Order parameter symmetry in ferromagnetic superconductors

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We analyze the symmetry and the nodal structure of the superconducting order parameter in a cubic ferromagnet, such as ZrZn$_2$. We demonstrate how the order parameter symmetry evolves when the electromagnetic interaction of the conduction electrons with the internal magnetic induction and the spin-orbit coupling are taken into account. These interactions break the cubic symmetry and lift the degeneracy of the order parameter. It is shown that the order parameter which appears immediately below the critical temperature has two components, and its symmetry is described by co-representations of the magnetic point groups. This allows us to make predictions about the location of the gap nodes.

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I. INTRODUCTION

A metallic ferromagnet is characterized by the fact that its electronic energy bands are split by the exchange interaction between the electrons so that the spin-up bands have different energies from the spin-down bands. This has important consequences for the symmetry and the gap structure of possible superconducting states. In this article, we study the symmetry properties of the superconducting order parameter in a cubic ferromagnetic superconductor, such as ZrZn$_2$, in the limit of weak spin-orbit coupling, thus complementing an earlier study by the authors [1] carried out in the strong spin-orbit coupling limit.

The formation of spin-singlet Cooper pairs in a ferromagnet is strongly inhibited because electrons with opposite momenta and spin have energies differing by the exchange splitting of the energy bands. Therefore we consider here only the case of spin-triplet pairing. In triplet superconductivity, the order parameter has three components: $\Delta_{\uparrow\uparrow}$ corresponding to the pairing of electrons in the spin-up band, $\Delta_{\downarrow\downarrow}$ corresponding to the pairing of electrons in the spin-down band, and $\Delta_{\uparrow\downarrow}$ corresponding to the pairing of one spin-up and one spin-down electron. The $\Delta_{\uparrow\downarrow}$ component is expected to be very small for the same reasons that inhibit the possibility of singlet superconductivity in a ferromagnet, and thus we generally neglect it. In the case of zero spin-orbit coupling, there is no coupling between the three components of the order parameter and thus, according to the Landau theory of second order phase transitions, only one of them will become nonzero immediately below the superconducting transition temperature. The turning on of a weak spin-orbit coupling has two effects: (i) there will be changes to each of the three components of the order parameter resulting from the lowering of the symmetry by the presence of the spin-orbit interaction, and (ii) the three components of the order parameter will be mixed together by the presence of the spin-orbit interaction. It will turn out that for the ferromagnetic magnetization directed along any high-symmetry axis, and for all possible symmetries of the superconducting gap function, at least one of the dominant components $\Delta_{\uparrow\uparrow}$ and $\Delta_{\downarrow\downarrow}$ has either line nodes or point nodes in the momentum space. These zeros will become deep minima in the energy gap in the presence of the component $\Delta_{\uparrow\downarrow}$. The bulk of this paper is devoted to a detailed demonstration of these results.

Recent discoveries of coexistence of superconductivity with itinerant ferromagnetism in ZrZn$_2$ [2] and UGe$_2$ [3] have renewed interest to the old problem of the interplay between the two phenomena. These materials exhibit a number of peculiar properties. First, in contrast to all previously known examples of ferromagnetic superconductors, such as ternary rare-earth compounds, ruthenocuprates, etc., the same band electrons ($d$-electrons in ZrZn$_2$, or $f$-electrons in UGe$_2$) are responsible for both the superconductivity and the ferromagnetism. Second, the superconductivity occurs only in the ferromagnetic phase. While the exchange splitting of the Fermi surfaces suppresses singlet Cooper pairing, it was shown that the exchange by spin fluctuations can lead to a triplet pairing both in the paramagnetic and the ferromagnetic phases [4], or to the enhancement of the superconducting critical temperature $T_c$ on the ferromagnetic side [5]. A prominent feature of the phase diagram of ZrZn$_2$ is that $T_c$ grows as pressure moves away from the ferromagnetic quantum critical point, which can be explained by the exchange-type interaction of the magnetic moments of the Cooper pairs with the magnetization density [6].

Even though the microscopic mechanism of pairing is not completely understood, one can use symmetry analysis to identify the possible order parameters and determine the structure of the superconducting gap. The symmetry group $\mathcal{G}$ of the system in the normal state is defined as a group of transformations which leave the system Hamiltonian $H_0$ invariant. If the spin-orbit coupling is sufficiently strong, $\mathcal{G}$ contains the operations which affect both the coordinate and the spin degrees of freedom. In non-magnetic superconductors, time reversal symmetry $K$ is not broken, and $\mathcal{G} = S \times K \times U(1)$, where $S$ is the space group of the crystal, and $U(1)$ is the gauge group [7]. In magnetic superconductors, time reversal symmetry is broken, and $\mathcal{G} = S_M \times U(1)$, where $S_M$ is
the magnetic space group whose elements leave both the microscopic charge density and the magnetization density \( M \) invariant \( \mathfrak{g} \). For example, if there is a crystal point group operation \( R \) which transforms \( M \) to \( -M \), then the combined operation \( KR \) will be an element of \( S_M \), because time reversal restores the original \( M \) not affecting the lattice symmetry. The combined operation \( KR \) is anti-linear and anti-unitary, which brings about a number of novel features in the symmetry analysis compared to the non-magnetic case. The symmetry properties of the superconducting state in \( \text{ZrZn}_2 \) assuming strong spin-orbit coupling have been studied in Ref. \([1]\) (see also Refs. \([10]\), \([11]\), and \([12]\), where various aspects of the theory of ferromagnetic superconductors have been considered). However, a rather weak magnetic anisotropy in \( \text{ZrZn}_2 \) \([3]\) points out that the spin-orbit coupling might be small, which requires a modification of the analysis of Ref. \([1]\). A peculiar feature of ferromagnetic superconductors, which was first emphasized by Ginzburg \([3]\), is that the internal magnetic induction in the normal state is always nonzero. This means that the orbital motion of electrons and therefore the symmetry of the superconducting order parameter will be affected by the ferromagnetic magnetization even in the absence of spin-orbit coupling. Another consequence is that the system undergoes the superconducting phase transition into a mixed state, even in the absence of an external field.

