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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 [1–4]. Blount [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 its 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 [6, 7]. 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 [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 non-symmorphic 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) non-symmorphic in space (allowing for odd-parity line nodes), (3) non-symmorphic in both space and time (allowing for even-parity line nodes in antiferromagnets), and (4) non-symmorphic 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 (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 pseudo-spin pairs formed out of the degenerate states ψ, $\theta I\psi$, $I\psi$, and $\theta\psi$ [8]. Pseudo spin-singlet and spin-triplet pairs correspond to the even, respectively odd, parity combinations [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 non-primitive translations,

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

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 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.

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

ρ	band sticking
+	$B_g + 3A_u$
$-$	$A_g + 3B_u$

TABLE II: Decompositions of Cooper-pair representations ($\Pi^{\rho}_{c_d}$) 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.

Throughout this work, we denote space group elements by $(g, \mathbf{t})$ with g a point group operation and $\mathbf{t}$ 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, $\mathbf{t}_\perp \equiv \mathbf{e}_z/2$, implies the presence of a two-fold screw axis $\mathcal{I}\Sigma'_z$. Despite its non-primitive 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 non-primitive translation $\mathbf{t}_\parallel$ 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.

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 non-primitive 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

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

Here E is the identity element of the point group, $\mathbf{t}_\theta$ the non-primitive 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 anti-symmetrized 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 anti-symmetrized products of the single particle 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 [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 co-representations 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 (left) 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 this 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 co-representations $\Gamma_{\mathbf{k}}$. Before doing so we first comment on implications of the four representations.

Decomposition into their irreducible components (Table I (right)) 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 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 (left) can be expressed in terms of the single-particle co-representation [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 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 co-representations 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 co-representations 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 representations $\Pi^\rho_{c_d}$ [15],

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

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

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 $\mathbf{t}_i$ 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 allows us to extend our results to more general conditions such as pairing of non-degenerate states in multi-band systems.

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 Π^+_0 (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 $\mathbf{t}_\theta$, $\mathbf{t}_i$, $\mathbf{t}_\sigma$, all four cases can be realized. The second entry in Table III, representation Π^-_1, has been previously discussed in Refs. [6, 7] and is here generalized to include glide plane symmetries [20] and coexistence with antiferromagnetic order. A scenario summarized by representation Π^-_0, third entry in the table, has recently been studied by Nomoto and Ikeda [4]. Finally, representation Π^+_1, given in the fourth entry, has to our knowledge not been discussed before.

$\mathbf{t}_\theta\vert(\mathbf{t}_\sigma-\mathbf{t}_i)$	pair-representation	implications
$\mathbf{T}\vert\mathbf{T}$	$\Pi^+_0 = A_g+2A_u+B_u$	"symmorphic behavior"
$\mathbf{T}\vert\mathbf{t}_\perp$	$\Pi^-_1 = A_g+3B_u$	"odd-parity line nodes"
$\mathbf{t}_\perp\vert\mathbf{t}_\perp$	$\Pi^-_0 = B_g+A_u+2B_u$	"nodal even-parity SC"
$\mathbf{t}_\perp\vert\mathbf{T}$	$\Pi^+_1 = B_g+3A_u$	"odd-parity line nodes" & "nodal even-parity SC"

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 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 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 AF phase.

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 [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), (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), (6) one readily verifies that the representation Π^-_1 also

	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	AF	line	Π_0^-
UNi_2Al_3	P6/mmm	AF	line	Π_0^-

TABLE IV: Properties of non-symmorphic (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 [15], H a helical magnet, and AF non-symmorphicity 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), (6). The parenthesis for UPt_3 for Rep indicates an additional possibility due to AF order.

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 AF Brillouin zone faces $k_x = \pi/\sqrt{3}$ and $k_y = \pi$. With $\mathbf{t}_\theta = \mathbf{t}_i = \mathbf{t}_a$ and $\mathbf{t}_\sigma = \mathbf{t}_z + \mathbf{t}_a$, respectively $\mathbf{t}_\sigma = \mathbf{t}_a$, one identifies with the help of Eqs. (5), (6) replacing as well k_z by k_x and k_y, respectively, the pair representation Π_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 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), (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), (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 AF 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 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, ψ, $\theta I\psi$, $I\psi$, and $\theta\psi$, all have the same mirror eigenvalue [24]. We provided simple formulas which allow 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), (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. Due to band degeneracies along symmetry lines on the zone face in the non-symmorphic 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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