Mixed-parity superconductivity in centrosymmetric crystals

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A weak-coupling formalism for superconducting states possessing both singlet (even parity) and triplet (odd parity) components of the order parameter in centrosymmetric crystals is developed. It is shown that the quasiparticle energy spectrum may be non-degenerate even if the triplet component is unitary. The superconducting gap of a mixed-parity state may have line nodes in the strong spin-orbit coupling limit. The pseudospin carried by the superconducting electrons is calculated, from which follows a prediction of a kink anomaly in the temperature dependence of muon spin relaxation rate. The anomaly occurs at the phase boundary between the bare triplet and mixed-parity states. The stability of mixed-parity states is discussed within Ginzburg-Landau theory. The results may have immediate application to the superconducting series Pr(Os$_{1-x}$Ru$_x$)$_4$Sb$_{12}$.

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I. INTRODUCTION

Very recently, magnetic susceptibility and electrical resistivity measurements on the filled skutterudite series Pr(Os$_{1-x}$Ru$_x$)$_4$Sb$_{12}$ found that superconductivity exists in the whole concentration range $0 \leq x \leq 1$. While PrRu$_4$Sb$_{12}$ is a conventional s-wave superconductor with $T_c=1$ K, PrOs$_4$Sb$_{12}$ is a heavy fermion material with $T_c=1.85$ K. There is experimental evidence that PrOs$_4$Sb$_{12}$ has two superconducting (SC) phases and that the quasiparticle energy spectrum has point nodes. These facts indicate that the SC order parameter is definitely unconventional. Zero-field muon-spin relaxation ($\mu$SR) measurements suggest that the pairing in PrOs$_4$Sb$_{12}$ can be triplet (odd parity). The competition between the conventional s-wave and triplet order parameters may result in the appearance of a new SC state in Pr(Os$_{1-x}$Ru$_x$)$_4$Sb$_{12}$ which has both singlet and triplet components and therefore is a mixed-parity (MP) state.

So far, several systems in which MP SC states may occur have been studied theoretically. Mineev and Samokhin showed that the normal state may be unstable with respect to a helical MP structure if the product of the two different parity representations of the symmetry group contains a vector representation. The possible occurrence of MP states due to inhomogeneity of the order parameter in the Larkin-Ovchinnikov-Fulde-Ferrel state was addressed in Refs. 11,12. MP states in two-dimensional superconductors, in which inversion symmetry is broken due to low dimensionality, were studied by Gor’kov and Rashba. Finally, an intriguing prediction was made by Volkov et al. about the possibility of generating a triplet condensate in mesoscopic ferromagnet/singlet superconductor multilayers.

In this paper, we analyse MP SC states in bulk crystals with inversion symmetry in zero magnetic field and describe the possible experimental manifestation of the MP state in Pr(Os$_{1-x}$Ru$_x$)$_4$Sb$_{12}$. We discuss the possibility of the realization of a MP state in terms of Ginzburg-Landau (GL) theory. We develop a weak-coupling formalism for MP states based on the generalized BCS approach. We obtain the quasiparticle energy spectrum and show that it may be non-degenerate even if the triplet component is unitary. It is shown that the gap function of the MP state in the strong spin-orbit limit may have line nodes, in contrast to bare triplet states. The Gor’kov formalism is used to obtain the self-consistent equation of the gap function and to calculate the pseudospin carried by the SC electrons. A kink anomaly in the temperature dependence of the muon spin relaxation rate is expected on the boundary between the bare triplet and MP states.

II. GINSBURG-LANDAU MODEL

The explicit form of the GL functional can be established only if the transformation properties of the multi-dimensional order parameters with respect to the spatial symmetry transformations are known. Thus far, the symmetry of the order parameter in PrOs$_4$Sb$_{12}$ has not been determined unambiguously. Also, the effects of multi-dimensionality of the order parameter are beyond the scope of this paper. Thus, we adopt an effective one-component model which only takes into account gauge, inversion and time reversal but not the crystallographic symmetry. We denote by $\eta = |\eta|e^{i\phi_1}$ the non-vanishing component of the singlet order parameter and by $\xi = |\xi|e^{i\phi_2}$ that of the triplet order parameter. A homogeneous situation in zero magnetic field is considered in the following, so that the gradient terms of $\eta$ and $\xi$ are neglected. The GL potential is

