RAPID COMMUNICATIONS

PHYSICAL REVIEW B **80**, 100506(R) (2009)

Odd parity and line nodes in nonsymmorphic superconductors

T. Micklitz and M. R. Norman

Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439, USA

(Received 26 August 2009; published 21 September 2009)

Group theory arguments have been invoked to argue that odd-parity order parameters cannot have line nodes in the presence of spin-orbit coupling. In this Rapid Communication we show that these arguments do not hold for certain nonsymmorphic superconductors. Specifically, we demonstrate that when the underlying crystal has a twofold screw axis, half of the odd-parity representations vanish on the Brillouin-zone face perpendicular to this axis. Many unconventional superconductors have nonsymmorphic space groups, and we discuss implications for several materials, including UPt_3, UBe_{13}, Li_2Pt_3B, and $Na_4Ir_3O_8$.

DOI: 10.1103/PhysRevB.80.100506 PACS number(s): 74.20.−z, 71.27.+a, 74.70.−b

I. INTRODUCTION

Unconventional superconducting materials include heavy fermion metals,[1] organics,[2] and cuprates.[3] The unconventionality of these materials is reflected in the symmetry of the Cooper pair wave function: in contrast to their "conventional" counterparts, unconventional Cooper pairing not only breaks gauge but also crystal symmetry. This opens the possibility of odd-parity pairing where by fermion antisymmetry, the spins are in a triplet state.

Among unconventional superconductors, an important class are those whose order parameter vanishes somewhere on the Fermi surface. The presence or absence of these nodes determines the low-energy excitations and thus the low-temperature thermodynamic and transport properties. It is generally stated that in the presence of spin-orbit interactions, an odd-parity order parameter cannot have a line of nodes on the Fermi surface. This is known as Blount's theorem.[4] In contrast, this restriction does not exist for an even-parity order parameter. There are, though, several heavy fermion superconductors where Knight-shift data indicate that the Cooper pair spins are in a triplet state, yet thermodynamic measurements imply the existence of a line of nodes.[5]

The aim of the present Rapid Communication is to investigate the generality of Blount's arguments. Specifically, we show that in crystals with a twofold screw axis, line nodes are possible whenever the Fermi surface intersects the Brillouin-zone face perpendicular to this axis even in the presence of spin-orbit interactions. Since many unconventional superconductors have nonsymmorphic space groups, it provides a large class of counterexamples to Blount's theorem. We discuss implications for several materials of interest.

In the presence of spin-orbit coupling, spin is no longer a good quantum number. On the other hand, Anderson showed that because of fermion antisymmetry, one can write down analogs of Cooper pair singlets and triplets.[6] By Kramers theorem, one has two degenerate states present at $\mathbf{k}$. Coupling them to the two degenerate states at $-\mathbf{k}$, one has an even-parity state that is a "pseudospin" singlet and an odd-parity state that is a pseudospin triplet. Blount has shown, though, that this puts restrictions on the form of the odd-parity state.[4] A node requires the simultaneous fulfilling of two real equations. Since two equations in three variables are commonly satisfied on curves, and these intersect the Fermi surface at isolated points, nodes for the odd-parity Cooper pair wave function should only occur for points on the Fermi surface. To assure that symmetry cannot force an increase in the size of the nodal regions, Blount discusses the presence of mirror planes. He argues that the pseudospin components of the odd-parity wave function form an axial vector, whose components parallel and perpendicular to the plane transform according to different representations. Symmetry may only force one of these components to vanish, and therefore a larger region of zero gap is "vanishingly improbable."

Blount's symmetry considerations obviously apply to point-group operations and, consequently, to any symmorphic space group. A nonsymmorphic space group, on the other hand, contains screw axes and glide planes, i.e., the combined operation of point-group elements with nonprimitive translations. The latter generate additional phase factors, which in special situations may conspire in a way that *all* of the order parameter's pseudospin components transform according to the *same* representation.[7] In this case, symmetry enforces the vanishing of the order parameter belonging to some representations. A particular example of such a case was encountered for the hexagonal close-packed lattice of UPt_3, where this was shown explicitly by construction from the single electron wave functions.[8] That is, for odd-parity representations that are also odd under the symmetry operation $z \to -z$, it was claimed that all pseudospin components vanish on the hexagonal zone face $k_z = \pi/c$. We will employ group theory arguments to illustrate the generality of this argument.

