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 nonprimitive 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 pseudospin-triplet pairs and two that exclude conventional fully gapped pseudospin-singlet pairs. We show that the former can only be realized in the presence of band-sticking degeneracies, and we 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 nonsymmorphic 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 [1–4]. Blount [5] has argued that odd-parity superconductivity should be free of nodal lines. Indeed, the vanishing of all three pseudospin triplet components is improbable for general points in the Brillouin zone, and line nodes may occur only on high-symmetry planes intersecting the Fermi surface. The pseudospin components of the odd-parity wave function form, however, an axial vector, and in symmorphic lattices its components parallel and perpendicular to the symmetry plane transform according to different representations. This excludes a symmetry-enforced vanishing of all three pseudospin components on the entire symmetry plane and allows for only point nodes.

The situation changes in the presence of nonsymmorphic space group symmetries. Nontrivial phase factors due to nonprimitive translations can conspire in a way to exclude representations on high-symmetry planes and open the possibility of nodal-line odd-parity superconductors [6,7]. A similar situation arises in superconducting materials coexisting with antiferromagnetic (AFM) order, where time-reversal symmetry exists only in conjunction with nonprimitive translations in the magnetic zone. In recent work, Nomoto and Ikeda [4] 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 nonsymmorphic crystal structures and coexistence with antiferromagnetic order.

Here, we give a full classification of possible representations on high-symmetry planes under such general conditions. There are four combinations of irreducible representations of the superconducting order parameter: (1) symmorphic (cases that obey Blount's theorem), (2) nonsymmorphic in space (allowing for odd-parity line nodes), (3) nonsymmorphic in both space and time (allowing for even-parity line nodes in antiferromagnets), and (4) nonsymmorphic 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 the 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 (θ) 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 pseudospin pairs formed out of the degenerate states ψ, $\theta I\psi$, $I\psi$, and $\theta\psi$ [8]. Pseudospin-singlet and -triplet pairs correspond to the even- and odd-parity combinations, respectively [9]. 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 σ_z, which may, however, be realized in combination with nonprimitive translations,

$$\Sigma_z' \equiv (\sigma_z, \mathbf{t}_\sigma'), \qquad \mathbf{t}_\sigma' = \begin{cases} 0 & \text{(mirror plane)} \\ \mathbf{t}_\perp & \text{(mirror plane}^*\text{)} \\ \mathbf{t}_\parallel & \text{(glide plane)} \end{cases} \tag{1}$$

Throughout this Letter, we denote space group elements by $(g, \mathbf{t})$, with g being a point group operation and $\mathbf{t}$ a possible nonprimitive translation, and we set the lattice constants to unity. Equation (1) is a mirror reflection for a vanishing translation vector. In centrosymmetric crystals, a nonprimitive translation perpendicular to the symmetry plane, $\mathbf{t}_\perp \equiv \mathbf{e}_z/2$, implies the presence of a twofold screw axis $\mathcal{I}\Sigma_z'$. Despite its nonprimitive translation, Σ_z' 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 nonprimitive translation $\mathbf{t}_\parallel$ within the symmetry plane, Eq. (1) is a (nonsymmorphic) 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.

Magnetism generally lifts the Kramer's degeneracy of single-particle states. In the presence of antiferromagnetic order, a generalized time-reversal symmetry operation is preserved which contains a nonprimitive translation in the magnetic Brillouin zone. Lattice symmetries may be affected in a similar fashion, and to account for these effects we introduce the generalized symmetries

$$\Theta \equiv (E, \mathbf{t}_\theta)\theta, \qquad \mathcal{I} \equiv (I, \mathbf{t}_i), \qquad \Sigma_z \equiv (\sigma_z, \mathbf{t}_\sigma). \tag{2}$$

Here, E is the identity element of the point group, $\mathbf{t}_\theta$ the nonprimitive magnetic translation which vanishes in the paramagnetic phase, and $\mathbf{t}_i = 0$ or $\mathbf{t}_\theta$, while $\mathbf{t}_\sigma = \mathbf{t}_\sigma'$ or $\mathbf{t}_\sigma' + \mathbf{t}_\theta$. We next aim to identify the allowed order parameter representations on symmetry planes $k_z = 0, \pi$, taking into account the constraints set by symmetries (2). The latter are derived from antisymmetrized products of the irreducible single-particle representations [10–13], as we discuss next.

