have studied Cooper pair representations for superconductors with spin-orbit and magnetic order. We have shown that on high symmetry planes there exist four possible representations. Two of these provide counter examples to Blount’s theorem, allowing for nodal-line odd-parity superconductivity, and two exclude conventional fully gapped even-parity pairing. The $A_u$ line node has been previously discussed [6, 7], and the $B_u$ line node has to our knowledge not been studied before. The latter can be readily understood noting that the degenerate states forming pseudo-spin pairs, $\psi, \theta\psi, \Gamma$, and $\psi, \theta\psi$, all have the same mirror eigenvalue [28]. We provided simple formulas which allow to identify the pair representation from the translation vectors $t_0, t_x, t_z$, of the (generalized) symmetries Eq. (3). We have illustrated how a straightforward application of the results gives interesting insights into the unconventional nodal structure of superconductors U$\text{Pt}_3$ and UPd$_2$Al$_3$, with other examples shown in Table IV that are discussed more in Ref. [15]. Given the simplicity of Eqs. (7), (9), we hope that they will prove useful in our understanding of known and yet to be discovered unconventional superconductors. Finally, we have verified topological stability of the encountered line nodes of odd parity superconductors. Due to band degeneracies along symmetry lines on the zone face in the non-symmorphic case, these nodes can form nodal loops [1, 2, 22], which implies a topological phase transition once the ratio of the superconducting gap to the spin-orbit splitting of the bands exceeds a critical value.

Consequences for possible topological surface states is an interesting question open for future investigation.

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| $t_0$ | pair-representation | implications |
|-------|---------------------|--------------|
| $T$ | $\Pi_0^\perp = A_0 + 2A_0 + B_0$ | “symmorphic behavior” |
| $T$ | $\Pi_1^\perp = A_0 + 3A_0$ | “odd-parity line nodes” |
| $t_x$ | $\Pi_1^\perp = B_0 + A_0 + 2A_0$ | “nodal even-parity SC” |
| $T$ | $\Pi_1^\perp = B_0 + 3A_0$ | “nodal even-parity SC” |

Table III: Summary of results where $T = \{0, t_0\}$ refers to translation vectors within the mirror plane and $t_{x,z}$ to a non-vanishing perpendicular component. Here “symmorphic behavior” refers to the absence of line nodes in odd-parity superconductors (Blount’s theorem) and the possibility of conventional fully gapped singlet pairing, and “nodal even-parity SC” to the impossibility of the latter. Entry 2 is realized for U$\text{Pt}_3$, Na$_x$CoO$_2$, Li$_2$Pt$_3$, and CrAs, entry 3 for UPd$_2$Al$_3$ and UNi$_2$Al$_3$, and entry 4 for U$\text{Pt}_3$ in the AF phase.
Notice that here and in the following a positive (negative) generator \( \gamma \) refers to the square \( \gamma^2 = 1 \) (\( \gamma^2 = -1 \)).

Notice that \( \varepsilon \), \( \zeta \), and \( \Theta \) individually invert momentum, but the above combinations leave \( k \) and thus the line node invariant.

Here and in the following a positive (negative) generator \( e_\pm \) are directed along \( e_x \). But long range order only sets in at very low temperatures, see Y. Koike, N. Metoki, N. Kimura, E. Yamamoto, Y. Haga, Y. Onuki and K. Maezawa, J. Phys. Soc. Japan 67, 1142 (1998).

The pair symmetry group on the Brillouin zone face \( k_z = \pi \) reads \( G_k \cup iG_k = \{ (E, 0), (\sigma_z, t_z + t_\alpha), (I, t_\alpha), (2\pi, t_z) \} \).

The small moments are directed along \( e_x \). But long range order only sets in at very low temperatures, see Y. Koike, N. Metoki, N. Kimura, E. Yamamoto, Y. Haga, Y. Onuki and K. Maezawa, J. Phys. Soc. Japan 67, 1142 (1998).