The paper is organized as follows. In Sec. II, the normal-state symmetry groups are derived assuming that spin-orbit coupling is negligibly small, focusing on the cubic crystal symmetry relevant for \( \text{ZrZn}_2 \). In Sec. III, the effect of the electromagnetic interaction on the symmetry of the spin-triplet order parameters is analyzed, and the predictions are made about the location of gap zeros. The lattice periodicity is taken into account properly, which allows us to list all possible gap nodes, including those at the surface of the first Brillouin zone. In Sec. IV, the evolution of the order parameter symmetry in the presence of spin-orbit coupling is studied, and it is shown how the order parameter is induced on both sheets of the Fermi surface. In Sec. V the Ginzburg-Landau free energy functionals are derived for different magnetic symmetries. Sec. VI concludes with a discussion of our results and their implications for the experiment.

II. DERIVATION OF THE SYMMETRY GROUP AT ZERO SPIN-ORBIT COUPLING

We consider the case of cubic symmetry appropriate for \( \text{ZrZn}_2 \), which has the cubic laves phase structure. Also, we consider a single spin-degenerate electron band which is split by an exchange field in the ferromagnetic state. The symmetry of the normal (i.e. non-superconducting) state will be analyzed in terms of the effective single-particle Hamiltonian

\[
H_0 = \int \frac{d^3r}{V} \psi_\alpha^\dagger(r) \left\{ \frac{1}{2m} \left[ -i\hbar \frac{\partial}{\partial r} + \frac{e}{c} A(r) \right]^2 \right\} \delta_{\alpha\beta} + U(r) \delta_{\alpha\beta} - \{ h_{ex} + g \mu_B B \cdot \sigma \} \psi_\beta(r),
\]

Here \( \epsilon \) is the absolute value of the electron charge, \( U(r) \) is the periodic crystal lattice potential, \( \sigma = (\sigma_1, \sigma_2, \sigma_3) \) are Pauli matrices, and \( h_{ex}(r) \) is the exchange field. The magnetic induction inside the ferromagnet (in the assumed long cylinder geometry) is \( B = \text{curl} A(r) = 4\pi M \), and \( g \) is the Landé growth-factor for electrons, which determines the Zeeman splitting. In the case of a collinear ferromagnet, which is assumed here, \( h_{ex}(r) = h_0 f(r) \), where \( f(r) \) has the same periodicity as \( U(r) \), and \( h_0 \) is the exchange field direction, which does not vary in the crystallographic unit cell. We also assume that \( B \) is uniform and there is no external magnetic field (otherwise \( B = H_{ex} + 4\pi M \)), so that the vector potential can, for example, be written as \( A(r) = [B \times r]/2 \). In principle, the magnetic induction varies both in magnitude and direction in the crystallographic unit cell, and our \( B \) is the unit cell average of the microscopic magnetic induction. If the variation of the magnetic induction in the unit cell were taken into account it would change the symmetry analysis given below. However, since \( B \) (approximately 400 Gauss at zero pressure) is much smaller than the exchange field in \( \text{ZrZn}_2 \), and since a spatial average of magnetic induction over the unit cell is usually assumed to be appropriate in the calculation of the effects of the magnetic induction on the orbital motion of the electrons, the approximation of a uniform \( B \) is sufficient. The exchange field \( h_{ex} \), the magnetization density \( M \), and the magnetic induction \( B \) all have a common direction.

The spin-orbit coupling in not included in Eq. \([1]\). It should be noted that when we refer to spin-orbit coupling in this article, we mean the single-particle spin-orbit coupling which is shown explicitly in Eq. \([25]\) below. In principle, the microscopic magnetic dipole-dipole interaction that gives rise to the internal magnetic induction \( B = 4\pi M \) couples the spin and orbital motions, but because we assume a uniform \( B \) this does not affect our symmetry analysis. Even in the absence of the spin-orbit coupling \([25]\), there is an effect of the ferromagnetic magnetization density on the orbital motion of the electrons, which we refer to as the electromagnetic interaction. This means that the symmetry and the free energy of the superconducting state will depend on the direction of \( M \).

At zero spin-orbit coupling, the symmetry operations act independently in the real (orbital) space and the spin space, so that the full symmetry group of \( H_0 \) is a direct product

\[
\mathcal{G} = G_{\text{orb}} \times G_{\text{spin}} \times U(1), \tag{2}
\]

where \( U(1) \) is the gauge group composed of phase rotations \( \Phi \phi_\alpha(r) \Phi^{-1} = e^{i\theta} \phi_\alpha(r) \). For our purposes, the
translations are not important, so that \( G_{\text{orb}} \) contains orbital rotations \( R_{\text{orb}} \):
\[
R_{\text{orb}} \psi_{\alpha}(r) R_{\text{orb}}^{-1} = \psi_{\alpha}(R_{\text{orb}}^{-1} r),
\]
and inversion:
\[
I \psi_{\alpha}(r) I^{-1} = \psi_{\alpha}(-r).
\]
Also, the effects of time-reversal symmetry are included in \( G_{\text{orb}} \). Below we shall use the notation \( C_{kn} \) for the rotations by an angle \( 2\pi/k \) about the axis \( \hat{n} \) in orbital space. The group \( G_{\text{spin}} \) contains spin rotations \( R_{\text{spin}} \):
\[
R_{\text{spin}} \psi_{\alpha}(r) R_{\text{spin}}^{-1} = [D(1/2)(R_{\text{spin}})]_{\alpha\beta} \psi_{\beta}(r),
\]
where \( D(1/2)(R) \) is the spinor \((j = 1/2)\) representation of rotations: for a rotation \( R \) by an angle \( \theta \) around \( \hat{n} \), \( D(1/2)(R) = \exp[-i(\theta)/2(\sigma \cdot \hat{n})] \). It is convenient to introduce an orthogonal basis of unit vectors \( \hat{e}_1, \hat{e}_2, \hat{e}_3 \) in the spin space, such that \( \hat{e}_3 \parallel \hat{B} \). We shall use the notation \( C_{kn} \) for the rotations by an angle \( 2\pi/k \) about the axis \( \hat{n} \) in spin space.

A standard representation for the time reversal operator \( K \) is \( K = C_{2ex}^0 K_0 \), where \( K_0 \) is the complex conjugation operator associated with the representation \( \{r, s_z\} \). The anti-unitary operator \( K_0 \) is defined more explicitly by the equation
\[
K_0[\psi_{\alpha}(r)] K_0 = c^* \psi_{\alpha}(r),
\]
where \( c \) is an arbitrary c-number. In the momentum representation, \( K_0 \) also reverses the sign of \( k \). It should be noted that, in the decomposition \( K = C_{2ex}^0 K_0 \), while \( C_{2ex}^0 \) is an operator in spin space only, \( K_0 \) operates in both spin and orbital space [as indicated, for example, by the result \( K_0 \partial_y K_0 = -s_y \), where \( s_y = (\hbar/2)\sigma_y \) is the \( y \)-component of the electron spin operator]. Nevertheless, in discussing the symmetry properties of the Hamiltonian \( H_0 \) given by Eq. (4) for the case where the common direction of \( h_{ex} \) and \( \hat{B} \) is along \( \hat{e}_3 \) (so that the Hamiltonian does not contain \( \sigma_z \)), it is useful to consider \( K_0 \) together with the symmetry operations in orbital space.

