Superconductivity in non-centrosymmetric LaNiC$_2$

Soumya P. Mukherjee and Stephanie H. Curnoe

Department of Physics and Physical Oceanography, Memorial University of Newfoundland, St. John’s, Newfoundland & Labrador A1B 3X7, Canada

(Dated: October 18, 2013)

Abstract

We present a discussion of superconductivity in non-centrosymmetric superconductors with spin-orbit coupling. A general expression for the quasiparticle excitation energy is derived. The superconducting states for the point group $C_2v$ are classified by symmetry in the limit of weak spin-orbit coupling. A non-unitary triplet pairing gap function can account for observations of broken time-reversal symmetry and nodes in the superconducting state of LaNiC$_2$; however such a gap function also has a gapless branch and requires vanishing spin-orbit coupling.

PACS numbers: 74.50.+r, 72.25.-b, 74.20.Rp, 74.70.Tx
I. INTRODUCTION

There are many non-centrosymmetric (NCS) superconductors, including CePt$_3$Si,$^1$ Cd$_2$Re$_2$O$_7$,$^{2,3}$ Mg$_{10}$Ir$_{19}$B$_{16}$,$^4$ Li$_2$Pd$_3$B$_5$,$^5$ Li$_2$Pt$_3$B,$^6$ UIr,$^7$ LaNiC$_2$,,$^8$ and BiPd.$^9$ The main consequence of broken inversion symmetry in superconductors is that it admits the possibility of mixed spin singlet and spin triplet pairing. However, the determination of the symmetry of the superconducting state follows the same principles as for centrosymmetric superconductors, namely the identification of the order parameter corresponding to an irreducible representation of the symmetry group of the crystal. The symmetry group of the normal state consists of the (magnetic) space group, $U(1)$ gauge symmetry, and $SU(2)$ spin rotation symmetry if spin-orbit coupling is sufficiently weak. Often, the magnetic space group is just the product of the ordinary space group with time reversal symmetry (TRS); however in some cases (such as CePt$_3$Si) the magnetic space group is more complicated because of the existence of magnetic order above the superconducting transition. Here we are concerned with the former type, among them LaNiC$_2$.

The various phenomena associated with broken gauge symmetry mark the onset of superconductivity. If gauge symmetry is the only symmetry that is broken at the transition then superconductivity is “conventional”, otherwise it is “unconventional”. In unconventional superconductors broken gauge symmetry may be accompanied by a lower point group symmetry, broken TRS, or even broken translation symmetry. There are few examples of superconductors with broken TRS. The most famous is Sr$_2$RuO$_4$,$^{10}$ and it has also been proposed for PrOs$_4$Sb$_{12}$.$^{11}$ A recent $\mu$SR experiment by Hillier et al.$^{12}$ showed that on entering the superconducting state at $T_c = 2.7K$, LaNiC$_2$ also simultaneously breaks TRS.

Various experiments performed on LaNiC$_2$ have led to different proposals for the symmetry of the superconducting gap function based on the presence of nodes. Early measurements of specific heat$^{13}$ and NQR $1/T_1$ relaxation time$^{14}$ suggested conventional BCS behaviour. Another early experiment on specific heat found evidence for point nodes.$^8$ Finally, a recent penetration depth measurement$^{15}$ found a power law dependence on temperature, indicative of nodes, most likely line nodes. Based on these experimental findings, we will explore the possible symmetry groups of the superconducting order parameter, especially those with broken TRS.

The outline for this article is as follows. We begin by examining band electrons in a
lattice without inversion symmetry with spin-orbit coupling. Using a spin helicity basis, we derive a general expression for the quasi-particle excitation energy. In order to classify superconducting states in LaNiC$_2$, two approaches are considered in the limit of weak spin-orbit coupling.$^{12,16}$ The type (line vs. point) and location of nodes are calculated and compared with experiment.

II. SUPERCONDUCTIVITY IN NON-CENTROSYMMETRIC CRYSTALS

The normal state Hamiltonian for band electrons in a lattice without inversion symmetry is

$$H_0 = \sum_{\mathbf{k},s} \xi_{\mathbf{k}} c_{\mathbf{k}s}^\dagger c_{\mathbf{k}s} + \sum_{\mathbf{k},s,s'} (\mathbf{g}_\mathbf{k} \cdot \sigma)_{ss'} c_{\mathbf{k}s}^\dagger c_{\mathbf{k}s'},$$

