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Relativistic analysis of the pairing symmetry of the noncentrosymmetric superconductor $LaNiC_2$

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We present a relativistic symmetry analysis of the allowed pairing states in the noncentroymmetric superconductor $LaNiC_2$. The case of zero spin-orbit coupling (SOC) is discussed first and then the evolution of the symmetry-allowed superconducting instabilities as SOC is adiabatically turned on is described. In addition to mixing singlet with triplet pairing, SOC splits some triplet pairing states with degenerate order-parameter spaces into nondegenerate pairing states with different critical temperatures. We address the breaking of time-reversal symmetry detected in recent muon spin-relaxation experiments and show that it is only compatible with such nonunitary triplet pairing states. In particular, an alternative scenario featuring conventional singlet pairing with a small admixture of triplet pairing is shown to be incompatible with the experimental data.

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I. INTRODUCTION

Noncentrosymmetric superconductors have been a subject of considerable interest since the discovery of superconductivity in the heavy-fermion material $CePt_3Si$.[1] In particular, it is the unique property of such noncentrosymmetric superconductors that in the presence of spin-orbit coupling (SOC) both spin singlet and spin triplet Cooper pairs can, and must, coexist within a single material. This is quite general as while in the complete absence of SOC the two kinds of pairing are distinguished by their different behavior under rotations in spin space, once SOC is finite then spin and space rotations cannot be separated and it is only the parity of the Cooper pair wave function under spatial inversion, P, which separates spin singlet (even) from spin triplet (odd) states.[2–6] In a noncentrosymmetric superconductor there is no lattice center of inversion and so the parity operator, P, is not a well-defined symmetry of the crystal, leading to mixing of singlet and triplet pairing states within a single material. An interesting analogy can be made with particle physics where the mixing of neutrino flavors is induced by violation of CP symmetry.[7] The implication is that in noncentrosymmetric superconductors the order parameter is always unconventional. On the other hand the experimental situation is quite complex as some noncentrosymmetric superconductors such as $CePt_3Si$ are additionally strongly correlated while the superconducting state of others such as Li_2Pd_3B, $BaPtSi_3$, or Re_3W appears to feature pure singlet pairing.[8–10]

An important recent development has been the observation, through zero-field muon spin resonance (μSR), of time-reversal symmetry (TRS) breaking at the superconducting instability of $LaNiC_2$.[11] Superconductivity in this intermetallic compound[12] was discovered in the mid 1990s with critical temperature T_c=2.7 K.[13] There was some discussion of whether it was a type-II or a dirty type-I superconductor[14] and the possibility that the symmetry of the superconducting order parameter was unconventional was debated.[13,14] At the time, however, the lack of inversion symmetry was largely overlooked. In contrast, very recently there has been a surge of experimental[11,15,16] and theoretical[11,17–19] work on this system. Some of this has been motivated by the results in Ref. 11 which constitute very strong and direct evidence of unconventional pairing. In addition to this dramatic dependences of T_c on Cu, Y, and Th doping have been identified.[15,16,20,21]

Two broad and mutually exclusive scenarios have been proposed to describe the breaking of TRS in the superconducting state of $LaNiC_2$.[11,19] In the first scenario, which is based on group-theoretical considerations,[11] the superconducting order parameter is intrinsically unconventional: a nonunitary triplet pairing state. In the second scenario, based on first-principles calculations,[19] $LaNiC_2$ is essentially a conventional superconductor but a small amount of triplet pairing is induced by SOC, as described above and is responsible for the observed breaking of TRS. Unfortunately both the group-theoretical analysis of Ref. 11 and the first-principles calculations of Ref. 19 ignore relativistic effects. It is therefore unclear whether any of the eight superconducting instabilities that are allowed by symmetry and that preserve TRS (Ref. 11) acquire a TRS breaking component when SOC is adiabatically turned on. More specifically it is not known whether the conventional superconducting state assumed in Ref. 19, which does not break TRS, can acquire the necessary TRS breaking component in this way. Indeed it is well known[22] that TRS breaking requires a superconducting order parameter with degeneracy. However no such degeneracy should occur in an orthorhombic crystal with finite SOC. In the present work we address this question directly by extending the previous symmetry analysis[11] to include the effect of SOC. The more general analysis that we present here allows us to conclude that the observation of time-reversal symmetry breaking at T_c is not compatible with a conventional mechanism of the type proposed in Ref. 19.