Following the argument presented in Ref. [2] for the \( A_n \) line node, it is verified that the (anti-)commutation relations \( \{ \Sigma_z, \Theta \} = 0 \), \( [\Sigma_z, \mathcal{I}] = 0 \) imply that for \( \Sigma_z \psi = i\psi \) also \( \Sigma_z \Theta \psi = i\Theta \psi \), \( \Sigma_z \mathcal{I} \psi = i\psi \), and \( \Sigma_z \mathcal{I} \Theta \psi = i\mathcal{I} \Theta \psi \).
In this Supplemental Material, we give details on the group theory calculation of the Cooper pair representations. We calculate characters of the induced representations and those entering Herring's criterion, and determine the single particle co-representations of the magnetic group. We further provide details on the Clifford algebra extension method and verify the topological stability of the line nodes of odd parity order parameters discussed in the main text. Finally, we discuss a number of other examples of non-symmetric and antiferromagnetic superconductors.

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I. PAIR REPRESENTATIONS

We present details on the group theory calculation of the pair representations summarized in Table I of the main text.

Characters of induced representations

Starting from induced representations Eqs. (3) and (4) in the main text, we define characters for the Cooper pair symmetry group $G_k \cup T Z G_k = \{ E, \Sigma_z, T, \Sigma_z \}$ where $G_k = \{ E, \Sigma_z \}$ is the little group. Anticipating two-fold degeneracy of the single-particle states (as confirmed by Herring’s criterion), all single-particle co-representations $\Gamma_k$ are two-dimensional, i.e. $\chi(P^{-}(E)) = \chi^{2}(\Gamma_k(E)) = 4$ and $\chi(P^{-}(T)) = -\chi(\Gamma_k(E)) = -2$. Employing the multiplication rule for non-symmetric group elements, $(g_1, t_1)(g_2, t_2) = (g_1g_2, t_1 + g_1t_2)$, one finds $|\Sigma_z|^2 = (\sigma_z^2, t_\sigma - t_\sigma (t_\sigma - t_\sigma))$ and $\chi(P^{-}(\Sigma_z)) = \chi(\Gamma_k(E, t_i - t_\sigma (t_\sigma - t_\sigma))) = 2e^{2ikz_e} \rho (t_{i_\sigma}t_\sigma)$, or $\rho = e^{2ikz_e} \rho (t_{i_\sigma}t_\sigma)$. Similarly, $\Sigma_z T = (E, t_i - \sigma_z t_i - 2t_\sigma) \Sigma_z$ and $\chi(P^{-}(\Sigma_z)) = e^{-ik(2t_\sigma + \sigma_z t_i - t_\sigma)} \chi^{2}(\Gamma_k(\Sigma_z))$.

Herring’s criterion

Degeneracies induced by $\Theta$ are conveniently detected by Herring’s criterion from summing characters of double-valued representations $\gamma_k$ of the little group $\{ I, \bar{I} \}$, $Z(\gamma_k) \equiv \sum_{m \in G_k} \chi(\gamma_k([I \Theta m]^2))$. For centrosymmetric crystals with (generalized) time-reversal symmetry, the two possible outcomes $Z = 0, 1$ indicate the presence of Kramer’s, respectively, band-sticking degeneracies.

To apply Herring’s criterion in our case, we need to sum two characters of the one-dimensional single-particle representations $\gamma_k$. That is, $\chi(\gamma_k([I \Theta E]^2)) = -1$, and $\chi(\gamma_k([I \Theta \Sigma_z]^2)) = \chi(\gamma_k(E, 2t_\sigma (t_\theta - t_\sigma) - t_\theta - t_\sigma)) = e^{ik(2t_\sigma + \sigma_z t_i - t_\sigma)} \chi(\bar{I} \Sigma_z)$. Here we used the multiplication rule for the magnetic group $g_1g_2 = -g_1g_2$, to find $[I \Theta E]^2 = -E$ and $[I \Theta \Sigma_z]^2 = -(\sigma_z^2, \sigma_z (t_\theta + t_\sigma - t_\theta) - t_\theta - t_\sigma + t_i)$.