(1)

where electrons with momentum $\mathbf{k}$ and spin $s$ (=↑ or ↓) are created (annihilated) by the operators $c_{\mathbf{k}s}^\dagger$ ($c_{\mathbf{k}s}$), $\xi_{\mathbf{k}}$ is the band energy measured from the Fermi energy $\epsilon_F$ and $\sigma$ are the Pauli matrices. The second term in the Hamiltonian (1) is spin-orbit coupling (SOC). The form of the SOC is governed by the symmetry of the underlying point group. In a non-centrosymmetric crystal it is common to assume that $\mathbf{g}_{-\mathbf{k}} = -\mathbf{g}_{\mathbf{k}}$. Because of broken parity and SOC, the spin degeneracy of the band is lifted. By diagonalizing $H_0$, one finds two non-degenerate bands with energies $\xi_{\mathbf{k}\lambda} = \xi_{\mathbf{k}} + \lambda|\mathbf{g}_{\mathbf{k}}|$ where $\lambda = \pm 1$ is “helicity” of the bands. Therefore in the diagonalized basis $H_0$ (1) becomes $H_0 = \sum_{\mathbf{k},\lambda} \xi_{\mathbf{k}\lambda} c_{\mathbf{k}\lambda}^\dagger c_{\mathbf{k}\lambda}$, where $c_{\mathbf{k}\lambda}^\dagger$ and $c_{\mathbf{k}\lambda}$ are the electron creation and annihilation operators for the band with helicity $\lambda$ and momentum $\mathbf{k}$. The unitary transformation from the spin basis to the helicity basis is

$$c_{\mathbf{k}\uparrow} = \frac{1}{\sqrt{2|\mathbf{g}_{\mathbf{k}}|}} \left[ \sqrt{|\mathbf{g}_{\mathbf{k}}| + \mathbf{g}_{\mathbf{k}} \cdot \mathbf{c}_{\mathbf{k}\uparrow} + \sqrt{|\mathbf{g}_{\mathbf{k}}|}} - \mathbf{g}_{\mathbf{k}} \cdot \mathbf{c}_{\mathbf{k}\downarrow} \right]$$

$$c_{\mathbf{k}\downarrow} = \frac{e^{i\phi_{\mathbf{k}}}}{\sqrt{2|\mathbf{g}_{\mathbf{k}}|}} \left[ \sqrt{|\mathbf{g}_{\mathbf{k}}| - \mathbf{g}_{\mathbf{k}} \cdot \mathbf{c}_{\mathbf{k}\uparrow} - \sqrt{|\mathbf{g}_{\mathbf{k}}|}} + \mathbf{g}_{\mathbf{k}} \cdot \mathbf{c}_{\mathbf{k}\downarrow} \right]$$

where $e^{i\phi_{\mathbf{k}}} = \frac{g_{\mathbf{k}x} + ig_{\mathbf{k}y}}{|\mathbf{g}_{\mathbf{k}}|}$.

To describe superconductivity, we add to $H_0$ (1) a superconducting pairing term $H_1$,

$$H = H_0 + H_1$$

$$H_1 = \frac{1}{2} \sum_{\mathbf{k},s,s'} \left[ \Delta_{ss'}(\mathbf{k}) c_{\mathbf{k}s}^\dagger c_{-\mathbf{k}s'}^\dagger - \Delta_{ss'}^*(-\mathbf{k}) c_{-\mathbf{k}s} c_{\mathbf{k}s'} \right]$$

(2)

where $\Delta(\mathbf{k})$ is the gap function, a $2 \times 2$ matrix in spin space of the form

$$\Delta(\mathbf{k}) = i\psi(\mathbf{k})\sigma_y, \quad \psi(\mathbf{k}) = \psi(-\mathbf{k})$$

(3)
for singlet spin pairing, or
\[
\Delta(k) = id(k) \cdot \sigma_y, \quad d(k) = -d(-k)
\]
for triplet pairing. \(\Delta(k)\) is associated with one of the irreducible representations of the point group. In a NCS superconductor, the gap function can be a mixture of even and odd representations,
\[
\Delta(k) = \psi(k) + d(k) \cdot \sigma_y
\]
If \(\Delta\Delta^\dagger\) is proportional to the unit matrix then superconductivity is “unitary”, otherwise it is “non-unitary”. In a centrosymmetric superconductor, non-unitarity arises in the triplet channel from broken TRS, which splits the quasi-particle energy degeneracy. In a NCS superconductor, the gap function (5) is non-unitary due to mixed parity.