To address the pairing symmetry in the $LaNiC_2$ crystal structure[12] we first consider, following the original analysis,[11] the possible pairing states if spin-orbit interaction is negligible. We then study how these states evolve when perturbed by SOC. In particular, we note in this paper that simply a combination of *s*-wave pairing and noncentrosymmetric crystal structure does not automatically lead to time-reversal symmetry breaking at T_c. It turns out that the low symmetry of the orthorhombic *Amm*2 structure leads to only a small number of time-reversal symmetry-breaking states in the absence of SOC, all of which have degeneracy which is lifted when spin-orbit interaction is finite. Therefore the observation of time-reversal symmetry breaking at T_c provides a very strong constraint on the pairing state and is not naturally consistent with the conventional electron-phonon pairing mechanism or s-wave pairing. Instead, the observation is only compatible with SOC being small and with the system entering a nonunitary triplet pairing state at T_c.

Our arguments are based on group theory and in that spirit the present analysis of the pairing symmetry in $LaNiC_2$ does not rely on any specific assumptions about the origin of the pairing interaction, the band structure or the strength of SOC. The method is very well established and has been very successful in the past for many other superconductors with a center of inversion, e.g., the cuprates.[23] More recently similar methods have been applied to noncentrosymmetric superconductors.[24–26] We will nevertheless describe some of the main arguments in considerable detail to highlight the issue of TRS breaking, both in the presence and absence of SOC, as well as the features specific to the point symmetry of $LaNiC_2$.

II. SYMMETRY ANALYSIS IN THE ABSENCE OF SPIN-ORBIT COUPLING

The possible symmetries of the superconducting instability in $LaNiC_2$ assuming that SOC can be neglected were enumerated in Ref. 11. In this section we give the details of the derivation emphasizing the similarities and differences with the case where there is a center of inversion. In the absence of spin-orbit coupling, the point group G is

$$G = G_c \times SO(3), \tag{1}$$

where $\times$ represents the direct product, G_c is the point group of the crystal structure and $SO(3)$ represents all spin rotations. The irreducible representations therefore have the form $\Gamma = \Gamma^c \times \Gamma^s$, where Γ^c and Γ^s are irreducible representations of G_c and $SO(3)$, respectively (in principle, the full space group of the crystal must be taken into account; however, we assume that the translational symmetries are the same above and below T_c, so it is enough to refer to the point group). A basis of Γ is given by the functions $\hat{\Gamma}_{mn}(\mathbf{k}) = \Gamma^c_m(\mathbf{k})\hat{\Gamma}^s_n$, where $\{\Gamma^c_m(\mathbf{k})\}_{m=1,\ldots,d_{\Gamma^c}}$ forms a basis of Γ^c and $\{\hat{\Gamma}^s_n\}_{n=1,\ldots,d_{\Gamma^s}}$ forms a basis of Γ^s. The dimensionality of Γ is $d_\Gamma = d_{\Gamma^c} d_{\Gamma^s}$. The gap function just below T_c is thus $\hat{\Delta}(\mathbf{k}) = \sum_{m=1}^{d_{\Gamma^c}} \sum_{n=1}^{d_{\Gamma^s}} \eta_{m,n} \Gamma^c_m(\mathbf{k}) \hat{\Gamma}^s_n$.