Co-representations

The only character of the induced representation that we need to explicitly calculate is $\chi(P^{-}(\Sigma_z)) = e^{-ik(2t_\sigma + \sigma_z t_i - t_\sigma)} \chi^2(\Gamma_k(\Sigma_z))$ fixing the mirror eigenvalue of the Cooper pairs. To this end we first need to specify co-representations for the two types of degeneracies. Notice that the one-dimensional single-particle representation $\gamma_k(\Sigma_z) = \pm e^{ik(\sigma_z t_\sigma + t_\sigma)/2}$ and $\gamma_k(\Sigma_z T) = \pm ie^{-ik(\sigma_z t_\sigma + t_\sigma)/2}$. Therefore $\Gamma_k(\Sigma_z) = \pm e^{ik(\sigma_z t_\sigma + t_\sigma)/2} (i \perp)$ in the case of a Kramer’s degeneracy and $\Gamma_k(\Sigma_z) = \pm e^{ik(\sigma_z t_\sigma + t_\sigma)/2} (i \perp)$ in the case of band sticking. That is, Kramer’s degeneracies lead to pairs of complex conjugate representations while band sticking doubles the representations. This implies that $\chi(P^{-}(\Sigma_z)) = 0$ and $\chi(P^{-}(\Sigma_z)) = -4e^{-2ikz_e} \rho (t_{i_\sigma}t_\sigma)$ for a Kramer’s degeneracy and band-sticking, respectively, or $\chi(P^{-}(\Sigma_z)) = -4e^{-2ikz_e} \rho$ as stated in the main text.

II. CLIFFORD ALGEBRA EXTENSIONS

We here discuss in detail the Clifford algebra extension method and verify the topological stability of line nodes of odd parity order parameters. Let us recall the criterion for band-sticking ($c_d = 1$), respectively Kramers degeneracy ($c_d = 0$) given in the main text,

$(-1)^c_d = e^{2ikz_e} \rho (t_\theta + t_\sigma - t_\theta)$.  
(7)

Only the former allow for line nodes of odd parity superconductors, and to study topological stability of this case we may thus concentrate on the Brillouin zone face $k_z = \pi$ and translations $t_\theta, t_\sigma, t_i \in \{ 0, t_\perp \}$. To simplify the presentation we first assume that $t_\theta = 0$ and then discuss what changes for $t_i = t_\perp$. Topological arguments
showing the absence of nodal line odd parity superconductors for $t_\theta, t_\sigma = 0$ have been introduced in Ref. 3. Moreover, topological stability of the $A_u$ line node for $t_\theta = 0$, $t_\sigma = t_1$ has been discussed in the recent work Ref. 4. We will first recall the calculation of Ref. 4 demonstrating topological stability of the latter has been discussed in the recent work Ref. 3. Here $\gamma$ represents the imaginary unit $i$, e.g. $\gamma^2 = 1$, and $J$ is negative, i.e. $J^2 = -1$.

The fundamental symmetries to be included into the algebra and discussed in the main text include combinations of particle-hole symmetry $C$, (generalized) time-reversal symmetry $T$ and inversion symmetry $I$ [4]. The latter have commutation relations (i.e., $i = 0, 1$)

$$\{\Theta, J\} = 0, \quad \{\Theta, \gamma_i\} = 0, \quad [\Theta, C] = 0, \quad [C, J] = 0, \quad \{I, J\} = 0, \quad \{I, \gamma_i\} = 0, \quad (8)$$

and we recall that $C$ and $I$ are both positive, i.e. $C^2 = 1$ and $I^2 = 1$. Anti-commutation between particle-hole and inversion symmetry accounts for the fact that we are here considering odd-parity superconductors. The commutation relation between $\Theta$ and $I$ and the sign of $\Theta^2$ both depend on the presence or absence of antiferromagnetic order, i.e.