Pair representations.—Starting from representations $\Gamma_\mathbf{k}$ of the "little" group of the symmetry planes, $G_\mathbf{k} = \{\mathcal{E}, \Sigma_z\}$, one can construct representations for the symmetry group of Cooper pairs. The latter reads $G_\mathbf{k} \cup \mathcal{I} G_\mathbf{k} = \{\mathcal{E}, \Sigma_z, \mathcal{I}, \mathcal{I}\Sigma_z\}$, where, for notational convenience, we introduced $\mathcal{E} \equiv (E, 0)$. Cooper pairs are constructed from antisymmetrized products of the single-particle wave functions with vanishing total momentum. For pair representations, one thus has to separate out the antisymmetric 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 [10,11]. Applying the general recipe to our case, we are left with [12,13]

$$\chi(P^-(m)) = \chi(\Gamma_\mathbf{k}(m))\chi(\Gamma_\mathbf{k}(\mathcal{I}m\mathcal{I})), \tag{3}$$

$$\chi(P^-(\mathcal{I}m)) = -\chi(\Gamma_\mathbf{k}(\mathcal{I}m\mathcal{I}m)), \tag{4}$$

where $m \in G_\mathbf{k}$ and the left-hand side defines the characters of P^- for the symmetry group of Cooper pairs. For our purposes, the single-particle representations $\Gamma_\mathbf{k}$ are double-valued corepresentations of the magnetic group $\mathcal{G}_\mathbf{k} = G_\mathbf{k} + \Theta\mathcal{I}G_\mathbf{k}$ 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 I (top), where the values for ρ and c_d depend on the translations $\mathbf{t}_\theta$, $\mathbf{t}_i$, $\mathbf{t}_\sigma$. We note that the first and third characters in the table formalize that centrosymmetric crystals with (generalized) time-reversal symmetry host four different pairs, one of which is even and three of which are odd parity [14]. A short calculation further shows [15] that $\rho = e^{2ik_z\mathbf{e}_z\cdot(\mathbf{t}_\sigma - \mathbf{t}_i)} = \pm 1$ fixes the sign of the last character. In the following, we refer to the two resulting representations as $\Pi^\pm$. We notice that Π^-, e.g., describes for vanishing $\mathbf{t}_i$ the Brillouin zone face of a mirror* symmetry. On the basal plane, on the other hand, Π^+ always applies. Finally, the second character in Table I 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 corepresentations $\Gamma_\mathbf{k}$. Before doing so, we first comment on implications of the four representations.

TABLE I. (Top) Character table for representations P^- of antisymmetrized 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. (Bottom) Character table for irreducible representations of the Cooper-pair wave function on high-symmetry planes.

ρ	$\mathcal{E}$	Σ_z	$\mathcal{I}$	$\Sigma_z\mathcal{I}$
$+$	4	$-4c_d$	-2	2
$-$	4	$4c_d$	-2	-2

	$\mathcal{E}$	Σ_z	$\mathcal{I}$	$\Sigma_z\mathcal{I}$
A_g	1	1	1	1
A_u	1	-1	-1	1
B_g	1	-1	1	-1
B_u	1	1	-1	-1

TABLE II. Decompositions of Cooper-pair representations ($\Pi^{\rho}_{c_d}$) into irreducible components summarized in Table I (bottom). Here, Kramer's degeneracy and band sticking refer to $c_d = 0$ and $c_d = 1$, respectively.

ρ	Kramer's deg.
+	$A_g + 2A_u + B_u$
−	$B_g + A_u + 2B_u$

ρ	Band sticking
+	$B_g + 3A_u$
−	$A_g + 3B_u$

Decomposing into their irreducible components (Table I, bottom), one arrives at Table II, 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 it 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 A_g.

Kramer's degeneracies and band sticking.—The second character in Table I (top) can be expressed in terms of the single-particle corepresentation [15] $\chi(P^{-}(\Sigma_z)) = e^{-i\mathbf{k}\cdot(2\mathbf{t}_\sigma+\sigma_z\mathbf{t}_i-\mathbf{t}_i)}\chi^2(\Gamma_{\mathbf{k}}(\Sigma_z))$, and to specify $\Gamma_{\mathbf{k}}$ one needs to account for degeneracies induced by Θ. 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]. In the absence of spin orbit, the latter occur for each spin component, and it is this fourfold degeneracy that the name alludes to [11,17,18]. Both types of degeneracies are accounted for by passing from double-valued representations $\gamma_{\mathbf{k}}$ of the little group to corresponding corepresentations of the magnetic group $\mathcal{G}_{\mathbf{k}}$. That is, $\gamma_{\mathbf{k}} \mapsto \Gamma_{\mathbf{k}} \equiv \begin{pmatrix} \gamma_{\mathbf{k}} & \\ & \bar{\gamma}_{\mathbf{k}} \end{pmatrix}$, where $\bar{\gamma}_{\mathbf{k}}(m) = \gamma^{*}_{\mathbf{k}}((\mathcal{I}\theta)^{-1}m\mathcal{I}\theta)$ for Kramer's and $\bar{\gamma}_{\mathbf{k}}(m) = \gamma_{\mathbf{k}}(m)$ for band-sticking degeneracies [19]. One readily verifies that corepresentations of the former come in pairs of opposite sign, i.e., $\chi(\Gamma_{\mathbf{k}}(\Sigma_z)) = 0$, independent of translations $\mathbf{t}_\theta, \mathbf{t}_i, \mathbf{t}_\sigma$. Representations of band-sticking degeneracies, on the other hand, come in identical pairs, i.e., $\chi(\Gamma_{\mathbf{k}}(\Sigma_z)) = \pm 2ie^{i\mathbf{k}\cdot(\mathbf{t}_\sigma+\sigma_z\mathbf{t}_\sigma)/2}$ and $\chi(P^{-}(\Sigma_z)) = -4\rho$, as summarized in Table I [15]. 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 the representations $\Pi^{\rho}_{c_d}$ [15],