If \( R_{\text{orb}} \) leaves the periodic potential \( U(r) \) and the exchange field \( h_{ex}(r) \) invariant, then the transform of the Hamiltonian \( H_0 \), namely \( R_{\text{orb}} H_0 R_{\text{orb}}^{-1} \), is the same as \( H_0 \) except that the vector potential \( \mathbf{A}(r) \) is replaced by \( \mathbf{A}'(r) = R_{\text{orb}} \mathbf{A}(r) R_{\text{orb}}^{-1} \). This means that the transformation rule for the magnetic induction under \( R_{\text{orb}} \) is \( \mathbf{B}(r) = \nabla \times \mathbf{A}(r) \rightarrow \mathbf{B}'(r) = \nabla \times \mathbf{A}'(r) = R_{\text{orb}}^{-1} \mathbf{B}(r) R_{\text{orb}}^{-1} \). Also, \( K_0 H_0 K_0 \) is the same as \( H_0 \) except that \( \mathbf{A}(r) \) is replaced by \( -\mathbf{A}(r) \), so that the transformation rule for the magnetic induction under \( K_0 \) is simply \( \mathbf{B} \rightarrow -\mathbf{B} \). Thus, if \( R_{\text{orb}} \) leaves \( U(r) \) and \( h_{ex}(r) \) invariant, and \( R_{\text{orb}} \mathbf{B} = -\mathbf{B} \), then \( K_0 R_{\text{orb}} \) is a member of the symmetry group of \( H_0 \). For convenience, such combined symmetry elements will be included with purely orbital elements in the definitions of the various orbital symmetry groups below.

In the non-magnetic case, i.e. at \( h_{ex} = \mathbf{B} = 0 \), the orbital symmetry of \( H_0 \) is determined by the symmetry of the lattice potential \( U(r) \). Since ZrZn\(_2\) has a cubic Laves phase structure, \( G_{\text{orb}} = O_h \times K_0 = O \times I \times K_0 \), where \( I = \{E, I\} \) and \( K_0 = \{E, K_0\} \). In addition, \( H_0 \) is invariant under arbitrary rotations in the spin space, so that \( G_{\text{spin}} = SU(2) \).

In the ferromagnetic case, where \( M, h_{ex} \) and \( \mathbf{B} \) are all nonzero, time reversal symmetry is broken, and, as noted above, the symmetry group of \( H_0 \) contains elements of the form \( K_0 R_{\text{orb}} \) as well as purely orbital transformations. In addition, the symmetry group of \( H_0 \) will contain operations that are purely spin-space rotations. More precisely, it is evident from Eqs. (4) and (5) that \( H_0 \) is invariant under the operators of the group \( C^*_\infty \), describing the set of all spin rotations about the axis \( \hat{e}_3 \), which, as always, is taken to lie along the common direction of \( M, h_{ex} \) and \( \mathbf{B} \). Therefore,
\[
G_{\text{spin}} = C^*_\infty.
\]
This spin-space symmetry group will be combined with a number of orbital symmetry groups to describe a number of different cases corresponding to different orientations for the ferromagnetic magnetization density. The different cases will be called Case A, Case B, ... Case E. The appropriate symmetry groups will be described immediately, and the order-parameter symmetries for each of the cases will be described later in section 11.

Case A. The orbital symmetry of the system is determined by the electromagnetic interaction of the conduction electrons with the induction \( \mathbf{B} \) via the vector potential \( \mathbf{A} \). If this interaction can be neglected, which amounts to setting \( c \rightarrow 0 \) in Eq. (4), then the Hamiltonian is real, so that the orbital symmetry is independent of \( M \) and is described by the cubic group \( O_h \), i.e.
\[
G_{\text{orb}} = O_h \times K_0 = O \times I \times K_0.
\]
In this case, which might be appropriate for a neutral Fermi system, such as the liquid \(^3\text{He}\) in magnetic field, or the “cold” atomic gases, only the spin symmetry is influenced by the presence of ferromagnetic magnetization.

In ferromagnetic metals, the electromagnetic interaction is always present, and the presence of the magnetization affects the orbital symmetry even in the absence of spin-orbit coupling. The structure of the orbital group depends on the direction of magnetization density. In ZrZn\(_2\), the magnetic anisotropy is sufficient weak that it should be possible to align the magnetization density along an arbitrary direction in the crystal by applying an external magnetic field along that direction. We now consider a number of possible orientations.

Case B. If the magnetization density lies along the [001] direction, the orbital symmetry group is
\[
G_{\text{orb}} = D_4(\mathbf{C}_4) \times I = \{E, C_{4z}, C_{2z}, C_{4z}^{-1}, K_0 C_{2z}, K_0 C_{2y}, K_0 C_{2a}, K_0 C_{2b}\} \times I.
\]
where \( \hat{a} = (\hat{x} + \hat{y})/\sqrt{2} \), and \( \hat{b} = (\hat{x} - \hat{y})/\sqrt{2} \). Here we use a standard notation for the magnetic group \( G(H) \) \([3]\), where the subgroup \( H \) in parentheses (the unitary subgroup) includes all elements of \( G \) which are not multiplied by the anti-unitary operation \( K_0 \). A useful observation is that any magnetic group \( G(H) \) can be expressed in terms of left cosets with respect to the unitary subgroup \( H: G(H) = H + AH \), where all elements of the coset \( AH \) are anti-unitary. The choice of the anti-unitary group element \( A \) is arbitrary and does not affect the final results, but once chosen it remains fixed. For the group \( D_4(C_4) \), we choose \( A = K_0C_{2\pi} \).

**Case C.** When the magnetization density lies along the [111] direction, the orbital symmetry group is

\[
G_{\text{orb}} = D_3(C_3) \times I = \{E, C_{3e}, C_{3e}^{-1}, K_0C_{2\pi}, K_0C_{2\pi}^* \} \times I, \tag{10}
\]

where \( \hat{b} = (\hat{x} + \hat{y} + \hat{z})/\sqrt{3}, \hat{b'} = C_{3e}\hat{b} = (\hat{y} - \hat{z})/\sqrt{2}, \) and \( \hat{b''} = C_{3e}^{-1}\hat{b} = (\hat{z} - \hat{x})/\sqrt{2} \). For this magnetic group, we choose \( A = K_0C_{2\pi} \).