In the helicity basis, \(H\) takes the form
\[
H = \sum_{k,\lambda} \left[ \xi_{k\lambda} \tilde{c}_{k\lambda}^\dagger \tilde{c}_{k\lambda} + \Delta_{\lambda}(k) \tilde{c}_{k\lambda}^\dagger \tilde{c}_{-k\lambda}^\dagger - \Delta_{-\lambda}^*(k) \tilde{c}_{-k\lambda} \tilde{c}_{k\lambda} \right] + \sum_{k,\lambda\lambda'} \left( \Delta_{\lambda\lambda'}(k) \tilde{c}_{k\lambda}^\dagger \tilde{c}_{-k\lambda'}^\dagger - \Delta_{-\lambda\lambda'}^*(k) \tilde{c}_{-k\lambda} \tilde{c}_{k\lambda'} \right),
\]
where
\[
\Delta_{\lambda}(k) = -\lambda e^{-i\phi} \left[ \psi(k) + \lambda(d(k) \cdot \hat{g}_k) \right]
\]
\[
\Delta_{\lambda\lambda'}(k) = \frac{\lambda e^{-i\phi}}{\sqrt{g_{kx}^2 + g_{ky}^2}} \left[ \{\hat{g}_k \times (d(k) \times \hat{g}_k)\} + i\lambda'(d(k) \times \hat{g}_k) \right]_z
\]
and \(\hat{g}_k\) is the unit vector along \(g_k\). Eq. (8) clearly indicates that for \(d(k)\) parallel to \(g_k\) the interband pairing term completely disappears. This results in less condensation energy for the superconducting state therefore stabilizing \(d(k) \parallel g_k\).

Neglecting interband pairing, we find the quasiparticle excitation energy,
\[
E_{k\lambda} = [\xi_{k\lambda}^2 + |\psi(k)|^2 + (d(k) \cdot \hat{g}_k)(d^*(k) \cdot \hat{g}_k) + \lambda(\psi(k)d^*(k) + \psi^*(k)d(k)) \cdot \hat{g}_k]^2, \tag{9}
\]
which is non-degenerate due to the lifting of band degeneracy in the normal state and a mixed parity superconducting gap function. When TRS is preserved (\(d\) and \(\psi\) are real), we have
\[
E_{k\lambda} = \left[ \xi_{k\lambda}^2 + (\psi(k) + \lambda(d(k) \cdot \hat{g}_k))^2 \right]^{1/2}, \tag{10}
\]
which is a well-known result for a general NCS superconductor. However, in LaNiC\(_2\), SOC is expected to be weak and therefore interband pairing should be considered.
TABLE I: Sample gap functions for singlet $\psi(k)$ and triplet $d(k)$ pairing for the point group $C_{2v}$ when SOC is included\textsuperscript{21}. The first column lists the irreducible representations of $C_{2v}$, the second and third columns list representative forms for the functions $\psi(k)$ and $d(k)$, the fourth column is the symmetry of the superconducting state and the fifth column lists symmetry-required nodes. $A$, $B$ and $C$ are arbitrary constants.

| $C_{2v}$ | $\psi(k)$ | $d(k)$ | Symmetry | Nodes |
| --- | --- | --- | --- | --- |
| $A_1$ | 1 | $(Ak_x, Bk_y, Ck_z)$ | $C_{2v} \times T$ | none |
| $A_2$ | $k_xk_y$ | $(Ak_y, Bk_x, Ck_xk_yk_z)$ | $C_{2v}(C_2^z) \times T$ | point [001] |
| $B_1$ | $k_xk_z$ | $(Ak_z, Bk_xk_yk_z, Ck_x)$ | $C_{2v}(\sigma_{xz}) \times T$ | point [010] |
| $B_2$ | $k_yk_z$ | $(Ak_xk_yk_z, Bk_x, Ck_x)$ | $C_{2v}(\sigma_{yz}) \times T$ | point [100] |

III. CLASSIFICATION OF SUPERCONDUCTING STATES

Now we perform a symmetry analysis of possible superconducting states. LaNiC\textsubscript{2} crystallizes into a single phase of orthorhombic space group $Amm2$ (No. 38, $C_{14}^{14}$). Possible superconducting states are derived from irreducible representations of the normal-state symmetry group. If we consider that SOC is weak then there are two approaches:

i) band splitting due to SOC is neglected, but the helicity basis is used to describe superconductivity, with interband pairing. Then the normal-state symmetry is $C_{2v} \times T \times U(1)$, where $T$ is time-reversal and $U(1)$ is gauge (phase) symmetry.\textsuperscript{16}

ii) spin-orbit coupling is completely neglected and so the symmetry group (for a pair of spins) is $SO(3) \times C_{2v} \times T \times U(1)$\textsuperscript{12}.