$$F = a_1[T - T_{c1}(x)]|\eta|^2 + b_1[T - T_{c2}(x)]|\xi|^2$$

$$+ a_2|\eta|^4 + b_2|\xi|^4 + c_1|\eta|^2|\xi|^2 + c_2(\eta^2\xi^*2 + \eta^*2\xi^2),$$

where $T$ is temperature and $T_{c1,2}(x)$ are concentration dependent transition temperatures for the singlet and triplet order parameters, respectively. The latter can be roughly fitted to the experimental data as linear functions $T_{c1}(x) = T_0[1 - \alpha(1 - x)], T_{c2}(x) = T_1(1 - 3\beta x)$ with

$$T_0 \approx 1 K, T_1 \approx 1.85 K.$$
\[ T_s = 1.2 \text{ K}, \quad T_l = 1.8 \text{ K}, \quad \alpha = 1.07, \quad \text{and} \quad \beta = 1.03. \]

The rest of the parameters in \( \Pi \) are assumed to be undetermined constants.\(^{16} \)

\( F \) can be immediately minimized with respect to the relative phase \( \Delta \phi = \phi_1 - \phi_2 \). Depending on the sign of \( c_2 \), the following MP states are energetically favoured

\[
\Delta \phi = \pi/2, 3\pi/2, \quad \eta \xi^* = \pm|\eta|/|\xi| \quad \text{for} \quad c_2 > 0; \quad (2a)
\]

\[
\Delta \phi = 0, \pi, \quad \eta \xi^* = \pm|\eta|/|\xi| \quad \text{for} \quad c_2 < 0. \quad (2b)
\]

The phase diagram of \( \Pi \) adapted for \( \text{Pr}(\text{Os}_{1-x}\text{Ru}_x)_{4}\text{Sb}_{12} \) is shown in Fig. 1. If \( 4a_2b_2 > (c_1 - 2|c_2|)^2 \), one of the MP states \( \Pi \) exists in the sector bounded by two second-order transition lines

\[
T(x) = \frac{ca_1 T_c(x) - 2a_2 b_1 T_c(x)}{ca_1 - 2a_2 b_1} \quad (3)
\]

on the singlet side and

\[
T(x) = \frac{2b_2 a_1 T_c(x) - 3b_1 T_c(x)}{2b_2 a_1 - b_1} \quad (4)
\]

on the triplet side. If \( 4a_2b_2 < (c_1 - 2|c_2|)^2 \), the MP states \( \Pi \) do not minimize \( F \) and a first-order phase transition between the bare singlet and triplet states occurs at the line

\[
T(x) = \frac{a_1 \sqrt{b_2} T_c(x) - b_1 \sqrt{a_2} T_c(x)}{a_1 \sqrt{b_2} - b_1 \sqrt{a_2}}. \quad (5)
\]

Phenomenologically, therefore, both types of the phase diagram shown in Fig. 1 may occur with the same probability in the sense that they are described by the same fourth-order model \( \Pi \). Another doped system \( \text{U}_{1-x}\text{Th}_x\text{Be}_{13} \) is an example in which the co-existence of two SC order parameters is preferred to the first-order phase transition scenario.\(^{17,18} \)

### III. GENERALIZED BCS APPROACH

A realistic description of superconductivity in \( \text{Pr}(\text{Os}_{1-x}\text{Ru}_x)_{4}\text{Sb}_{12} \) should be based on a strong-coupling approach which would incorporate the superconductivity mechanism and coupling of SC electrons to the Os(Ru) ions. However, at present even the superconductivity mechanism of pure \( \text{PrOs}_4\text{Sb}_{12} \) remains vague. In this paper our goal is to elucidate the qualitative features of MP states rather than to make quantitative predictions. Hence, we use the weak-coupling approach, implicitly assuming that the main ingredients of the theory, the band energy relative to the chemical potential \( \epsilon(k) \) and the pairing interaction matrix element \( V_{s_1,s_2,s_3,s_4}(k,k') \), depend on the Ru concentration \( x \).