$$(-1)^{c_d} = e^{2ik_z\mathbf{e}_z\cdot(\mathbf{t}_\theta+\mathbf{t}_\sigma-\mathbf{t}_i)}, \quad (5)$$

$$\rho = e^{2ik_z\mathbf{e}_z\cdot(\mathbf{t}_\sigma-\mathbf{t}_i)}. \quad (6)$$

Equations (5) and (6) are a central result and allow us to identify the pair representation from the translation vectors defining the basic symmetries Eq. (2). Band sticking occurs for vanishing $\mathbf{t}_i$ on the Brillouin zone face of a mirror* symmetry in the absence of magnetic order, or a mirror symmetry with coexistent antiferromagnetic order $\mathbf{t}_\theta = \mathbf{t}_\perp$. We also notice that glide and mirror symmetries have identical implications for the nodal structure. We also verified [15] the topological stability of the encountered line nodes using a Clifford algebra technique [3]. There, we show that topological protection arises under the conditions of Eq. (5), which indicate band sticking and allow us to extend our results to more general conditions such as the pairing of nondegenerate states in multiband systems.

Applications.—Our results are summarized in Table III. On the basal plane, the absence of nontrivial phase factors associated with nonprimitive translations implies symmorphic behavior of representation Π^{+}_{0} (the 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 the 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 $\mathbf{t}_\theta$, $\mathbf{t}_i$, $\mathbf{t}_\sigma$, all four cases can be realized. The second entry in Table III, representation Π^{-}_{1}, has previously been discussed in Refs. [6,7] and is here generalized to include glide-plane symmetries [20] and coexistence with the antiferromagnetic order. A scenario summarized by representation Π^{-}_{0}, the third entry in the table, was recently studied by Nomoto and Ikeda [4]. Finally, representation Π^{+}_{1}, given in the fourth entry, has, to our knowledge, not been discussed before.

Table IV lists a number of nonsymmorphic and antiferromagnetic superconductors with their space group symmetry, nonsymmorphic group operations (GO), the

TABLE III. Summary of results where $\mathbf{T} = \{0, \mathbf{t}_\parallel\}$ refers to translation vectors within the mirror plane and $\mathbf{t}_\perp$ to a nonvanishing 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 UPt_3, Na_xCoO_2, Li_2Pt_3B, and CrAs, entry 3 for UPd_2Al_3 and UNi_2Al_3, and entry 4 for UPt_3 in the AFM phase.

$\mathbf{t}_\theta \| (\mathbf{t}_\sigma - \mathbf{t}_i)$	Pair representation	Implications
$\mathbf{T}\|\mathbf{T}$	$\Pi^{+}_{0} = A_g + 2A_u + B_u$	Symmorphic behavior
$\mathbf{T}\|\mathbf{t}_\perp$	$\Pi^{-}_{1} = A_g + 3B_u$	Odd-parity line nodes
$\mathbf{t}_\perp\|\mathbf{t}_\perp$	$\Pi^{-}_{0} = B_g + A_u + 2B_u$	Nodal even-parity SC
$\mathbf{t}_\perp\|\mathbf{T}$	$\Pi^{+}_{1} = B_g + 3A_u$	Odd-parity line nodes and nodal even-parity SC

TABLE IV. Properties of nonsymmorphic (the first six entries) and antiferromagnetic superconductors (the last two entries). For GO (group operations), S indicates a screw axis, G a glide plane, I a lack of inversion [15], H a helical magnet, and AFM nonsymmorphicity induced by antiferromagnetism. Node means the experimentally known nodal structure [line, point, or ? (for unknown)], and Rep refers to the pair representation obtained from Eqs. (5) and (6). The parentheses for UPt_3 for Rep indicate an additional possibility due to AFM order.