These approaches differ from the limit of strong SOC when interband pairing can be neglected.\textsuperscript{20}

The first approach yields functions $\psi(k)$ and $d(k)$ that are the same as strong SOC in a centrosymmetric superconductor, therefore the trial functions listed in Table I are the same as those for $D_{2h}$\textsuperscript{21}. The only difference between the NCS and centrosymmetric cases is that mixed parity states are allowed. The magnitude of the gap of a mixed-parity centrosymmetric superconductor is $|\Delta_{\pm}(k)|^2 = |\psi(k)|^2 + |d(k)|^2 \pm |p(k) + q(k)|$, where $p(k) = \psi(k)d^*(k) + \psi^*(k)d(k)$ and $q(k) = i[d(k) \times d^*(k)]$.\textsuperscript{22} TRS is not broken for any of the phases involving the 1D order parameters listed in Table I, but the gap function is
TABLE II: Sample gap functions for singlet and triplet pairing for the point group $C_{2v}$ when there is no SOC.$^{21}$ The first column lists the irreducible representations of $SO(3) \times C_{2v}$, the second column lists representative forms of $\psi(k)$ and $d(k)$, the third column lists the symmetries of the superconducting states and the fourth column lists symmetry-required nodes.

| $\psi(k)$ | Symmetry | Nodes |
|-----------|-----------|-------|
| $^{1}A_1$ | $SO(3) \times C_{2v} \times T$ | none |
| $^{1}A_2$ | $k_x k_y$ | $SO(3) \times C_{2v}(C_2^z) \times T$ | lines $k_x, k_y = 0$ |
| $^{1}B_1$ | $k_x k_z$ | $SO(3) \times C_{2v}(\sigma_{xz}) \times T$ | lines $k_x, k_z = 0$ |
| $^{1}B_2$ | $k_y k_z$ | $SO(3) \times C_{2v}(\sigma_{yz}) \times T$ | lines $k_y, k_z = 0$ |

| $d(k)$ | Symmetry | Nodes |
|--------|-----------|-------|
| $^{3}A_1$ | $\psi(k)$ | $D_{\infty}(C_{\infty}) \times C_{2v} \times T$ | lines $k_x, k_y, k_z = 0$ |
| $^{3}A_2$ | $\psi(k)$ | $D_{\infty}(C_{\infty}) \times C_{2v}(C_2^z) \times T$ | line $k_x = 0$ |
| $^{3}B_1$ | $\psi(k)$ | $D_{\infty}(C_{\infty}) \times C_{2v}(\sigma_{xz}) \times T$ | line $k_y = 0$ |
| $^{3}B_2$ | $\psi(k)$ | $D_{\infty}(C_{\infty}) \times C_{2v}(\sigma_{yz}) \times T$ | line $k_x = 0$ |

non-unitary because $\Delta \Delta^\dagger$ is not proportional to the identity matrix and the magnitude of the gap is $|\Delta_{\pm}(k)| = |(|\psi(k)| \pm |d(k)|)|$. Symmetry-required nodes are those which occur in $\Delta_{\pm}(k)$ for any values of the parameters $A$, $B$ and $C$; lines nodes may also be found for $\Delta_{-}(k)$ depending on the choice of parameters.$^{22}$

The gap functions resulting from the second approach are tabulated in Refs. 12,16 and reproduced in Table II. Table II also gives the symmetry$^{21}$ and symmetry-required nodes of each possible phase. In the singlet cases, $SO(3)$ spin symmetry is preserved. However, in the triplet cases two possibilities are realised. In the first possibility the triplet spin state is of the form $|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle$. The symmetry of this spin state is $D_{\infty}(C_{\infty}) \times T$. This possibility
is shown in the upper rows of the triplet cases in Table II. The other possibility is that the spin state is of the form \( |↑↑⟩ \), that is, the spin points in a definite direction. This state breaks TRS; its symmetry group is \( D_∞(E) \). Combined with the real-space part of the gap functions, we find twelve distinct superconducting phases. In all cases except the trivial \( 1A_1 \) case the gap function has line nodes; in the non-unitary case these occur in \( \Delta_±(k) \), where

\[
|\Delta_±(k)| = \sqrt{|d(k)|^2 ± |q(k)|}
\]

and \( q(k) = id(k) \times d^∗(k) \), while the \( \Delta_−(k) \) is gapless.\(^\text{12} \)

We now discuss those phases that have broken TRS, as observed in Ref. 12. According to the symmetry classifications, the only phases that break TRS are found in the weak SOC classification scheme (Table II) and are non-unitary. These always occur with line nodes and gapless excitations.\(^\text{12} \) Gaplessness should be reflected in power laws, but it seems unlikely that any of the early specific heat experiments\(^\text{8,13} \) are compatible with gapless superconductivity. Therefore, it is difficult to reconcile a state with broken TRS with these measurements.