The generalized mean-field BCS Hamiltonian is

\[
H = \sum_{k,s} \epsilon(k)a^\dagger_{ks}a_{ks} + \frac{1}{2} \sum_{k,s_1,s_2} \left[ \Delta_{s_1,s_2}(k)a^\dagger_{ks_1}a^\dagger_{-k}\Delta^*_{s_1,s_2}(-k)a_{-k,s_2} \right] - \Delta_{s_1,s_2}^*(k)a_{k,s_1}a_{-k,s_2}, \quad (6)
\]

where \( a^\dagger_{ks} \) (\( a_{ks} \)) is the creation (annihilation) operator of an electron with wave vector \( k \) and pseudospin \( s \) and the gap function matrix is

\[
\Delta_{s_1,s_2}(k) = -\sum_{k',s_3,s_4} V_{s_2,s_3,s_4}(k,k') \langle a_{k's_3}a_{-k',s_4} \rangle. \quad (7)
\]

The gap function is conveniently parametrized by an even scalar function \( \psi(k) = \sum_\eta \psi_\eta(k) \) for the singlet component and an odd vectorial function \( d(k) = \sum_\xi d_\xi(k) \) for the triplet component. Here \( \psi_\eta(k) \) and \( d_\xi(k) \) are basis functions of the irreducible representations of the point group and \( \eta \) and \( \xi \) are the corresponding order parameters.\(^{13} \) In the MP state the gap function takes the form

\[
\hat{\Delta}(k) = [\psi(k)\hat{\sigma}_0 + d(k)\hat{\sigma}]i\hat{\sigma}_y, \quad (8)
\]

where \( \hat{\sigma}_0 \) is the \( 2 \times 2 \) unit matrix and \( \hat{\sigma} = (\hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z) \) are the Pauli matrices.

The Bogoliubov transformation for the diagonalization of \( \hat{\Delta}(k) \) yields the quasiparticle energy spectrum

\[
E_{k\pm} = \sqrt{\epsilon(k)^2 + \Delta^2_{k}(k)^2}, \quad (9)
\]

with two gaps \( \Delta_{\pm}(k) \) defined by

\[
\Delta_{\pm}(k)^2 = |\psi(k)|^2 + |d(k)|^2 \pm |p(k) + q(k)|, \quad (10)
\]

where two real vectors \( p(k) = \psi(k)d^*(k) + \psi^*(k)d(k) \) and \( q(k) = i[d(k) \times d^*(k)] \) are introduced. They are orthogonal to each other, therefore

\[
|p(k) + q(k)| = \sqrt{p(k)^2 + q(k)^2}. \quad (11)
\]

Note that if \( q(k) \neq 0 \), i.e., \( d(k) \) and \( d^*(k) \) are not collinear, then \( p(k) \) is finite in the MP state.

It follows that the quasiparticle spectrum \( \Pi \) is degenerate only if \( p(k) = q(k) = 0 \). Such a state corresponds
to 20. It is not invariant with respect to time reversal $K$, but it possesses a combined symmetry element $U_1(\pi)JK$, where $U_1$ is the gauge transformation and $I$ is inversion. In a time reversal invariant MP state, $q(k) = 0$ and $p(k) = 2|\psi(k)||d(k)|$ [See 20]. Then, the gap acquires the form

$$\Delta_{\pm}(k)^2 = \left(|\psi(k)| \pm |d(k)|\right)^2. \quad (12)$$

As follows from 10, the gap of a MP state vanishes if both singlet and triplet components have nodes, i.e., $\psi(k) = 0$ and $|d(k)| = |d(k) \times d'(k)|$. In the strong spin-orbit coupling limit 20 these nodes can be found only at isolated points on the Fermi surface unless the Fermi surface crosses the boundary of the Brillouin zone. However, $\Delta_-$ may have additional line nodes if $p \neq 0$, as illustrated by the following example.

Keeping in mind the possible application to Pr(01−2Ru4)4Sb12, we consider a $p$-wave state which may arise under $T_h$ crystallographic symmetry. Time reversal symmetry is broken in the SC state of PrOs4Sb12. Here, for the sake of simplicity, a time-reversal invariant admixture of $s$- and $p$-wave states is considered, in which the gap takes the simple form 12. We can show that this simplification does not affect the main result, line nodes may exist for finite $q$ as well.

Let us take a $p$-wave state belonging to the irreducible representation $T_w$ of $T_h$. This representation has two linearly independent sets of basis functions. Therefore, in general, one should take into account two order parameters of the same symmetry. We consider the state denoted $(0, 0, 1)$ in the order parameter space. The MP gap function is given by

$$\psi(k) = \eta, \quad d(k) = \xi_1k_x\hat{y} + \xi_2k_y\hat{x}, \quad (13)$$

where $\eta, \xi_1$ and $\xi_2$ are the $T$ and $x$ dependent order parameters. $\Delta_{-}(k)$ vanishes at two lines defined by the equation

$$|\xi_1|^2k_x^2 + |\xi_2|^2k_y^2 = |\eta|^2. \quad (14)$$

The line nodes exist while $|\eta| \leq \max(|\xi_1|, |\xi_2|)$. This condition is obeyed close to the boundary with the bare triplet state. Fig. 2 shows the line nodes on a unit spherical Fermi surface for $|\xi_1| > |\xi_2|$. Note that in this example the line nodes are not remnants of line nodes of the singlet state, which is fully gapped, but rather they appear due to a distortion of point nodes of the triplet component.