The spin rotation group $SO(3)$ is the same for all crystals. As is well known it has two irreducible representations (irreps). The first of these is the singlet representation, of dimension 1. This corresponds to order parameters of the form $\hat{\Delta}(\mathbf{k}) = \sum_{m=1}^{d_{\Gamma^c}} \eta_{m,0} \Gamma^c_m(\mathbf{k}) \hat{\Gamma}^s_{\text{singlet}}$. Crucially, $\hat{\Gamma}^s_{\text{singlet}} = -(\hat{\Gamma}^s_{\text{singlet}})^T$ meaning that we must have $\Gamma^c_m(\mathbf{k}) = \Gamma^c_m(-\mathbf{k})$. Thus for singlet order parameters only the first term in

$$\hat{\Delta}(\mathbf{k}) = \Delta(\mathbf{k}) i\hat{\sigma}_y + [\mathbf{d}(\mathbf{k}) \,.\, (\hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z)]\hat{\sigma}_y \tag{2}$$

is finite. The second irrep of $SO(3)$ is the triplet representation, of dimension 3. For it we thus have $\hat{\Delta}(\mathbf{k}) = \sum_{m=1}^{d_{\Gamma^c}} \sum_{n=-1,0,+1} \eta_{m,n} \Gamma^c_m(\mathbf{k}) \hat{\Gamma}^s_{\text{triplet},n}$. Moreover we have $\hat{\Gamma}^s_{\text{triplet},n} = (\hat{\Gamma}^s_{\text{triplet},n})^T$ whereby the G_c basis functions must be odd, $\Gamma^c_m(\mathbf{k}) = -\Gamma^c_m(-\mathbf{k})$, meaning that for triplet pairing in Eq. (2) has only the second term.

The above results are very well known from the group-theory analysis of centrosymmetric superconductors.[22,23,27] They are also valid in the noncentrosymmetric case as long as SOC can be neglected. In particular, the pairing symmetry must be purely of the singlet or triplet type in the limit in which SOC does not play a role. The only difference with the case of centrosymmetric superconductors is that in a noncentrosymmetric superconductor the irreps of the crystal point group do not have distinct symmetries under inversion, so each of them is compatible with both singlet and triplet pairing. Thus in $LaNiC_2$, where $G_c = C_{2v}$, each of the four irreps A_1, A_2, B_1, and B_2 [Table I in Ref. 11] is compatible with singlet and triplet superconducting instabilities. Since in this case all four irreps of G_c are one-dimensional, this leads to a total of 12 possible instabilities: four in the singlet channel and eight in the triplet channel (see Ref. 11 for details). The possible symmetries of the gap function are reproduced in Table I here for completeness. Note that the nonunitary triplet pairing instabilities $^3A_1(b)$, $^3A_2(b)$, $^3B_1(b)$, and $^3B_2(b)$ are the only ones that break TRS, leading to the conclusion that the superconducting state just below T_c features nonunitary triplet pairing.[11] As noted in that reference one of these four forms of the gap function has the same point-group symmetry as the crystal, which would not have been possible for triplet pairing in a centrosymmetric superconductor. The other three break additional symmetries. In the following

TABLE I. Possible symmetries of the gap function of $LaNiC_2$ just below T_c in the case where SOC can be neglected, written in terms of $\Delta_0(\mathbf{k})$ and $\mathbf{d}(\mathbf{k})$ in Eq. (2). Each of the functions X, Y, and Z depend on the wave vector $\mathbf{k}$ and they have the same symmetries under the operations of the point group C_{2v} as its three components k_x, k_y, and k_z, respectively.

Irrep of $SO(3)\times C_{2v}$	$\Delta_0(\mathbf{k})$	$\mathbf{d}(\mathbf{k})$
$^1A_1$	1	0
$^1A_2$	XY	0
$^1B_1$	XZ	0
$^1B_2$	YZ	0
$^3A_1(a)$	0	$(0,0,1)Z$
$^3A_2(a)$	0	$(0,0,1)XYZ$
$^3B_1(a)$	0	$(0,0,1)X$
$^3B_2(a)$	0	$(0,0,1)Y$
$^3A_1(b)$	0	$(1,i,0)Z$
$^3A_2(b)$	0	$(1,i,0)XYZ$
$^3B_1(b)$	0	$(1,i,0)X$
$^3B_2(b)$	0	$(1,i,0)Y$

section we analyze how this conclusion is affected by the inclusion of SOC in the analysis.