**Case D.** When the magnetization density lies along the [110] direction, the orbital symmetry group is

\[
G_{\text{orb}} = D_2(C_2) \times I = \{E, C_{2\pi}, K_0C_{2\pi}, K_0C_{2\pi} \} \times I. \tag{11}
\]

In this case, we also choose \( A = K_0C_{2\pi} \).

**Case E.** For the magnetization along a general direction, the orbital symmetry group is

\[
G_{\text{orb}} = C_1 = C \times I, \tag{12}
\]

where \( C_1 \) consists of the unity operation \( E \). This group is trivial and does not contain anti-unitary elements.

In the next section, we study the symmetry properties of the superconducting order parameter at \( M \neq 0 \) using \( G_{\text{spin}} \) from Eq. (11), and \( G_{\text{orb}} \) from Eqs. (10) and (12). The microscopic origins of the ferromagnetism and the superconductivity are not important for the symmetry analysis.

### III. SUPERCONDUCTING ORDER PARAMETER AT ZERO SPIN-ORBIT COUPLING

In ZrZn$_2$, the exchange band splitting is \( E_{\text{ex}} \simeq 5\text{mRy} \simeq 800\text{K} \), which greatly exceeds the superconducting critical temperature \( T_c \simeq 0.2\text{K} \). In this conditions, the usual Chandrasekhar-Clogston arguments \( \square \) make any pairing of electrons with opposite spins, in particular in the singlet channel, strongly suppressed. The general form of a spin-triplet superconducting order parameter is \( \Delta_{\sigma\beta}(k, r) = (i\sigma \sigma_{\alpha \beta})d(k, r) \) \([11]\). It is convenient to use the following representation: \( d(k) = \hat{e}_+d_+(k) + \hat{e}_-d_-(k) + \hat{e}_3d_3(k), \) where \( \hat{e}_\pm = (\hat{e}_1 \pm i\hat{e}_2)/\sqrt{2} \) and \( d_\pm = (d_1 \pm id_2)/\sqrt{2} \).

According to the Landau theory of phase transitions, the spin vector \( d \), which appears at the critical temperature \( T_c \), should correspond to an irreducible representation of the normal state symmetry group \( G \). The easiest way to obtain the transformation properties of the order parameter under the operations from \( G \), i.e. the orbital and the spin rotations, and also the operation \( K_0 \), is to use the mean-field expression for the pairing Hamiltonian:

\[
H_{\text{sc}} = \sum_k \sum_{\alpha, \beta = \uparrow, \downarrow} \left[ \Delta_{\alpha\beta}(k) c_{k\alpha}^\dagger c_{-k, \beta}^\uparrow + \text{H.c.} \right]. \tag{13}
\]

Here \( \Delta_{\uparrow\uparrow} = -\sqrt{2}d_- \), which corresponds to a gap on the spin-up Fermi surface; \( \Delta_{\downarrow\downarrow} = \sqrt{2}d_+ \), which corresponds to a gap on the spin-down Fermi surface; and \( \Delta_{\uparrow\downarrow} = \Delta_{\downarrow\uparrow} = d_3 \), which corresponds to a pairing of a spin-up electron with a spin-down electron. Because of the Pauli principle, \( d(\mathbf{k}) = -d(\mathbf{k}) \). From Eqs. (13), (11), and \( \square \), we obtain

\[
R_{\text{orb}}d_\alpha(k) = d_\alpha(R_{\text{orb}}^{-1}k)
\]

\[
R_{\text{spin}}d_\alpha(k) = [D^{(1)}(R_{\text{spin}})]_{\beta\beta}d_\beta(k) \tag{14}
\]

\[
K_0d_\alpha(k) = d_\alpha(-k),
\]

where \( \alpha = \pm, 3 \), and \( D^{(1)}(R) \) is the vector \( (j = 1) \) representation of rotations.

Since \( G \) is a direct product of the independent orbital and spin symmetry groups \( \square \), the basis functions of the irreducible representations of \( G \) are given by products of the basis functions of \( G_{\text{orb}} \) and \( G_{\text{spin}} \). An important point here is that, because of the presence of the anti-unitary operations \( K_0R_{\text{orb}} \) in \( G_{\text{orb}} \), the symmetry analysis should be modified. The order parameter should transform according to one of the irreducible co-representations of \( G_{\text{orb}} = G(H) \), which can be derived from the irreducible representations of the unitary subgroup \( H \) \([11]\).

At \( M = 0 \), \( G_{\text{spin}} = SU(2) \), and \( d \) transforms according to the three-dimensional vector representation of \( SU(2) \), whose basis functions are \( \hat{e}_x \) and \( \hat{e}_y \). All three spin components \( d_\uparrow \) and \( d_3 \) have the same critical temperature. At \( M \neq 0 \), the spin symmetry is reduced to \( G_{\text{spin}} = C_{3\alpha e_3} \) \([11]\), and the vector representation is split into three one-dimensional representations of the group \( C_{3\alpha e_3} \). The spin components \( d_\uparrow \) and \( d_3 \) have different critical temperatures, and we assume that the maximum \( T_c \) is achieved for \( d_- \). Thus, the order parameter can be represented as an expansion

\[
d_\Gamma(k, r) = i\hat{e}_+ \sum_{i=1}^{n_\Gamma} \eta_i(r) f_{\Gamma,i}(k). \tag{15}
\]

Here \( f_{\Gamma,i}(k) \) are the odd basis functions of a \( n_\Gamma \)-dimensional irreducible co-representation \( \Gamma \) of \( G_{\text{orb}} \) (the parity of the spin-triplet order parameter is fixed, and the inversion operation can be omitted from \( G_{\text{orb}} \)). The action of the orbital symmetry elements on the functions
f_{Γ,i}(k) in the momentum space is defined as follows: under the crystal rotations, \( R_{orb} f(k) = f(R^{-1}_{orb} k) \), under the combined operations, \( K_0 R_{orb} f(k) = f^*(-R^{-1}_{orb} k) \). The expansion coefficients \( η_i(r) \) play the role of the order parameter components, which enter the Ginzburg-Landau free energy functional. The factor \( i \) on the right-hand side of Eq. (15) is introduced so that, as we shall see in Sec. IV, the anti-unitary combined operations \( KR \) are equivalent to complex conjugation when acting on \( η_i \).