$$[\Theta, I] = 0, \quad \Theta^2 = -1, \quad (PM)$$

$$\{\Theta, I\} = 0, \quad \Theta^2 = 1, \quad (AF), \quad (11)$$

where in the second line we restricted ourselves to the case of interest $t_\theta = t_1$ and the Brillouin zone face $k_z = \pi$. Finally, the mirror symmetry $\Sigma_z$ is negative, i.e. $\Sigma_z^2 = -1$, and has the following commutation relations

$$\{\Sigma_z, \gamma_i\} = 0, \quad [\Sigma_z, J] = 0, \quad C\Sigma_z = \eta_C \Sigma_z C, \quad \{9\}$$

In the last equation $\eta_C = +/-$ applies for pairs with positive/negative mirror eigenvalues, i.e. for order parameters from representations $B_u$ and $A_u$, respectively. Commutation relations involving $\Sigma_z$ depend on the absence/presence of magnetic order and of a non-primitive translation. That is, for the cases of interest (and concentrating here on $t_i = 0$)

$$[\Theta, \Sigma_z] = 0 \quad (PM), \quad [\Sigma, \Sigma_z] = 0 \quad (mirror), \quad (13)$$

$$\{\Theta, \Sigma_z\} = 0 \quad (AF), \quad \{\Sigma, \Sigma_z\} = 0 \quad (mirror), \quad (14)$$

where the second line applies for $t_\theta, t_\sigma = t_1$, and we again used that for our purposes $k_z = \pi$. In the absence of time-reversal and mirror plane symmetries, the Clifford algebra accounting for all symmetries leaving the line node invariant reads

$$Cl_{2,2} = \{\gamma_0, \gamma_1, \gamma_2 \equiv JCI, \gamma_3 \equiv CI\}, \quad (15)$$

where 2, 2 refers to the two positive ($\gamma_0, \gamma_1$) and two negative ($\gamma_2, \gamma_3$) elements.

*Extension problem:*—Eq. (15) is the starting algebra to which then generators $\gamma_4, \gamma_5$ representing $\Theta$ and $\Sigma_z$, respectively, are added. As detailed below, we will encounter the following three situations: (i) the elements $\gamma_0, ..., \gamma_5$ can all be chosen to mutually anti-commute and define a real Clifford algebra $Cl_{p,6-p}$, where $p = (6-p)$ refers to the number of negative (positive) generators. (ii) five out of the six elements mutually anti-commute, but commute with the remaining positive element $\gamma_i$. The latter effectively decouples, reducing the real Clifford algebra to $Cl_{6-p,p}$. (iii) a situation as in (ii) with negative $\gamma_i$, which defines a complex algebra and the resulting complex Clifford algebra of anti-commuting elements $Cl_5$. The extension problem then compares symmetry groups of the Clifford algebra obtained after $\gamma_0$ has been removed with that of the full algebra. The latter is a subset of the former and their quotient defines the manifold of mass terms, i.e. the classifying space $Q$. Removing $\gamma_0$ from the algebra corresponds to passing from $Cl_{p,q}$ (with $\gamma_0$) to $Cl_{p,q-1}$ (without $\gamma_0$) in the real cases, and correspondingly from $Cl_6$ to $Cl_4$ in the complex case. The invariance groups of the corresponding algebras and their quotients define the (symmetric) classifying space $Q$ of the extension problem. Finally, classifying spaces $R_i$ and $C_i$ for all real and complex extension problems, respectively, as well as their homotopy groups can be looked up in Ref. 5. As discussed in the main text, we will find that in our context only the complex extension problem $Cl_4 \rightarrow Cl_5$ has a topologically nontrivial classifying space, $\pi_0(Q) = Z$. That is, the presence of a commuting negative symmetry-element $\gamma_i$ is equivalent to the topological protection of a nodal-line superconductor and should be related to the band sticking.

*Paramagnet with screw axis*—From commutation relations summarized in Table IV, one notices that the negative element $\Theta C$ anti-commutes with all Clifford algebra elements [15]. That is, the time-reversal invariant system defines the Clifford algebra $Cl_{3,2} = \{\gamma_0, \gamma_1, \gamma_2 \equiv JCI, \gamma_3 \equiv CI, \gamma_4 \equiv \Theta C\}$. Next, we include the mirror
mirroring eigenvalues, i.e. order parameters from representations resulting from a twofold screw axis, i.e. order parameters from representations resulting from a twofold screw axis, i.e.