	Space group	GO	Node	Rep
UPt_3	$P6_3/mmc$	S, G	Line	Π_1^- (Π_1^+)
Na_xCoO_2	$P6_3/mmc$	S, G	Line	Π_1^-
Li_2Pt_3B	$P4_132$	S, I	Line	Π_1^-
UBe_{13}	$Fm\bar{3}c$	G	Point	Π_0^+
CrAs	$Pnma$	S, G, H	Line	Π_1^-
MnP	$Pnma$	S, G, H	?	Π_1^-
UPd_2Al_3	$P6/mmm$	AFM	Line	Π_0^-
UNi_2Al_3	$P6/mmm$	AFM	Line	Π_0^-

experimentally indicated nodal structure (Node) and pair representation (Rep) obtained from our analysis. As we discuss next, for several of these examples, the observed nonsymmorphic behavior is in agreement with the indicated pair representations [15].

As pointed out in several recent works [1,2,6,7], the pair representation Π_1^- may be realized in UPt_3, where the Fermi surface intersects the symmetry plane $k_z = \pi$ of a mirror* symmetry $\Sigma_z = (\sigma_z, \mathbf{e}_z/2)$. As discussed in Ref. [15], the same may occur for Na_xCoO_2, Li_2Pt_3B, and CrAs. This is readily verified from Eqs. (5) and (6), noting that $\mathbf{t}_\theta$, $\mathbf{t}_i = 0$ and $\mathbf{t}_\sigma = \mathbf{e}_z/2$. Our above analysis further shows that the resulting A_u line node for UPt_3 also persists in the presence of weak antiferromagnetic order along the hexagonal a axis, $\mathbf{t}_\theta = \mathbf{t}_a = (\sqrt{3}\mathbf{e}_x - \mathbf{e}_y)/2$ [21]. Indeed, translation vectors defining pair symmetries on the Brillouin zone face $k_z = \pi$ are $\mathbf{t}_\sigma = \mathbf{t}_z + \mathbf{t}_a$ and $\mathbf{t}_i = \mathbf{t}_a$ [22,23]. Inserting these vectors into Eqs. (5) and (6), one readily verifies that the representation Π_1^- also applies in the presence of the antiferromagnetic order. Moreover, symmetry planes $\Sigma_x = (\sigma_x, \mathbf{t}_z + \mathbf{t}_a)$ and $\Sigma_y = (\sigma_y, \mathbf{t}_a)$ lead to interesting behavior on the AFM Brillouin zone faces $k_x = \pi/\sqrt{3}$ and $k_y = \pi$. With $\mathbf{t}_\theta = \mathbf{t}_i = \mathbf{t}_a$ and $\mathbf{t}_\sigma = \mathbf{t}_z + \mathbf{t}_a$ ($\mathbf{t}_\sigma = \mathbf{t}_a$), one identifies, with the help of Eqs. (5) and (6) and by replacing k_z by k_x (k_y), the pair representation Π_1^+ on both zone faces. Since Fermi surfaces intersect both of these zone faces, this opens up the possibility for B_u line nodes for AFM UPt_3 and also implies the absence of conventional fully gapped even-parity pairing.

UPd_2Al_3 provides a further interesting example, as recently discussed in Ref. [4]. The Fermi surface intersects the symmetry plane $k_z = \pi$ of a mirror σ_z symmetry. For antiferromagnetic order along the c axis and orientation of the moments within the basal plane, the translations are $\mathbf{t}_\theta = \mathbf{e}_z/2$, $\mathbf{t}_\sigma = \mathbf{e}_z/2$ and $\mathbf{t}_i = 0$. From Eqs. (5) and (6), one readily finds the pair representation Π_0^-, 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, $\mathbf{t}_\sigma = 0$, while the other translations are unchanged. A brief glance at Eqs. (5) and (6) then shows that the pair representation on the Brillouin zone face is Π_1^+ 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_2Al_3 for the c-axis zone face, since the AFM wave vector along c is the same as UPd_2Al_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 counterexamples 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 by noting that the degenerate states forming pseudospin pairs, ψ, $\theta I\psi$, $I\psi$, and $\theta\psi$, all have the same mirror eigenvalue [24]. We have provided simple formulas which allow us to identify the pair representation from the translation vectors $\mathbf{t}_\theta$,$\mathbf{t}_i$,$\mathbf{t}_\sigma$ of the (generalized) symmetries Eq. (2). We have illustrated how a straightforward application of the results gives interesting insights into the unconventional nodal structure of superconductors UPt_3 and UPd_2Al_3 (with other examples shown in Table IV that are discussed more in Ref. [15]). Given the simplicity of Eqs. (5) and (6), 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. Owing to band degeneracies along symmetry lines on the zone face in the nonsymmorphic case, these nodes can form nodal loops [1,2,20], 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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