The physical meaning of Eq. (15) is that the order parameter appears only on the spin-up sheet of the Fermi surface, while the spin-down sheet remains normal (for the order parameter on the spin-down sheet, one would have \( d_+ ≠ 0 \), i.e. \( d ∝ \hat{e}_- \)). It should be mentioned here that the band structure of ZrZn\(_2\) is quite complex \([10, 11]\), but we neglect such complication here and assume that there are only two exchange-split bands. This assumption should not affect the essence of our results. In contrast to the strong spin-orbit coupling case considered in Ref. \([9]\), the interband interactions \( c_{k\uparrow} c_{-k\downarrow} c_{-k\uparrow} c_{k\downarrow} \), which could induce the order parameters of the same symmetry on both sheets of the Fermi surface, are absent due to the spin conservation. The critical temperature for the order parameter \( d_3 \), which describes the Cooper pairing of electrons with opposite spins, is expected to be much smaller than those for \( d_+ \), because of the large value of the exchange splitting in ZrZn\(_2\), mentioned in the beginning of this Section. For the same reason, we also neglect the possibility of a superconducting state with a non-zero momentum, i.e. with \( ⟨c_{k\uparrow}, c_{-k\downarrow}⟩ ≠ 0 \) (Larkin-Ovchinnikov-Fulde-Ferrell state) \([12]\).

When the symmetry is described by one of the magnetic point groups \([4]\), \([10]\), \([11]\), or \([12]\), \( G_{orb} \) has only one-dimensional co-representations (see below), therefore Eq. (15) reduces to the form

\[
d_+(k, r) = i\hat{e}_+ η(r)f_{Γ}(k).
\]

Thus, the order parameter has one component, and the Ginzburg-Landau functional has the same form as for the conventional s-wave pairing. This means that the phase transition from the normal ferromagnetic state to the superconducting state occurs into the usual mixed state with a lattice of the Abrikosov vortices. However, in contrast to the s-wave case, the orbital symmetry is non-trivial, in particular, there are zeros in the spectrum of elementary excitations where \( f_{Γ}(k) = 0 \). Below we examine the order parameter symmetry for different cases and determine the positions of the gap zeros dictated by the magnetic symmetry.

**Case A:** \( G_{orb} = O × I × K_0 \)

In this case, which is relevant for the superconductivity in a neutral ferromagnetic Fermi system, the orbital symmetry is not affected by the presence of a non-zero \( M \). The order parameter is given by Eq. (15). The group \( O \) has 2 one-dimensional \((A_1 \text{ and } A_2)\), 1 two-dimensional \((E)\), and 2 three-dimensional \((F_1 \text{ and } F_2)\) representations. The examples of the basis functions are given in Table I. One-component order parameters \( d_{A_1}(k) \) and \( d_{A_2}(k) \) have line zeros at the Fermi surface, which do not depend on the choice of the basis functions. For the higher-dimensional representations, the form of the order parameter and its gap structure are obtained by minimizing the free energy in the superconducting state. The explicit expressions for the Ginzburg-Landau functionals and the phase diagrams for the multi-component order parameters can be found, e.g. in Ref. \([8]\).

In a charged Fermi system, where the vector potential created by the internal magnetization affects the single-electron wave functions, the cubic symmetry is reduced to one of the magnetic groups \([10]\), \([11]\), or \([12]\), and the degeneracy of the two- and three-dimensional order parameters is lifted. Mathematically, this corresponds to the splitting of higher-dimensional representations of \( O \) into several one-dimensional co-representations. If \( M \parallel [001] \) and \( O \to D_3(C_3) \), then it is easy to check, using Table I, that

\[
\begin{align*}
A_1 & \to A \\
A_2 & \to B \\
E & \to A + B \\
F_1 & \to A + 1E + 2E \\
F_2 & \to B + 1E + 2E.
\end{align*}
\]

We also gave here the correspondence between the one-dimensional representations of \( O \) and the co-representations of \( D_3(C_3) \). If \( M \parallel [111] \) and \( O \to D_3(C_5) \), then, using Table I, that

\[
\begin{align*}
A_1 & \to A \\
A_2 & \to A \\
E & \to 1E + 2E \\
F_1 & \to A + 1E + 2E \\
F_2 & \to A + 1E + 2E.
\end{align*}
\]
If \( M \parallel [110] \) and \( \mathbf{O} \rightarrow \mathbf{D}_2(\mathbf{C}_2) \), then, using Table II,

\[
\begin{align*}
A_1 & \rightarrow A \\
A_2 & \rightarrow B \\
E & \rightarrow A + B \\
F_1 & \rightarrow A + B + B \\
F_2 & \rightarrow A + A + B.
\end{align*}
\]

(19)

The physical origin of the order parameter splitting can be easily traced using the phenomenological Ginzburg-Landau theory. For example, consider an uncharged Fermi liquid as above and let \( \eta = (\eta_x, \eta_y, \eta_z) \) be a three-component order parameter corresponding to the vector representation \( F_1 \) of the orbital group \( \mathbf{G}_{\text{orb}} = \mathbf{O} \times \mathbf{I} \times \mathbf{K}_0 \) and corresponding to a gap function on the spin-up Fermi surface. Then the Ginzburg-Landau free energy describing a homogeneous phase is

\[
F = \alpha \eta^* \cdot \eta + \beta_1 (\eta^* \cdot \eta)^2 \\
+ \beta_2 |\eta|^4 + \beta_3 (|\eta_x|^4 + |\eta_y|^4 + |\eta_z|^4),
\]

(20)

where \( \alpha = a(T - T_{c,0}), \) and \( T_{c,0} \) is the critical temperature at \( e = 0 \). There are a number of physically different states that minimize this free energy, depending on the values of the parameters of the fourth-order terms [1]; for example, one of these solutions has the form \( \eta = \eta_0(1,1,1) \).