Accounting for all symmetry elements, one thus arrives at the Clifford algebra generators. That is, we start from the Clifford algebra accounting for all symmetry elements is complex, and we then include the mirror plane symmetry.

The extension problem then reads $Cl_{4,1} \rightarrow Cl_{4,2}$ with classifying space $R_5$. The trivial topology $\pi_0(R_5) = 0$ confirms the absence of protected line nodes for odd-parity superconductors from $B_u$ also encountered from the group theory analysis. For order parameters from $A_u$ with negative mirror eigenvalue, one finds that the negative element $\gamma_5 \equiv J\Sigma_\gamma$ anti-commutes with all Clifford algebra generators. This element generates the algebra $Cl_{4,0} = \{\gamma_5\}$ which introduces the complex unit $i$ into the Clifford algebra accounting for all symmetries. That is the latter is the complex algebra $Cl_5 = \{\gamma_0, \gamma_1, \gamma_2, \gamma_3, \gamma_4\} \otimes Cl_{4,0}$, and the extension problem reads $Cl_4 \rightarrow Cl_5$ with classifying space $C_0$ and non-trivial topology $\pi_0(C_0) = \mathbb{Z}$. The latter shows the topological protection of line nodes for odd-parity superconductors from $A_u$ discussed in the second entry of Table III in the main text. The above example has been first mentioned in Ref. [4]. We next discuss how the results change in the presence of antiferromagnetic order corresponding to the cases summarized in the third and fourth entries of Table III in the main text.

“Antiferromagnet with screw axis”:—From commutation relations summarized in Table VI, one notices that the negative element $\gamma_4 \equiv \Theta CJ$ anti-commutes with all other Clifford algebra elements. Upon inclusion of a (generalized) time-reversal symmetry, one thus arrives at the Clifford algebra $Cl_{3,2} = \{\gamma_0, \gamma_1, \gamma_2 \equiv JCI, \gamma_3 \equiv CI, \gamma_4 \equiv \Theta CJ\}$. Concentrating first on order parameters from $B_u$, it can be verified that the positive element $\gamma_5 \equiv C\Theta J\Sigma_\gamma$ commutes with all other Clifford algebra generators. The latter defines the algebra $Cl_{0,1} = \{\gamma_5\}$ and the conjunction of all symmetry elements defines the algebra $Cl_{3,2} \otimes Cl_{0,1}$. The extension problem is not modified by the second tensor component, i.e. is given by $Cl_{3,1} \rightarrow Cl_{3,2}$ with a topologically trivial classifying space $R_6$ with $\pi_0(R_6) = 0$. For order parameters from $A_u$, one finds that the positive element $\gamma_5 \equiv \Sigma_\gamma \gamma_1$ anti-commutes with all Clifford algebra generators, defining the algebra $Cl_{3,3} = \{\gamma_0, \gamma_1, \gamma_2 \equiv JCI, \gamma_3 \equiv CI, \gamma_4 \equiv \Theta CJ, \gamma_5 \equiv \Sigma_\gamma \gamma_1\}$. The extension problem then reads $Cl_{3,2} \rightarrow Cl_{3,3}$ with again a topologically trivial classifying space $R_7$ with $\pi_0(R_7) = 0$. This shows that antiferromagnetic order destabilizes the line node encountered for crystals with twofold screw axes, as also found from our group theory analysis summarized in the third entry of Table III of the main text.