II. GROUP THEORY

The group theory approach to Cooper pair wave functions of unconventional superconductors goes back to Anderson.[6] Classifications of pair states at the zone center rely on irreducible representations of point groups and have been listed for many relevant crystal symmetries.[9] Building on work on antisymmetrized Kronecker squares of induced representations,[10] a more general space-group approach has been developed to deduce which Cooper pair symmetries are allowed at arbitrary points in the Brillouin zone.[11]

Here, we consider a general nonsymmorphic space-group symmetry G, containing inversion symmetry $(I,0)$ and a twofold screw axis $(2_z,\mathbf{t}_2)$. The latter is a symmetry operation combining a π rotation 2_z around some axis with a non-primitive translation $\mathbf{t}_2=\frac{c}{2}\mathbf{e}_z$ along the axis by half of the lattice displacement c (we choose this axis to define the z direction). $(E,0)$ denotes the identity element and $\sigma_z=I2_z$. Also, we assume the presence of spin-orbit interactions.

The space-group approach calculates representations $\mathcal{P}(\mathbf{k})$ of the Cooper pair wave function at a given $\mathbf{k}$ point in the Brillouin zone by the method of induced representations,[10–12]

$$\mathcal{P}(\mathbf{k}) = \sum_{\sigma} P_{\sigma}^{-}\uparrow G. \tag{1}$$

To explain this notation, we proceed in two steps: (i) we outline the construction of representations P_{σ}^{-} and (ii) we indicate a prescription how induced representations $P_{\sigma}^{-}\uparrow G$ may be calculated.

Concerning (i), representations P_{σ}^{-} at a $\mathbf{k}$ point in the zone are constructed from small representations $\gamma_{\mathbf{k}}$ of the symmetry group of wave vector $\mathbf{k}$ ("little group" $G^{\mathbf{k}}$). Referring for details to Refs. 10–12, we merely state the procedure: the sum σ in Eq. (1) extends over those representatives d_σ in a double coset decomposition $G=\Sigma_\alpha G^{\mathbf{k}} d_\alpha G^{\mathbf{k}}$, for which $\mathbf{g}=\mathbf{k}+d_\alpha \mathbf{k}$ is a vector of the reciprocal lattice. This latter condition accounts for the Cooper pair's vanishing total momentum (modulo a reciprocal lattice vector). Introducing the intersection of wave-vector groups $M_\sigma=G^{\mathbf{k}}\cap d_\sigma G^{\mathbf{k}} d_\sigma^{-1}$ and choosing an element $a\in d_\sigma G^{\mathbf{k}}\cap G^{\mathbf{k}} d_\sigma^{-1}$, P_{σ}^{-} is then the representation of $\tilde{M}_\sigma=M_\sigma+aM_\sigma$ induced from $\gamma_{\mathbf{k}}$ by the following definition of its characters ($m\in M_\sigma$)

$$\chi[P_{\sigma}^{-}(m)] = \chi[\gamma_{\mathbf{k}}(m)]\chi[\gamma_{\mathbf{k}}(d_\sigma^{-1} m d_\sigma)], \tag{2}$$

$$\chi[P_{\sigma}^{-}(am)] = -\chi[\gamma_{\mathbf{k}}(amam)]. \tag{3}$$

Turning to (ii), induced representations are conveniently calculated with the help of the "Frobenius reciprocity theorem."[12] In the context of Eq. (1), the theorem states that the number of times n_j an irreducible representation Γ^j of G appears in the decomposition $\mathcal{P}(\mathbf{k})=\Sigma_j n_j \Gamma^j$ equals the number of times P_{σ}^{-} appears in the decomposition of Γ^j into irreducible representations $\tilde{\Gamma}^j$ of the "subduced" group $G\cap\tilde{M}$. Here, both Γ^j and $\tilde{\Gamma}^j$ are representations at the zone center. We summarize $\tilde{\Gamma}^j$ for points of interest in Table I. Line nodes of the odd-parity Cooper pair wave function may arise if any of the odd-parity representations $\tilde{\Gamma}_u^j$ are absent in the decomposition $P_{\sigma}^{-}=\Sigma_j m_j \tilde{\Gamma}^j$ in a symmetry plane of the zone that intersects the Fermi surface.