IV. GREEN’S FUNCTIONS AND GAP EQUATION

Beginning with the equations of motion for Heisenberg operators, the Gor’kov equations 23 for the normal $G_{ss'}(k, \tau)$ and anomalous $F_{ss'}(k, \tau)$, $F_{ss'}^\dagger(k, \tau)$ temperature Green’s functions in the MP state are obtained in the usual way 20. The Green’s functions are defined as

$$G_{ss'}(k, \tau) = -\langle T_\tau \{a_{ks}(\tau)a^\dagger_{ks'}(0)\} \rangle, \quad F_{ss'}(k, \tau) = \langle T_\tau \{a_{ks}(\tau)a_{-ks'}(0)\} \rangle, \quad F_{ss'}^\dagger(k, \tau) = \langle T_\tau \{a^\dagger_{-ks}(\tau)a^\dagger_{ks'}(0)\} \rangle, \quad (15)$$

where $T_\tau$ is the imaginary time ordering operator. The Fourier transform is $\hat{A}(k, \tau) = T\sum_\omega \hat{A}(k, \omega)e^{-i\omega_\tau}$, where $\hat{A}$ stands for $\hat{G}$, $\hat{F}$, or $\hat{F}^\dagger$; $T$ is temperature and $\omega_\tau = \pi T(2n+1)$ is the Matsubara frequency for fermions.

The resulting Gor’kov equations for the Fourier transforms are

$$[i\omega_n - \varepsilon(k)]\hat{G}(k, \omega_n) + \hat{\Delta}(k)\hat{F}^\dagger(k, \omega_n) = \hat{\sigma}_0, \quad [i\omega_n + \varepsilon(k)]\hat{F}^\dagger(k, \omega_n) + \hat{\Delta}^\dagger(k)\hat{G}(k, \omega_n) = 0. \quad (16)$$

They are solved by

$$\hat{G}(k, \omega_n) = \frac{-[\omega_n^2 + \varepsilon(k)^2 + |\psi(k)|^2 + |d(k)|^2]|\sigma_0 + [p(k) + q(k)]|\bar{\sigma}}{(\omega_n^2 + E_{k+}^2)(\omega_n^2 + E_{k-}^2)}[i\omega_n + \varepsilon(k)], \quad (17)$$

$$\hat{F}(k, \omega_n) = \frac{[\omega_n^2 + \varepsilon(k)^2 + |\psi(k)|^2 + |d(k)|^2]|\Delta(k) - [p(k) + q(k)]\bar{\Omega}(k)}{(\omega_n^2 + E_{k+}^2)(\omega_n^2 + E_{k-}^2)}.$$

where

$$\bar{\Omega}(k) = \frac{d(k)p(k)\bar{\sigma}_0 + [\psi(k)p(k) + iq(k) \times d(k)]\bar{\sigma}}{|p(k) + q(k)|}(i\bar{\sigma}_y). \quad (18)$$

The denominator introduced in the definition of $\bar{\Omega}(k)$ allows one to put the self-consistent gap equation in a...
concise form. Using (7), (15), and (17) one obtains

$$\Delta_{s_1s_2}(\mathbf{k}) = - \sum_{\mathbf{k}',s_3s_4} V_{s_3s_4s_1s_2}(\mathbf{k},\mathbf{k}') \mathcal{F}_{s_3s_4}(\mathbf{k}',T),$$

where

$$\tilde{\mathcal{F}}(\mathbf{k},T) = \frac{\Delta(\mathbf{k}) + \tilde{\Omega}(\mathbf{k})}{4E_{k+}} \tanh \left( \frac{E_{k+}}{2T} \right) + \frac{\Delta(\mathbf{k}) - \tilde{\Omega}(\mathbf{k})}{4E_{k-}} \tanh \left( \frac{E_{k-}}{2T} \right).$$