“Symmorphic antiferromagnet”:—In the case where $\Sigma_z$ is a conventional mirror symmetry with $t_\sigma = t_\perp$, we again include $\gamma_4 \equiv \Theta CJ$ to account for a generalized time-reversal symmetry. That is, we start from the Clifford algebra $Cl_{3,2} = \{\gamma_0, \gamma_1, \gamma_2 \equiv JCI, \gamma_3 \equiv CI, \gamma_4 \equiv \Theta CJ\}$, to which we then include the mirror plane symmetry. Concentrating on order parameters from $B_u$ with positive mirror eigenvalue, we find from commutation relations summarized in Table VI that the negative element $\gamma_5 \equiv C\Theta J\Sigma_\gamma$ commutes with all other Clifford algebra generators. The situation is then similar to that encountered for $A_u$ order parameters in a paramagnet with a twofold screw axis. The Clifford algebra accounting for all symmetry elements is complex, $Cl_5 = Cl_{3,2} \otimes Cl_{1,0}$, giving rise to the extension problem $Cl_4 \rightarrow Cl_5$ with classifying space $C_0$. The nontrivial topology $\pi_0(C_0) = \mathbb{Z}$ again indicates the topological protection of line nodes, now for a representation $B_u$ as defined in the fourth entry of Table VII:

| $\Theta$ | $C$ | $J$ | $\bar{T}$ | $\gamma_1$ | $\gamma_0$ | $\Sigma_z$ |
|----------|-----|-----|-----------|------------|------------|------------|
| $\gamma_0$ | $-$ | $+$ | $-$ | $-$ | $-$ | $+$ |
| $\gamma_1$ | $-$ | $-$ | $-$ | $-$ | $-$ | $-$ |
| $\gamma_2 \equiv JCI$ | $-$ | $-$ | $-$ | $-$ | $-$ | $-$ |
| $\gamma_3 \equiv CI$ | $-$ | $-$ | $-$ | $-$ | $-$ | $-$ |
| $\gamma_4 \equiv \Theta CJ$ | $-$ | $-$ | $-$ | $-$ | $-$ | $-$ |
Table III in the main text. Finally, for order parameters from $A_u$ with negative mirror eigenvalue, one finds that the negative element $\gamma_5 \equiv J\Sigma_z \gamma_1$ anti-commutes with all Clifford algebra generators. Including this element, one arrives at the Clifford algebra $Cl_{4,2} = \{\gamma_0, \gamma_1, \gamma_2 \equiv JC I, \gamma_3 \equiv CI, \gamma_4 \equiv \Theta C J, \gamma_5 \equiv J\Sigma_z \gamma_1\}$. This defines the extension problem $Cl_{3,2} \rightarrow Cl_{4,2}$ with trivial classifying space $R_3$, with $\pi_0(R_3) = 0$.

Inversion with finite translation:—We may now straightforwardly extend the above analysis to the case $t_0 = t_L$. To this end we notice that for general $t_i, t_\sigma$ the second of Eq. (13) changes to

$$\Sigma_z = e^{2ik_z \cdot \mathbf{R}} e^{(t_x - t_y)I_z} I_x,$$  \hspace{1cm} (16)

where we employed that $t_\sigma, t_i = \{0, t_L\}$. It is then evident that leaving $t_i \in \{0, t_L\}$ unspecified, the above calculation can be repeated and generalizes the demonstration of topological stability of an $A_u$, respectively $B_u$, line node to those conditions leading to band sticking ($c_d = 1$) in Eq. (7).

III. MORE EXAMPLES

In the main text, we concentrated on the well studied case of UPt$_3$. But there are a number of other unconventional superconductors which are characterized by non-symmorphic space groups, many of which are suspected to be odd-parity superconductors. These are tabulated in Table VIII along with the two antiferromagnetic superconductors discussed in the text. Much of the information on the uranium-based superconductors can be found in Ref. 7. There are others we do not discuss, since not enough is known about their properties. For instance, the topological semimetal Cd$_3$As$_2$ becomes superconducting under pressure with the space group P$2_1/c$ 8, but its nodal properties and Fermi surface (in the high pressure phase) are not known at present.

We now discuss each of these cases in turn. The nodal properties of UPt$_3$ have been known for a long time 7,8,11. Strong evidence for line nodes have been found from specific heat 12, thermal conductivity 13, and transverse ultrasound 14, with the lack of a change in the Knight shift below $T_c$, indicating triplet behavior 15. An $E_{2u}$ order parameter has been inferred from phase sensitive Josephson tunneling 16. Two of the five Fermi surfaces cross the zone face along the $k_z$ direction 17.