There is second issue related to broken TRS in a \( C_2v \) crystal that is difficult to resolve. According to the results of symmetry classification, a TRS breaking state is possible only when SOC is completely neglected. However, SOC exists in the normal state\(^\text{23} \), and while its effects are smaller than that of CePt\(_3\)Si, it is large enough to justify a strong SOC approach.\(^\text{23} \) However, there are no broken TRS states in this approach. Therefore, in order for TRS to be broken there must be a decoupling of the orbital and spin degrees of freedom in the superconducting phase.

To summarise, beginning with the most general description of superconductivity in non-centrosymmetric crystals, we have analysed possible superconducting phases for the point group \( C_2v \), assuming weak spin-orbit coupling. In order to account for TRS breaking, superconductivity in LaNiC\(_2\) should be described by a non-unitary order parameter in the triplet channel with SOC neglected. Such a gap function has line nodes in its upper branch while its lower branch is gapless. In order to confirm this phase, further investigations that can establish the existence and positions of line nodes and gapless superconductivity are required.

\(^1\) Bauer E, Hilscher G, Michor H, Paul Ch, Scheidt E W, Gribanov A, Seropegin Yu, Noël H, Sigrist M and Rogl P 2004 Phys. Rev. Lett. 92 027003.
2 Hanawa M, Muraoka Y, Tayama T, Sakakibara T, Yamaura J, and Hiroi Z 2001, Phys. Rev. Lett. 87, 187001.
3 Castellan J P, Gaulin B D, van Duijn J, Lewis M J, Lumsden M D, Jin R, He J, Nagler S E and Mandrus D 2002 Phys. Rev. B 66 134528.
4 Klimczuk T, Ronning F, Sidorov V, Cava R J and Thompson J D 2007 Phys. Rev. Lett. 99 257004.
5 Togano K, Badica P, Nakamori Y, Orimo S, Takeya H and Hirata K 2004 Phys. Rev. Lett. 93 247004.
6 Badica P, Kondo T and Togano K 2005 J. Phys. Soc. Jpn.74 1014.
7 Akazawa T, Hidaka H, Fujiwara T, Kobayashi T C, Yamamoto E, Haga Y, Settai R and Onuki Y 2004 J. Phys.: Condens. Matter L29.
8 Lee W H, Zeng H K, Yao Y D and Chen Y Y 1996 Physica C 266 138.
9 Joshi B, Thamizhavel A and Ramakrishnan S 2011 Phys. Rev. B 84 064518.
10 Luke G M, Fudamoto Y, Kojima K M, Larkin M I, Merrin J, Nachumi B, Uemura Y J, Maeno Y, Mao Z Q, Mori Y, Nakamura H and Sigrist M, 1998 Nature 394 558.
11 Aoki Y, Tsuchiya A, Kanayama T, Saha S R, Sugawara H and Sato H, Phys. Rev. Lett. 91, 067003 (2003).
12 Hillier A D, Quintanilla J and Cywinski R 2009 Phys. Rev. Lett. 102 117007, Hillier A D, Quintanilla J and Cywinski R 2010 Phys. Rev. Lett. 105 229001(E).
13 Pecharsky V K, Miller L L and Gschneidner K A 1998 Phys. Rev. B 58 497.
14 Iwamoto Y, Iwasaki Y, Ueda K and Kohara T 1998 Phys. Lett. A 250 439.
15 Bonalde I, Ribeiro R L, Syu K J, Sung H H and Lee W H 2011 New J. Phys. 13 123022.
16 Quintanilla J, Hillier A D, Annett J F and Cywinski R 2010 Phys. Rev. B 82 174511.
17 Mineev V P 2004 Int. J. Mod. Phys. B 18 2963.
18 Samokhin K V and Mineev V P 2008 Phys. Rev. B 77 104520.
19 Frigeri P A, Agterberg D F, Koga A and Sigrist M 2004 Phys. Rev. Lett. 92 097001.
20 Sergienko I A and Curnoe S H 2004 Phys. Rev. B 70 214510.
21 Annett J F 1990 Adv. Phys. 39 83.
22 Sergienko I A 2004 Phys. Rev. B 69 174502.
23 Hase I and Yanagisawa T 2009 J. Phys. Soc. Jpn.78 084724.