To apply the outlined procedure, we need to identify small representations $\gamma_{\mathbf{k}}$. Our main focus is on $\mathbf{k}$ vectors on the zone face (ZF) $k_z=\pi/c$. For purpose of illustration we also discuss the symmetry plane (SP) $k_z=0$ and a general $\mathbf{k}$ point (GP). In the presence of spin-orbit interactions, spin and real spaces do not transform independently, and the spin rotation group is absorbed into the crystal's space group. Moreover, extra degeneracies may occur due to time-reversal symmetry. Both effects are taken into account when considering co-representations of the little group $G^{\mathbf{k}}$.

For illustration, let us derive representations P_{σ}^{-} for a general $\mathbf{k}$ point: the little group G^{GP} consists only of the identity and its multiplication with primitive translations. A co-representation γ_{GP} is characterized by the identity's character, $\chi[(E,0)]$, which is two from the fact that any point in the zone is twofold degenerate (Kramers theorem). The only double coset representative satisfying the zero-momentum condition is $d_1=(I,0)$. M_1 is identical to G^{GP} and $a=(I,0)$. The representation P_1^{-} is then readily deduced from Eqs. (2) and (3), see Table II (top). The decomposition of P_1^{-} into representations $\tilde{\Gamma}^j$ of Table I (top) results in $P_1^{-}=\Gamma_g+3\Gamma_u$. This corresponds to Anderson's classification of the Cooper pair wave function into an even-parity pseudospin singlet and an odd-parity pseudospin triplet. At a general $\mathbf{k}$ point, there is no symmetry reason for any of them to vanish.

Next, we turn to points in the symmetry planes: little groups G^{SP} and G^{ZF} are both formed by $(E,0)$, $(\sigma_z,\mathbf{t}_2)$, and their multiplication with primitive translations. To account for the appearance of nontrivial phase factors, one has to resort to the little groups' central extensions and look at their projective representations.[12] One may readily convince oneself of the absence of nontrivial phase factors for wave vec-

TABLE I. Characters of representations $\tilde{\Gamma}^j$ of the subduced groups. The table (top) applies to the group $G\cap\tilde{M}$ for a general point in the zone; the table (bottom) applies to the group $G\cap\tilde{M}$ for points in the planes $k_z=0$ and $k_z=\pi/c$. Here g refers to even parity and u odd parity refers to representations.

$\tilde{\Gamma}^j$	$(E,0)$	$(I,0)$
Γ_g	1	1
Γ_u	1	−1

$\tilde{\Gamma}^j$	$(E,0)$	$(2_z,\mathbf{t}_2)$	$(I,0)$	$(\sigma_z,\mathbf{t}_2)$
A_g	1	1	1	1
B_g	1	−1	1	−1
A_u	1	1	−1	−1
B_u	1	−1	−1	1

TABLE II. Representations P_i^{-} induced by $\gamma_{\mathbf{k}}$. Top table: representation for a general $\mathbf{k}$ point. Bottom table: representations for $k_z=0$ and $k_z=\pi/c$ are given by the first and second line, respectively.

P_1^{-}	$(E,0)$	$(I,0)$
GP	4	−2

$P_{1,2}^{-}$	$(E,0)$	$(2_z,\mathbf{t}_2)$	$(I,0)$	$(\sigma_z,\mathbf{t}_2)$
SP	4	2	−2	0
ZF	4	−2	−2	4

tors that satisfy $k_z=0$. For points on the zone face, however, nontrivial phase factors arise. As a result, G^{SP} and G^{ZF} define different groups. They can be identified by their multiplication table, and their co-representations can be looked up. The (relevant) characters of the co-representations are as follows: for $k_z=0$, there are two identical co-representations γ_{SP} characterized by $\chi[(E,0)]=2$ and $\chi[(\sigma_z,\mathbf{t}_2)]=0$. At the zone face, on the other hand, there are two complex conjugate co-representations γ_{ZF} with characters $\chi[(E,0)]=2$ and $\chi[(\sigma_z,\mathbf{t}_2)]=\pm 2i$. The different characters $\chi[(\sigma_z,\mathbf{t}_2)]$ for these two cases reflect the different type of degeneracy encountered, i.e., a pairing degeneracy and a doubling degeneracy, respectively.[13]