III. SYMMETRY ANALYSIS IN THE PRESENCE OF SPIN-ORBIT COUPLING

Now suppose that spin-orbit coupling is strong enough that it cannot be neglected. Then, as in the case of centrosymmetric superconductors, $G=G_{c,J}$, which is the "double group" obtained by appending to each rotation carried out on the coordinates in G_c an equivalent operation carried out on the spins. Take, for example, the reflection through the x-z plane contained in the point group of the $LaNiC_2$ crystal structure, C_{2v}. This is $\sigma_v=IC_2^y$, where I represents inversion through the central point and C_2^y a rotation by 180° around the y axis. Then $G_{c,J}$ contains the similar operation, $\sigma_{v,J}$, involving this reflection as well as a C_2^y rotation carried out on the spins (i.e., a rotation of the **d** vector). The gap function just below T_c is now $\hat{\Delta}(\mathbf{k})=\sum_{i=1}^{d_\Gamma}\eta_i\hat{\Gamma}_i(\mathbf{k})$, where $\hat{\Gamma}_i(\mathbf{k})$ is the ith basis function of the irrep Γ of $G_{c,J}$. In general, unlike the case of vanishing SOC, the gap function is not of the singlet or triplet forms. Note, however, that such mixture of the singlet and triplet channels occurs only when *both* of the following conditions are met: (i) there is no center of inversion *and* (ii) SOC cannot be neglected. As has been extensively remarked[1,28–30] this makes noncentrosymmetric superconductors special in that SOC has a more dramatic effect on the pairing symmetry than it has in centrosymmetric superconductors.[23,27] On the other hand that is quite different from saying that SOC has to be strong in these systems. Indeed, as we will see shortly in the case of $LaNiC_2$ it is difficult to reconcile the observation of TRS breaking[11] with SOC being strong.

Through SOC, spin rotations cease to be independent degrees of freedom. Thus unlike the case of zero SOC the irreps of $G_{c,J}$ are in one-to-one correspondence to those of G_c. For $LaNiC_2$ this leads to a dramatic reduction in the number of symmetry-allowed superconducting instabilities of the normal state from 12 when SOC can be neglected (see above) to only four, corresponding to the four irreps of the point group of the crystal structure. The basis functions depend both on **k** and the spin indices (i.e., they are matrices), just like the basis functions of the irreps of $G_c\times SO(3)$. Constructing the four symmetry operations E_J, $C_{2,J}$, $\sigma_{v,J}$, and $\sigma'_{v,J}$ in the way described above one can find a set of basis functions that is compatible with the group's character table [Table I in Ref. 11]. One such set is given in Table II. The A, B, C, and D coefficients should be determined by a microscopic theory but should be real. Note that, as a direct result of all the irreps of G_c being one-dimensional [Table I in Ref. 11], all the possible order parameters just below T_c are one-dimensional, too. Since a one-dimensional order parameter cannot break TRS (Ref. 22) we are led to the inescapable conclusion that *the superconducting instability in* $LaNiC_2$ can only break TRS if SOC is negligible. In view of the experimental observation of TRS breaking,[11] this suggests that the effect of SOC on the superconductivity must be small and confirms our original conclusion,[11] reached on the basis of a nonrelativistic analysis, of nonunitary triplet pairing.

TABLE II. Possible symmetries of the gap function of $LaNiC_2$ just below T_c in the case where SOC cannot be neglected. A, B, C, and D denote four **k**-independent quantities with the same phase. All other notations as in Table I.