Superconducting sodium-doped (and water intercalated) CoO$_2$, with the same space group as UPt$_3$, has been heavily studied as well 18. Band structure calculations 19 reveal Fermi surfaces that also cross the zone face along the $k_z$ direction (later found to be consistent with ARPES 20). Specific heat 21, Knight shift 22, and the spin lattice relaxation rate 23 are consistent with line nodes. Knight shift data 22 have been interpreted as either a singlet or a triplet with the d-vector orthogonal to $c$.

| Space Group | GO | Node | Spin |
|-------------|----|------|------|
| UPt$_3$     | P$\bar{6}$/mmc | S,G | line | T |
| Na$_x$CoO$_2$ | P$\bar{6}$/mmc | S,G | line | S,T |
| Li$_2$Pd$_3$B | P$\bar{4}$/32 | S,I | line | T |
| UBe$_{13}$  | Pnma | S,G,H | line | ? |
| CrAs        | Pnma | S,G,H | line | ? |
| MnP         | Pnma | S,G,H | ?   | ? |
| UPd$_2$Al$_3$ | P6/mmm | AF | line | S |
| UNi$_2$Al$_3$ | P6/mmm | AF | line | T |

Table VIII: Properties of non-symmorphic superconductors (first six entries) and antiferromagnetic superconductors (last two entries). For GO (group operations), S indicates a screw axis, G a glide plane, I a lack of inversion symmetry, H a helical magnet, and AF non-symmorphicity induced by antiferromagnetism. Node means the experimentally indicated nodal structure (line, point, or ? for unknown), and Spin denotes singlet (S) or triplet (T) behavior (both have been advocated for Na$_x$CoO$_2$).

Li$_2$Pd$_3$B and Li$_2$Pt$_3$B have the P$\bar{4}$/32 chiral space group that breaks inversion 24. The Pd version appears to be a fully gapped superconductor, but for the Pt version, specific heat 25, penetration depth 26 and NMR 27,28 are consistent with line nodes. A lack of change of the Knight shift below $T_c$ 27,28 indicates triplet behavior. Band structure calculations 29,30 predict Fermi surfaces at the zone face. Thus, all of these cases (UPt$_3$, Na$_x$CoO$_2$, and Li$_2$Pt$_3$B) are consistent with our analysis indicating the possibility of line nodes at the zone face for odd-parity representations, though for Li$_2$Pt$_3$B, parity mixing is possible that could alter the nodal structure.

The well known heavy fermion superconductor UBe$_{13}$ also has a non-symmorphic space group, but one which only has glide operations. Specific heat 31 and penetration depth 32 are consistent with point nodes, which agrees with our previous analysis 32 that glide operations do not induce line nodes. A lack of change of the Knight shift below $T_c$ 34 indicates triplet behavior.

Recently, the helical magnets CrAs 35 and MnP 36 have been found to be superconducting under high pressures. Both are characterized by the space group Pnma, which has screw axes associated with all three crystallographic axes, and glide planes associated with two of them. NQR on CrAs is consistent with line nodes 37, and band structure calculations 38 indicate small pockets around the $Y$ point on the zone face. Again, this is consistent with our analysis.

The case of UPd$_2$Al$_3$ was discussed extensively by Nomoto and Ikeda 39. Its sister compound, UNi$_2$Al$_3$, is strongly suspected of being a triplet superconductor given the lack of change of the Knight shift below $T_c$ 40, as opposed to UPd$_2$Al$_3$ that appears to be a singlet 13. NMR indicates line nodes 41. UNi$_2$Al$_3$ is an incommen-
surate antiferromagnet with a $Q$ vector of $(1/2 \pm \delta, 0, 1/2)$ and moments perpendicular to $c$ [42]. Thus for the zone face perpendicular to $c$, these two cases are the same since $Q_z$ is the same, as discussed in the main text.

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