Now, for a charged (metallic) ferromagnet, it is important to include the gradient terms in the free energy, so that the terms in the free energy of second order in the order parameter becomes [20]

\[
F = a(T - T_{c,0})|\eta|^2 + K_1 (D_i \eta_j)^* (D_i \eta_j) \\
+ K_2 (D_i \eta_j)^* (D_i \eta_j) + K_3 (D_i \eta_j)^* (D_i \eta_j) \\
+ K_4 (D_i \eta_j)^* (D_i \eta_j) \\
= a(T - T_{c,0})|\eta|^2 + i\gamma|\eta|^2 \times |\eta| B + K_1 (D_i \eta_j)^* (D_i \eta_j) \\
+ K_2 (D_i \eta_j)^* (D_i \eta_j) + (D_i \eta_j)^* (D_i \eta_j) \\
+ K_4 (D_i \eta_j)^* (D_i \eta_j). 
\]

(21)

Here \( \mathbf{D} = \nabla + i(2\pi/\Phi_0)\mathbf{A}, \Phi_0 = \hbar c/e \) is the flux quantum, \( K_23 = (K_2 + K_3)/2 \), and \( \gamma = \pi(K_3 - K_2)/\Phi_0 \). In the second part of Eq. \( (21) \), we regrouped the gradient terms using the identity \( [D_i, D_j] = -(2\pi i/\Phi_0)e_{ijk}B_k \). The quantity \( i\gamma|\eta|^2 \times |\eta| \) can be interpreted, up to a factor, as the density of the orbital magnetization of Cooper pairs [8]. The second order terms given by Eq. \( (21) \) are sufficient to calculate the critical temperature describing the phase transition from the normal state to the superconducting mixed state. The free energy of the superconducting state will depend on the direction of the flux lines (determined by the direction of \( M \) relative to the underlying crystal lattice).

Here we consider only the case \( M \parallel [001] \), so that \( \mathbf{G}_{\text{orb}} = \mathbf{D}_4(\mathbf{C}_4) \). The critical temperature for the order parameter component \( \eta_z \) can be calculated exactly, while the critical temperatures for \( \eta_{\pm} = \eta_x \pm i\eta_y \) can be found using the variational approach similar to that of Ref. [21], with the result:

\[
T_{c,+} = T_{c,0} - \frac{8\pi^2}{a\Phi_0} \left( K_1 + K_3 + \frac{K_4}{2} \right) M \\
T_{c,-} = T_{c,0} - \frac{8\pi^2}{a\Phi_0} \left( K_1 + K_2 + \frac{K_4}{2} \right) M \\
T_{c,z} = T_{c,0} - \frac{8\pi^2}{a\Phi_0} K_1 M. 
\]

Barring accidental degeneracies, these critical temperatures are all different, so that, at \( e \neq 0 \), the three-component order parameter is split. The difference between the critical temperatures \( T_{c,+} \) and \( T_{c,-} \) is proportional to \( \gamma \), and is entirely due to the interaction of the orbital pair magnetization with \( \mathbf{B} \). It is easy to see, using Table I, that the order parameter components \( \eta_+ , \eta_- \), and \( \eta_z \) correspond to the following one-dimensional co-representations of \( \mathbf{D}_4(\mathbf{C}_4) \); \( \eta_+ \sim A, \eta_+ \sim 1E, \eta_- \sim 2E \).

It may be that as the temperature is lowered below this critical temperature into the superconducting state and the fourth-order terms in the free energy become more important, there will be a second phase transition into a state that does a better job of minimizing the fourth-order contributions to the free energy.

**Case B:** \( \mathbf{G}_{\text{orb}} = \mathbf{D}_4(\mathbf{C}_4) \times \mathbf{I} \) \( (M \parallel [001]) \)

The order parameter is given by Eq. \( (16) \), and the irreducible co-representations are listed in Table II. We see that the order parameters \( d_{A}(k) \) and \( d_{E}(k) \) vanish on the line \( k_z = 0 \) at the Fermi surface, while \( d_{E}(k) \) and \( d_{E}(k) \) vanish at the points \( k_z = k_y = 0 \) [note that here the label \( \Gamma \) refers to the orbital symmetry, whereas in Ref. [8] we labelled the co-representations by their total (orbital plus spin) symmetry]. These zeros are not accidental in the sense that they are independent of the choice of the basis functions. Indeed, one of the elements of the magnetic point group \( \mathbf{D}_4(\mathbf{C}_4) \) is the two-fold rotation \( C_{2z} \). Therefore,

\[
C_{2z} f_{A,B}(k) = f_{A,B}(k_x, -k_y, k_z) \\
= -f_{A,B}(k_x, k_y, -k_z) = f_{A,B}(k),
\]

(23)

**TABLE II:** The character table and the examples of the odd basis functions for the irreducible co-representations of the magnetic point group \( \mathbf{D}_4(\mathbf{C}_4) \). The overall phases of the basis functions are chosen so that \( K_0 C_{2z}, f_{1}(k) = f_1(k) \). \( \lambda_{1,2} \) are arbitrary real constants.

| \( \Gamma \) | \( E \) | \( C_{4z} \) | \( f_1(k) \) |
|---|---|---|---|
| \( A \) | 1 | 1 | \( k_x \) |
| \( B \) | 1 | -1 | \( k_z \) |
| \( 1E \) | 1 | 1 | \( k_y + ik_x \) |
| \( 2E \) | 1 | -1 | \( k_y - ik_x \) |
so that \( f_{A,B}(k_x, k_y, 0) = 0 \). Similarly, under a four-fold rotation around the \( z \) axis:

\[
C_{4z} f_B(k) = f_B(k_y, -k_x, k_z) = -f_B(k),
\]

therefore \( f_B(0, 0, k_z) = 0 \). Also,

\[
C_{4z} f_{1E,2E}(k) = f_{1E,2E}(k_y, -k_x, k_z) = \pm i f_{1E,2E}(k),
\]

hence \( f_{1E,2E}(0, 0, k_z) = 0 \).

It also follows from Eq. (23) that \( f_A(k) \) and \( f_B(k) \) go to zero at the surface of the Brillouin zone, i.e. at \( k_z = \pm \pi/a \) (\( a \) is the lattice constant), because \((k_x, k_y, \pi/a) \) and \((k_x, k_y, -\pi/a) \) are equivalent points. In order to take into account the crystal periodicity leading to the presence of these additional gap zeros, one has to represent the basis functions as the lattice Fourier series \( f(k) = \sum_n f_n e^{i k n R_n} \), where summation goes over the sites \( R_n \) of the Bravais lattice of the crystal. The expansion appropriate for an odd order parameter has the form

\[
f(k) = \sum_n c_n \sin k \cdot R_n, \tag{24}
\]

where \( R_n \) are the sites of a fcc cubic lattice, which cannot be transformed one into another by inversion. In the nearest-neighbor approximation, we choose the following set of \( R_n \): \( \{R_n\} = \{(a/2)\{110\}, (101), (011), (110), (110)\} \). Using Table III we obtain the basis functions which have symmetry-imposed zeros at the surface of the Brillouin zone:

\[
f_A(k) = \sin \frac{k_z a}{2} \left( \cos \frac{k_x a}{2} + \cos \frac{k_y a}{2} \right),
\]