Irrep of $C_{2v,J}$	$\Delta_0(\mathbf{k})$	$\mathbf{d}(\mathbf{k})$
A_1	A	$(BY,CX,DXYZ)$
A_2	AXY	(BX,CY,DZ)
B_1	AXZ	$(BXYZ,CZ,DY)$
B_2	AYZ	$(BZ,CXYZ,DX)$

Note that the case of the orthorhombic-symmetry group C_{2v} appropriate for $LaNiC_2$ is quite different from the tetragonal C_{4v} appropriate to $CePt_3Si$.[24–26] For C_{4v} one of the irreducible representations is two-dimensional so time-reversal symmetry breaking is allowed even in the presence of strong SOC. The point-group studied here is also somewhat different from the monoclinic C_2, studied by Sergienko and Curnoe.[24] In this case there is only one twofold rotation axis and hence only two irreducible representations, A_1 and A_2, both one-dimensional. Nevertheless the general pattern of possible symmetry breakings for C_2 is similar to those given in Tables I and II. Under C_2 the A_1 representation is equivalent to both A_1 and A_2 of C_{2v} while the A_2 representation of C_2 is equivalent to B_1 and B_2 under C_{2v}.

IV. SPIN-ORBIT COUPLING-INDUCED SPLITTING OF THE SUPERCONDUCTING INSTABILITY

Our main conclusion so far is that the observation of TRS symmetry breaking implies that SOC must be very weak, for no TRS breaking superconducting instability of the normal state is compatible with the crystal's symmetry in the presence of SOC. One the other hand, a small amount of SOC must be present in any crystal, which raises the question of how the results of Secs. II and III can be reconciled. To clarify this we consider the evolution of the instability as a small amount of SOC is adiabatically turned on.

Each of the symmetry-allowed superconducting instabilities listed in Table I will evolve into one of those listed in Table II, as shown in Fig. 1. To ascertain the relationships depicted in the figure, we must express the gap function given in Table I as a linear combination of those in Table II. Such linear combinations are unique. In particular, the **k** dependences of the gap function just below the singlet superconducting instabilities are given by

$$\hat{\Gamma}{}^1{}_{A_1}(\mathbf{k})=\hat{\Gamma}_{A_1}(\mathbf{k})|_{A,B,C,D=1,0,0,0}, \tag{3}$$

$$\hat{\Gamma}{}^1{}_{A_2}(\mathbf{k})=\hat{\Gamma}_{A_2}(\mathbf{k})|_{A,B,C,D=1,0,0,0}, \tag{4}$$

$$\hat{\Gamma}{}^1{}_{B_1}(\mathbf{k})=\hat{\Gamma}_{B_1}(\mathbf{k})|_{A,B,C,D=1,0,0,0}, \tag{5}$$

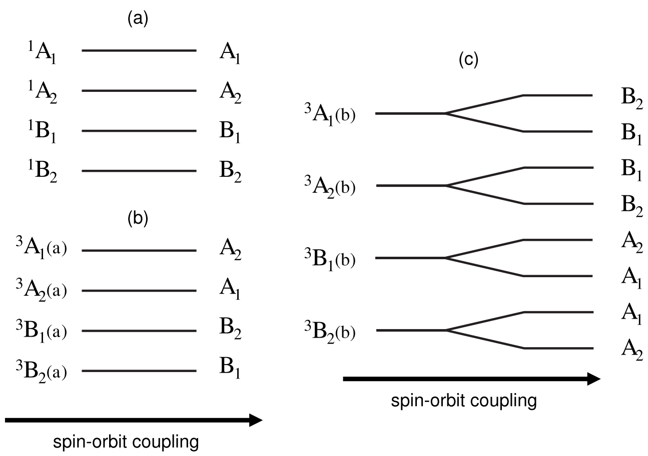

FIG. 1. Evolution of all the superconducting instabilities of the normal state of $LaNiC_2$ allowed by symmetry in the absence of SOC as the latter is adiabatically turned on: (a) singlet pairing instabilities; (b) unitary triplet pairing instabilities; and (c) nonunitary triplet pairing instabilities. The relative temperatures of the different instabilities in this diagram are arbitrary.