Wave vectors for both symmetry planes allow for $d_1=(I,0)$ and $d_2=(2_z,\mathbf{t}_2)$, resulting in $M_{1,2}$ both identical to the little group. Also, it is always possible to choose $a=(I,0)$. Application of Eqs. (2) and (3) to $k_z=0$ and d_1 results in the first line of Table II (bottom).[14] Using instead d_2 leads to the identical result in the second line (thus $P_1^- \equiv P_2^-$). The decomposition into irreducible components $\tilde{\Gamma}^j$ of Table I (bottom) is $P_i^-=A_g+2A_u+B_u$, showing that half of the even-parity representations (B_g) vanish for $k_z=0$. Odd-parity representations, on the other hand, are all present, indicating the absence of line nodes. This is a consequence of Blount's argument since phase factors related to the twofold screw axis are all trivial.

At the zone face, d_1 and d_2 lead again to identical representations. Also, results for both co-representations γ_{ZF} (i.e., for characters $\chi[(\sigma_z,\mathbf{t}_2)]=\pm 2i$) are identical. The result is shown in the second line of Table II (bottom).[15] The decomposition

$$P_{1,2}^- = A_g + 3B_u \tag{4}$$

implies that half of the odd-parity representations (A_u) vanish. Equation (4) is the main result of this Rapid Communication. It shows that in crystals with a twofold screw axis, line nodes for odd-parity Cooper pair wave functions may occur whenever the Fermi surface intersects the Brillouin-zone face perpendicular to the screw axis. Our finding has relevance for a variety of unconventional superconductors.

III. IMPLICATIONS

We first discuss the heavy fermion metal UPt_3, which was mentioned before. Its nonsymmorphic space group $P6_3/mmc$ possesses a twofold screw axis perpendicular to the $k_z=\pi/c$ face of the hexagonal zone. Two of the Fermi-surface sheets intersect this zone face.[16] From our above analysis, it follows that for $k_z=\pi/c$, only those odd-parity representations (of point group $6/mmm$) are allowed that are even under the operation $z\rightarrow -z$. That is, an odd-parity wave function belonging to the representations A_{1u}, A_{2u}, or E_{2u} has line nodes on the Fermi surface. This potentially clears up a major puzzle in this material, where various measurements are consistent with a line of nodes,[17] but the Knight shift indicates a spin triplet order parameter.[5] We note that an E_{2u} order parameter has been proposed to explain various experimental properties of UPt_3,[18] and recent phase sensitive measurements are in support of this proposal.[19]

Another heavy fermion superconductor to which our observation applies is UBe_{13}. Again, the Knight shift suggests a spin triplet state,[5] while measurements of the NMR relaxation rate find a power law consistent with the presence of a line of nodes.[20] UBe_{13} has the nonsymmorphic space group $Fm\bar{3}c$ that has twofold screw axes perpendicular to the square faces of the face-centered-cubic zone. The Fermi surface is predicted to have pockets that intersect these faces.[21] Therefore, odd-parity Cooper pair wave functions belonging to the representations (of point group $m\bar{3}m$) A_{1u}, A_{2u}, or E_u should have line nodes on the Fermi surface.