\[
f_B(k) = \sin \frac{k_z a}{2} \left( \cos \frac{k_x a}{2} - \cos \frac{k_y a}{2} \right),
\]

\[
f_{1E}(k) = \cos \frac{k_z a}{2} \left( \sin \frac{k_y a}{2} + i \sin \frac{k_x a}{2} \right) + \lambda_1 \left[ e^{\mp i \pi} \sin \left( \frac{k_x a}{2} + \frac{k_y a}{2} \right) - e^{\mp i \pi} \sin \left( \frac{k_x a}{2} - \frac{k_y a}{2} \right) \right],
\]

\[
f_{1E}(k) = \cos \frac{k_z a}{2} \left( \sin \frac{k_y a}{2} - i \sin \frac{k_x a}{2} \right) + \lambda_2 \left[ e^{-\mp i \pi} \sin \left( \frac{k_x a}{2} + \frac{k_y a}{2} \right) - e^{-\mp i \pi} \sin \left( \frac{k_x a}{2} - \frac{k_y a}{2} \right) \right].
\]

Here \( \lambda_{1,2} \) are arbitrary real constants. The polynomial expressions for the basis functions from Table III are recovered in the limit of a “small” Fermi surface \( k \to 0 \) [note that \( f_B(k) \) from Table I can be obtained by including the next-nearest-neighbors in the expansion (24)]. It should be noted that these nearest-neighbor results give also gap zeros not required by symmetry, e.g. \( f_B(k) = 0 \) on the plane \( k_x = k_y \). These “accidental” zeros will be removed if higher-neighbor terms are included, but if the nearest-neighbor terms turn out to be dominant, experiment could find indications of these accidental zeros.

### Table III: The character table and the examples of the odd basis functions for the irreducible co-representations of the magnetic point group \( D_3(C_3) \). The overall phases of the basis functions are chosen so that \( K_0 C_{2b} f_1(k) = f_1(k) \).

| \( \Gamma \) | \( E \) | \( C_{2a} \) | \( C_{2a}^{-1} \) | \( f_1(k) \) |
|---|---|---|---|---|
| \( A \) | 1 | 1 | 1 | \( k_z + k_y + k_x \ |
| \( E \) | 1 | \( \omega \) | \( \omega^* \) | \( e^{-i\pi/3} k_x - k_y + e^{i\pi/3} k_z \) |
| \( E \) | 1 | \( \omega^* \) | \( \omega \) | \( e^{i\pi/3} k_x - k_y + e^{-i\pi/3} k_z \) |

### Table IV: The character table and the examples of the odd basis functions for the irreducible co-representations of the magnetic point group \( D_3(C_3) \). The overall phases of the basis functions are chosen so that \( K_0 C_{2b} f_1(k) = f_1(k) \) is an arbitrary real constant.

| \( \Gamma \) | \( E \) | \( C_{2a} \) | \( f_1(k) \) |
|---|---|---|---|
| \( A \) | 1 | 1 | \( k_z + k_y \) |
| \( B \) | 1 | \(-1\) | \( k_z + i\lambda (k_x - k_y) \) |

Case C: \( G_{orb} = D_3(C_3) \times I \) \( (M \parallel [111]) \)

The order parameter is given by Eq. (16), and the irreducible co-representations are listed in Table III. The order parameters \( d_{1E}(k) \) and \( d_{2E}(k) \) vanish at the points where the line \( k_x = k_y = k_z \) crosses the Fermi surface, but \( d_A(k) \) does not have zeros. The zeros of \( d_{1E,2E}(k) \) are imposed by symmetry, because under a three-fold rotation about the axis \( \hat{e} \),

\[
f_{3E} f_{1E,2E}(k) = f_{1E,2E}(k_z, k_x, k_y) = e^{\pm 2\pi i/3} f_{1E,2E}(k),
\]

so that \( f_{1E,2E}(k_x = k_y = k_z) = 0 \).

We also give the expressions for the basis functions of the magnetic point group \( D_3(C_3) \) in terms of the lattice Fourier series in the nearest-neighbor approximation:

\[
f_A(k) = S_1^+ + S_2^+ + S_3^+ + i\lambda_1 (S_1^- + S_2^- + S_3^-)
\]

\[
f_{1E}(k) = \omega^* S_1^+ + \omega S_2^+ + S_3^+
\]

\[
+ i\lambda_2 (\omega^* S_1^- + \omega S_2^- + S_3^-)
\]

\[
f_{2E}(k) = \omega S_1^+ + \omega^* S_2^+ + S_3^+
\]

\[
+ i\lambda_3 (\omega S_1^- + \omega^* S_2^- + S_3^-),
\]

where \( S_1^\pm = \sin(k_x a/2 \pm k_y a/2) \), \( S_2^\pm = \sin(k_y a/2 \pm k_z a/2) \), and \( S_3^\pm = \sin(k_z a/2 \pm k_x a/2) \), and \( \lambda_{1,2,3} \) are arbitrary real constants.

Case D: \( G_{orb} = D_2(C_2) \times I \) \( (M \parallel [110]) \)

The order parameter is given by Eq. (16), and the irreducible co-representations are listed in Table IV. The order parameter \( d_{2a}(k) \) does not have zeros, but \( d_{3a}(k) \) has the symmetry-imposed lines of zeros where the plane
\[ k_x = -k_y \] crosses the Fermi surface, because under a two-fold rotation about the axis \( \vec{a} \),
\[ C_{2\alpha} f_A(k) = f_A(k_y, k_x, -k_z) = -f_A(-k_y, -k_x, k_z) = f_A(k), \]
so that \( f_A(k_x = -k_y) = 0 \).

The basis functions of the magnetic point group \( D_{4h}(C_3) \) in terms of the lattice Fourier series in the nearest-neighbor approximation:
\[
\begin{align*}
  f_A(k) &= \cos \frac{k_x a}{2} \left( \sin \frac{k_x a}{2} + \sin \frac{k_y a}{2} \right) \\
  &+ \lambda_1 \sin \left( \frac{k_x a}{2} + \frac{k_y a}{2} \right) \\
  f_B(k) &= \sin \frac{k_x a}{2} \left( \cos \frac{k_x a}{2} + \cos \frac{k_y a}{2} \right) \\
  &+ i\lambda_2 \sin \left( \frac{k_x a}{2} - \frac{k_y a}{2} \right),
\end{align*}
\]
where \( \lambda_{1,2} \) are arbitrary real constants.