$$\hat{\Gamma}_{^1B_2}(\mathbf{k}) = \hat{\Gamma}_{B_2}(\mathbf{k})|_{A,B,C,D=1,0,0,0}. \tag{6}$$

Thus the $^1A_1$, $^1A_2$, $^1B_1$, and $^1B_2$ instabilities evolve into instabilities with A_1, A_2, B_1, and B_2 symmetries, respectively. Moreover adiabatic continuity in the limit of vanishing SOC places constraints on the coefficients A, B, C, and D in Table II: in order that the coefficients A, B, and C vanish in the limit of zero SOC, it is necessary for them to be small, compared to A, when SOC is weak but finite. By this mechanism a small triplet component [i.e., a finite $\mathbf{d}(\mathbf{k})$] could be induced in an otherwise singlet superconductor by the action of SOC alone. Note, however, that such triplet component does not break TRS. This is at variance with the claim made in Ref. 19, as we discuss in detail in Sec. V.

Similarly, the $\mathbf{k}$ dependences of the gap function just below the four unitary triplet pairing instabilities are also in one-to-one correspondence with those of the relativistically allowed ones

$$\hat{\Gamma}_{^3A_1(a)}(\mathbf{k}) = \hat{\Gamma}_{A_2}(\mathbf{k})|_{A,B,C,D=0,0,0,1}, \tag{7}$$

$$\hat{\Gamma}_{^3A_2(a)}(\mathbf{k}) = \hat{\Gamma}_{A_1}(\mathbf{k})|_{A,B,C,D=0,0,0,1}, \tag{8}$$

$$\hat{\Gamma}_{^3B_1(a)}(\mathbf{k}) = \hat{\Gamma}_{B_2}(\mathbf{k})|_{A,B,C,D=0,0,0,1}, \tag{9}$$

$$\hat{\Gamma}_{^3B_2(a)}(\mathbf{k}) = \hat{\Gamma}_{B_1}(\mathbf{k})|_{A,B,C,D=0,0,0,1}. \tag{10}$$

Finally, for the four nonunitary triplet pairing instabilities the situation is somewhat more complicated. Since they break TRS, they cannot evolve smoothly into one of the four symmetry-allowed instabilities as SOC is turned on, as all of them preserve TRS. Indeed the gap matrix just below T_c is a linear combination of two of the forms allowed in the presence of SOC

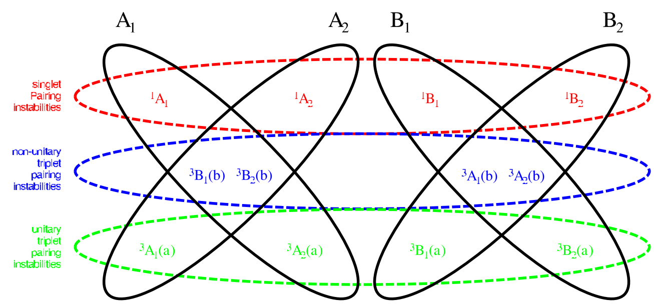

FIG. 2. (Color online) Venn-Euler diagram showing how the four pairing states allowed just below T_c in the presence of spin-orbit coupling decompose into the 12 singlet, nonunitary triplet, and unitary triplet states allowed in its absence.