Our next example concerns the recently discovered noncentrosymmetric superconductor Li_2Pt_3B.[22] Measurements of the temperature-dependent penetration depth point toward the existence of line nodes. This finding has been attributed to a mixing of even- and odd-parity components of the Cooper pair wave function.[23] In crystals without inversion symmetry, spin-orbit coupling lifts the Kramers degeneracy of the $\mathbf{k}$ states. If the energy splitting s resulting from this is sufficiently large compared to the superconducting gap, Cooper pairs can be admixed, $\Delta_\pm=\psi\pm t$, with pseudospin singlet and triplet components, ψ and t, respectively.[24] If t is large enough, Δ_- may change sign, and thus a line of nodes is possible. Given our above findings, we propose a second mechanism for the appearance of a line of nodes in Li_2Pt_3B that would occur in the opposite limit of weak spin-orbit splitting of the bands. Li_2Pt_3B has the space-group symmetry $P4_132$. This exhibits a twofold screw axis perpendicular to the faces of the simple cubic zone. The Fermi surface of Li_2Pt_3B is predicted to have several small pockets that intersect these faces.[25] If s is small enough that the mixing of odd- and even-parity components is not important, then Cooper pair wave functions belonging to the representations (of point group $m\bar{3}m$) A_{1u}, A_{2u}, or E_u can have line nodes on the Fermi surface. In contrast to the first scenario, these line nodes are now constrained by symmetry. Experiments should be able to differentiate between these two scenarios.

Finally, we mention the more exotic example of $Na_4Ir_3O_8$, which is a candidate for a three-dimensional (3D) spin liquid.[26] It has been proposed that this material possesses a "spinon" Fermi surface.[27,28] At the lowest temperatures, however, the specific heat decreases to zero as T^2, indicating (within this scenario) a line of nodes on this spinon surface. This phenomenon has been recently attributed to pairing of the spinons in a mixed state as described above for Li_2Pt_3B.[28] Interestingly, $Na_4Ir_3O_8$ has the same space group $P4_132$ and the predicted spinon Fermi surface also intersects the simple cubic zone faces. Therefore, our previous discussion for Li_2Pt_3B applies to this material as well, and we conclude that a pure triplet state with a line of nodes is also possible.

IV. CONCLUSIONS

We have shown that in some nonsymmorphic superconductors, it is possible to reconcile the existence of line nodes of an odd-parity Cooper pair wave function with the presence of (strong) spin-orbit interactions. Specifically, we have proven that Blount's theorem is superseded for superconductors possessing a twofold screw axis with a Fermi surface intersecting the zone face perpendicular to this axis. Our observation has potential relevance to a variety of unconventional superconductors and spin liquids.

ACKNOWLEDGMENT

Work at Argonne National Laboratory was supported by the U.S. DOE, Office of Science, under Contract No. DE-AC02-06CH11357.

[1] F. Steglich, J. Aarts, C. D. Bredl, W. Lieke, D. Meschede, W. Franz, and H. Schafer, Phys. Rev. Lett. **43**, 1892 (1979).

[2] D. Jerome, A. Mazaud, M. Ribault, and K. Bechgaard, J. Phys. (France) Lett. **41**, L95 (1980).

[3] J. G. Bednorz and K. A. Müller, Z. Phys. B: Condens. Matter **64**, 189 (1986).

[4] E. I. Blount, Phys. Rev. B **32**, 2935 (1985).

[5] H. Tou, K. Ishida, and Y. Kitaoka, J. Phys. Soc. Jpn. **74**, 1245 (2005).

[6] P. W. Anderson, Phys. Rev. B **30**, 4000 (1984).

[7] To be more specific, consider the eigenfunction of some space-group element $(R,\mathbf{t})f_{\mathbf{k}}=cf_{\mathbf{k}}$ (R is a point-group operation and $\mathbf{t}$ a translation vector). The action of time-reversal symmetry θ and inversion symmetry $(I,0)$ generates new eigenfunctions with eigenvalues c and $e^{2i\mathbf{kt}}c$, respectively, as can be checked by noting that θ and $(R,\mathbf{t})$ commute while $(R,\mathbf{t})(I,0)=(E,2\mathbf{t})(I,0)(R,\mathbf{t})$, where E is the point-group identity. It is then evident that symmetries involving nonprimitive translations generate different phase factors for the different pseudospin triplet components at different points in the zone.

[8] M. R. Norman, Phys. Rev. B **52**, 15093 (1995).

[9] G. E. Volovik and L. P. Gor'kov, Sov. Phys. JETP **61**, 843 (1985); K. Ueda and T. M. Rice, Phys. Rev. B **31**, 7114 (1985); M. Sigrist and K. Ueda, Rev. Mod. Phys. **63**, 239 (1991).

[10] C. J. Bradley and B. L. Davies, J. Math. Phys. **11**, 1536 (1970).