V. MUON SPIN ROTATION IN MIXED-PARITY STATES

$\mu$SR measurements are widely used to reveal the nature of a SC state as they provide invaluable information about the distribution of the local magnetic field $\mathbf{H}$. There are several possible sources of internal magnetic fields in superconductors. They include magnetic moments of localized states, two-dimensional imperfections such as domain walls and the surface, and magnetic moment of Cooper pairs. Sigrist and Rice showed that the latter contribution always vanishes in singlet pairing states, and it is non-vanishing in bare triplet states only if $\mathbf{q}(\mathbf{k}) \neq 0$. The zero-field $\mu$SR spectra are usually fitted using the Kubo-Toyabe function

$$g(t) = \frac{1}{3} + \frac{2}{3} (1 - \delta^2 t^2) \exp(-\frac{1}{2} \delta^2 t^2),$$

where $t$ is time and the relaxation rate $\delta$ is proportional to $\sqrt{\langle \mathbf{H}^2 \rangle}$. The temperature dependence of $\delta$ in the MP states can be obtained using the Green’s functions.

A calculation of the actual magnetic moment with strong spin-orbit coupling requires detailed knowledge of the electronic band structure. At every point $\mathbf{k}$ in momentum space, the operators $a_{\mathbf{k}\uparrow}^\dagger$ and $a_{\mathbf{k}\downarrow}$ can be expressed as linear combinations of Bloch sums consisting of orbital and spin parts. In the calculation of the magnetic moment, a quadratic form of the coefficients of this transformation will be an additional factor in the summand of the resulting expression (see below). However, the qualitative features of $\delta(T)$ may be discerned by calculating the average pseudospin of the Cooper pairs. The pseudospin operator is defined as

$$S_x = \frac{1}{2} \sum_{\mathbf{k}} (a^\dagger_{\mathbf{k}\uparrow} a_{\mathbf{k}\downarrow} + a^\dagger_{\mathbf{k}\downarrow} a_{\mathbf{k}\uparrow}),$$

$$S_y = i \frac{1}{2} \sum_{\mathbf{k}} (-a^\dagger_{\mathbf{k}\uparrow} a_{\mathbf{k}\downarrow} + a^\dagger_{\mathbf{k}\downarrow} a_{\mathbf{k}\uparrow}),$$

$$S_z = \frac{1}{2} \sum_{\mathbf{k}} (a^\dagger_{\mathbf{k}\uparrow} a_{\mathbf{k}\downarrow} - a^\dagger_{\mathbf{k}\downarrow} a_{\mathbf{k}\uparrow}),$$

where the indices $\uparrow$ and $\downarrow$ denote the pseudospin-up and down states, respectively. Using Eqs. (15), (17), (22), and the oddness of $\mathbf{p}(\mathbf{k})$, one obtains the average pseudospin of the Cooper pairs,

$$S(T) = \sum_{\mathbf{k}} \frac{\varepsilon(\mathbf{k}) \mathbf{q}(\mathbf{k})}{|\mathbf{p}(\mathbf{k}) + \mathbf{q}(\mathbf{k})|} \left[ \frac{\tanh(E_{k-}/2T)}{4E_{k-}} - \frac{\tanh(E_{k+}/2T)}{4E_{k+}} \right].$$

Hence, as in the case of a bare triplet state, $S(T)$ vanishes if $\mathbf{q}(\mathbf{k}) = 0$. If the bare triplet state is nonunitary and magnetic, then, as follows from (23), the temperature dependence of $\delta$ has a kink at the point of the bare triplet-to-MP phase transition with a discontinuity in $d\delta/dT$ proportional to $d\mathbf{p}(\mathbf{k})^2/dT$.

VI. SUMMARY

Using a GL-type model, we showed that a MP SC state can be stable in a finite region of the $T$-$\mu$ plane of Pr(1-x)Ru$_x$Sb$_{12}$. The phase transitions from the bare singlet and triplet states to the MP state are second-order. The general formalism describing the MP states within BCS approach is developed. The quasiparticle energy spectrum is degenerate only if $\mathbf{p}(\mathbf{k}) = \mathbf{q}(\mathbf{k}) = 0$. The gap in the MP state can have line nodes in strong spin-orbit coupling limit if $\mathbf{p}(\mathbf{k}) \neq 0$. Normal and anomalous Green’s functions and the self-consistent gap equation are obtained. The MP state may be experimentally indicated by line nodes in the gap of the quasiparticle spectrum and a kink in $\mu$SR relaxation rate $\delta(T)$.

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