$$\hat{\Gamma}_{^3A_1(b)}(\mathbf{k}) = \hat{\Gamma}_{B_2}(\mathbf{k})|_{A,B,C,D=0,1,0,0} + i\hat{\Gamma}_{B_1}(\mathbf{k})|_{A,B,C,D=0,0,1,0}, \tag{11}$$

$$\hat{\Gamma}_{^3A_2(b)}(\mathbf{k}) = \hat{\Gamma}_{B_1}(\mathbf{k})|_{A,B,C,D=0,1,0,0} + i\hat{\Gamma}_{B_2}(\mathbf{k})|_{A,B,C,D=0,0,1,0}, \tag{12}$$

$$\hat{\Gamma}_{^3B_1(b)}(\mathbf{k}) = \hat{\Gamma}_{A_2}(\mathbf{k})|_{A,B,C,D=0,1,0,0} + i\hat{\Gamma}_{A_1}(\mathbf{k})|_{A,B,C,D=0,0,1,0}, \tag{13}$$

$$\hat{\Gamma}_{^3B_2(b)}(\mathbf{k}) = \hat{\Gamma}_{A_1}(\mathbf{k})|_{A,B,C,D=0,1,0,0} + i\hat{\Gamma}_{A_2}(\mathbf{k})|_{A,B,C,D=0,0,1,0}. \tag{14}$$

This implies that, unlike the singlet and unitary triplet instabilities *the nonunitary triplet instabilities split under the influence of SOC*: as SOC is increased the critical temperature T_c splits into two transitions, one in which the order parameter takes one form and a second one where another component develops. The first transition does not break TRS but the second one does (it wouldn't if the system went into that state straight from the normal state; TRS breaking is due to the presence of the other component of the order parameter and their relative phase, which is fixed by the requirement that the correct form is recovered in the limit of zero SOC). In the limit of weak SOC, the two transitions happen so close that they are indistinguishable from a single transition going straight into the state with broken TRS.

V. DISCUSSION

Figure 1 shows the evolution of the superconducting instabilities allowed by symmetry in the absence of SOC as the latter is adiabatically turned on. We can pose the opposite question, which is: in the presence of strong SOC, how is a general pairing state decomposed into the components that would be allowed in its absence? This is shown in Fig. 2. We note that in general the pairing states allowed in the presence of SOC contain singlet, unitary and nonunitary triplet components. Interestingly, the nonunitary states, which are the only ones that can break TRS, are always shared between two different strong SOC pairing states. On the other hand the singlet s-wave state never contributes to a TRS breaking instability. Also interestingly, as shown in Fig. 2, the singlet $^1A_1$ state does mix with several triplet states, including part of the nonunitary triplet pairings $^3B_1(b)$ and $^3B_2(b)$. Nevertheless, and somewhat counterintuitively, none of these combinations break TRS.

In the light of the above analysis let us now consider possible pairing states in $LaNiC_2$. The authors of Ref. 19 have argued that the normal state of $LaNiC_2$ is weakly correlated and that the superconducting instability is of the conventional, s-wave type, resulting from phonon-mediated pairing of electrons. The justification provided for these assumptions is that a value of T_c very close to that encountered in the experiments follows from them. To explain the observation[11] of TRS breaking, a small triplet component induced by SOC is invoked. Indeed an order parameter with $^1A_1$ symmetry would develop a small triplet component as a result of SOC, as shown in Eq. (3) and Fig. 2. Unfortunately, however, such triplet component is not TRS breaking: only the nonunitary triplet pairing instabilities can break TRS. These instabilities, on the other hand, only have a small s-wave component, which vanishes completely as SOC is turned off. Our results imply that *only nonunitary triplet pairing is compatible with the observation of TRS breaking.*

A second consequence of our results, as shown in Fig. 1, is that *the superconducting instability must be split by SOC.* Since this only happens for the nonunitary triplet pairing instabilities, the observation of a split transition would be a direct consequence of TRS breaking and confirm the nonunitary triplet pairing in this system. On the other hand, given that it has not been detected in any experiment to date, the splitting must be quite small. Its observation may require the availability of single crystals, where any splitting may be more easily observed.