[11] V. G. Yarzhemsky, Phys. Status Solidi B **209**, 101 (1998); V. G. Yarzhemsky and E. N. Murav'ev, J. Phys.: Condens. Matter **4**, 3525 (1992).

[12] C. J. Bradley and A. P. Cracknell, *The Mathematical Theory of Symmetry in Solids* (Oxford University Press, Oxford, 1972).

[13] M. Lax, *Symmetry Principles in Solid State and Molecular Physics* (Wiley, New York, 1974), p. 309.

[14] Notice that the characters are those of double groups, and therefore for a 2π rotation, $\chi[(2_z 2_z,0)]=-1$.

[15] Notice the additional factor -1 for $\mathbf{k}$ points on the zone face compared to $k_z=0$. This arises from $\chi[\gamma_{\mathbf{k}}(d_\sigma^{-1}(\sigma_z,\mathbf{t}_2)d_\sigma)] =\chi[\gamma_{\mathbf{k}}(\sigma_z,-\mathbf{t}_2)]=-\chi[\gamma_{\mathbf{k}}(\sigma_z,\mathbf{t}_2)]$, i.e., the action of the translation group, $e^{2i\mathbf{k}\mathbf{t}_2}=-1$. Here $d_\sigma=(I,0)$ or $(2_z,\mathbf{t}_2)$, and we used the identity $(R,\mathbf{v})^{-1}(S,\mathbf{w})(R,\mathbf{v})=(R^{-1}SR,R^{-1}S\mathbf{v}+R^{-1}\mathbf{w}-R^{-1}\mathbf{v})$.

[16] G. J. McMullan, P. M. C. Rourke, M. R. Norman, A. D. Huxley, N. Doiron-Leyraud, J. Flouquet, G. G. Lonzarich, A. McCollam, and S. R. Julian, New J. Phys. **10**, 053029 (2008).

[17] R. Joynt and L. Taillefer, Rev. Mod. Phys. **74**, 235 (2002).

[18] M. R. Norman, Physica C **194**, 203 (1992); J. A. Sauls, Adv. Phys. **43**, 113 (1994).

[19] J. D. Strand, D. J. van Harlingen, J. B. Kycia, and W. P. Halperin, arXiv:0907.0225 (unpublished).

[20] A. Amato, Rev. Mod. Phys. **69**, 1119 (1997). On the other hand, specific heat and penetration depth data on UBe_{13} are more consistent with point nodes.

[21] M. R. Norman, W. E. Pickett, H. Krakauer, and C. S. Wang, Phys. Rev. B **36**, 4058 (1987); K. Takegahara and H. Harima, Physica B **281-282**, 764 (2000); T. Maehira, A. Higashiya, M. Higuchi, H. Yasuhara and A. Hasegawa, *ibid.* **312-213**, 103 (2002).

[22] P. Badica, T. Kondo, and K. Togano, J. Phys. Soc. Jpn. **74**, 1014 (2005).

[23] H. Q. Yuan, D. F. Agterberg, N. Hayashi, P. Badica, D. Vandervelde, K. Togano, M. Sigrist, and M. B. Salamon, Phys. Rev. Lett. **97**, 017006 (2006).

[24] L. P. Gor'kov and E. I. Rashba, Phys. Rev. Lett. **87**, 037004 (2001); P. A. Frigeri, D. F. Agterberg, A. Koga, and M. Sigrist, *ibid.* **92**, 097001 (2004).

[25] S. Chandra, S. Mathi Jaya, and M. C. Valsakumar, Physica C **432**, 116 (2005); K.-W. Lee and W. E. Pickett, Phys. Rev. B **72**, 174505 (2005).

[26] Y. Okamoto, M. Nohara, H. Aruga-Katori, and H. Takagi, Phys. Rev. Lett. **99**, 137207 (2007).

[27] M. J. Lawler, A. Paramekanti, Y. B. Kim, and L. Balents, Phys. Rev. Lett. **101**, 197202 (2008).

[28] Y. Zhou, P. A. Lee, T.-K. Ng, and F.-C. Zhang, Phys. Rev. Lett. **101**, 197201 (2008).