An outstanding issue is the quantitative estimation of the size of SOC in $LaNiC_2$. The band splitting has been calculated perturbatively using as the starting point a band structure obtained in the local-density approximation (LDA).[17] An average band splitting of $\sim$3.1 mRy, about half the value of that obtained by a similar method in the noncentrosymmetric heavy fermion superconductor $CePt_3Si$,[25,26] was found. Given that the critical temperature of $LaNiC_2$ is about three times higher than that of $CePt_3Si$ this suggests that the possible role played by SOC in $LaNiC_2$ is smaller. That said, even in this case the obtained splitting is an average and for some parts of the Fermi surface it can be either larger or smaller than that value.[17] The importance of SOC thus depends on a number of details that are as yet unknown, such as the exact functional form of the superconducting order parameter. In any case the average value is much larger than the superconducting gap and of the same order of magnitude as the Debye energy.[17] Yet as we have shown above if SOC had a strong effect on the superconducting instability the latter would not break TRS, which is at variance with the experimental data.[11] We note that LDA-based estimates of SOC have been called into question in the case of the heavy fermion noncentrosymmetric superconductor $CePt_3Si$ (Ref. 31) where de Haas-van Alphen oscillations have failed to detect the predicted band splitting.[32]

All discussions so far of the implications of the observation of TRS breaking in $LaNiC_2$,[11,19] including the one presented here, assume that this is a bulk phenomenon. However albeit very pure, the samples on which this was observed were polycrystalline.[11] A distinct possibility is that the observations could correspond to a breaking of TRS at the boundaries between crystallites.[33] On such surfaces the crystal symmetry is broken and the list of symmetry-allowed superconducting instabilities is altered. On the other hand in the experiment described in Ref. 11 muons were deposited uniformly throughout the bulk of the sample. Any magnetic fields occurring only at the boundaries between crystallites would have been screened over distances of the order of the penetration depth, λ. In order to discard completely this possibility it would therefore be required to know this number, which can be obtained for example in a transverse-field μSR experiment.

VI. CONCLUSION

In conclusion, we have studied, on the basis of group-theoretical considerations, the effect of SOC of arbitrary strength on the superconducting instability of the noncentrosymmetric intermetallic compound $LaNiC_2$. We have paid particular attention to the issue of TRS breaking. While in the absence of SOC there are 12 possible superconducting instabilities, of which four break TRS, when SOC is taken into account there are only four superconducting instabilities of the normal state and none of them break TRS. To reconcile this result with the experimental observation of TRS breaking on entering the superconducting state[11] we have studied the evolution of the superconducting instability as a small amount of SOC is adiabatically turned on. We have found that each of the eight TRS preserving singlet and unitary triplet instabilities evolve smoothly into one of the four that are allowed in the presence of SOC and we have obtained the form these must take when SOC is small but finite. In particular, our analysis shows a small triplet component developing on top of an s-wave order parameter. However, this mechanism is found *not* to lead to TRS breaking. A similar analysis for the case of the four nonunitary triplet pairing instabilities reveals that each of them splits into two distinct transitions: an instability of the normal state where superconductivity emerges without the breaking of TRS, followed by a second superconducting instability where the order parameter acquires an additional component and TRS is broken. We thus conclude that the superconducting instability must be of the nonunitary triplet type and that SOC must be comparatively small in this system so as to make the first and second transitions indiscernible. A distinct prediction of this analysis is a splitting of the superconducting transition that could be observed in single crystals and enhanced by the application of pressure. Since only the nonunitary triplet pairing instabilities are split in this way, its observation would be a direct consequence of the broken TRS and constitute definitive proof of nonunitary triplet pairing in this system.

Nonunitary triplet pairing is believed to be realized in the ferromagnetic superconductors.[34–38] In contrast, the normal state of $LaNiC_2$ just above T_c is paramagnetic. This material therefore constitutes an example of an “intrinsically” nonunitary triplet superconductor where the pairing of electrons with only one value of the spin does not result from a pre-existing exchange splitting. Elucidating the mechanism by which this comes about and the possible role that the lack of inversion symmetry may play in it, is an outstanding challenge.

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