**Case E**: \( G_{orb} = C_1 \times I \)

The group \( C_1 \) has single one-dimensional odd representation, which is realized by any odd function of \( k \). Therefore, there are no symmetry-imposed gap nodes in this case.

**IV. SUPERCONDUCTING ORDER PARAMETER AT WEAK SPIN-ORBIT COUPLING**

Now let us turn on a weak spin-orbit coupling neglected in the previous discussion. We shall see that the effect of spin-orbit coupling is two-fold. First, it mixes together the order parameters on different sheets. Second, similar to the electromagnetic interaction studied in the previous sections, it reduces the symmetry of the order parameter and changes the gap structure on each sheet of the Fermi surface.

In the presence of spin-orbit coupling, the normal state Hamiltonian \( \text{[1]} \) contains an extra term:
\[
H_{0,s-o} = H_0 + \frac{\hbar}{4m^2c^2} \left[ \nabla U(r) \times \left( p + \frac{e}{c} A \right) \right] \cdot \sigma. \tag{25}
\]
Spin is no longer a good quantum number and should be replaced by pseudospin \( \text{[22]} \). In contrast to Eq. \( \text{[2]} \), the symmetry group of Eq. \( \text{[25]} \) cannot be represented as a product of independent orbital and spin groups. Instead, we have, neglecting the translations,
\[
\mathcal{G} = G_{s-o} \times U(1), \tag{26}
\]
where \( G_{s-o} \) consist of rotations which affect both the orbital and the pseudospin degrees of freedom:
\[
R \psi_\alpha(r) R^{-1} = [D^{(1/2)}(R)]_{\alpha \beta} \psi_\beta(R^{-1}r), \tag{27}
\]
and also the combined operations \( KR \), where \( K = C_{2\pi} \).

This results in the electromagnetic interaction studied in the previous discussion. We shall see that the effect of this case.

Therefore, there are no symmetry-imposed gap nodes in \( k \) we have, neglecting the translations.

The group \( \Gamma \) in terms of the lattice Fourier series in the nearest-neighbor approximation:
\[
\begin{align*}
  f_A(k) &= \cos \frac{k_x a}{2} \left( \sin \frac{k_x a}{2} + \sin \frac{k_y a}{2} \right) \\
  &+ \lambda_1 \sin \left( \frac{k_x a}{2} + \frac{k_y a}{2} \right) \\
  f_B(k) &= \sin \frac{k_x a}{2} \left( \cos \frac{k_x a}{2} + \cos \frac{k_y a}{2} \right) \\
  &+ i\lambda_2 \sin \left( \frac{k_x a}{2} - \frac{k_y a}{2} \right),
\end{align*}
\]
where \( \lambda_{1,2} \) are arbitrary real constants.

**Case E**: \( G_{orb} = C_1 \times I \)

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H_{0,s-o} = H_0 + \frac{\hbar}{4m^2c^2} \left[ \nabla U(r) \times \left( p + \frac{e}{c} A \right) \right] \cdot \sigma. \tag{25}
\]
Spin is no longer a good quantum number and should be replaced by pseudospin \( \text{[22]} \). In contrast to Eq. \( \text{[2]} \), the symmetry group of Eq. \( \text{[25]} \) cannot be represented as a product of independent orbital and spin groups. Instead, we have, neglecting the translations,
\[
\mathcal{G} = G_{s-o} \times U(1), \tag{26}
\]
where \( G_{s-o} \) consist of rotations which affect both the orbital and the pseudospin degrees of freedom:
\[
R \psi_\alpha(r) R^{-1} = [D^{(1/2)}(R)]_{\alpha \beta} \psi_\beta(R^{-1}r), \tag{27}
\]
and also the combined operations \( KR \), where \( K = C_{2\pi} \).

This results in the electromagnetic interaction studied in the previous discussion. We shall see that the effect of this case.

Therefore, there are no symmetry-imposed gap nodes in \( k \) we have, neglecting the translations.

The group \( \Gamma \) in terms of the lattice Fourier series in the nearest-neighbor approximation:
\[
\begin{align*}
  f_A(k) &= \cos \frac{k_x a}{2} \left( \sin \frac{k_x a}{2} + \sin \frac{k_y a}{2} \right) \\
  &+ \lambda_1 \sin \left( \frac{k_x a}{2} + \frac{k_y a}{2} \right) \\
  f_B(k) &= \sin \frac{k_x a}{2} \left( \cos \frac{k_x a}{2} + \cos \frac{k_y a}{2} \right) \\
  &+ i\lambda_2 \sin \left( \frac{k_x a}{2} - \frac{k_y a}{2} \right),
\end{align*}
\]
where \( \lambda_{1,2} \) are arbitrary real constants.
assuming \( M \parallel [001] \). For the moment, we neglect the electromagnetic interaction and omit the gradient terms in the free energy. At zero spin-orbit coupling, the orbital symmetry is cubic, and \( \Gamma_+ = \Gamma_- = F_1 \). It is convenient to use the following set of the basis functions of \( F_1 \):

\[
 f_1(k) = \frac{k_y + ik_x}{\sqrt{2}}, \quad f_2(k) = \frac{k_y - ik_x}{\sqrt{2}}, \quad f_3(k) = k_z, \quad (31)
\]

then \( \eta_\pm = (\eta_{\pm,1}, \eta_{\pm,2}, \eta_{\pm,3}) \), and the quadratic part of the free energy is

\[
 F_0 = a_+ (T - T_{c,+}) |\eta_+|^2 + a_- (T - T_{c,-}) |\eta_-|^2. \quad (32)
\]

The critical temperatures \( T_{c,-} \) and \( T_{c,+} \) for the spin-up and the spin-down order parameters are different, in general (we assume that \( T_{c,-} > T_{c,+} \)). There are no mixed terms of the form \( \eta^*_+, \eta_- \) and c.c. in Eq. (32), because of the spin rotation symmetry \( U(1) \). Indeed, under a spin rotation by an angle \( \theta \) about \( e_3 \), we have \( d_\pm \to e^{\pm i\theta} d_\pm \), which can be interpreted as an operation acting on the order parameter components: \( \eta_\pm \to e^{\pm i\theta} \eta_\pm \). The mixed terms are not invariant under such transformations and therefore are not allowed. This is, of course, the same continuous symmetry which is responsible for the spin conservation.

Now, if a weak spin-orbit coupling is turned on, we can treat it as a symmetry-breaking perturbation in the phenomenological Ginzburg-Landau functional. The spin rotations are no longer symmetry elements on their own, and, in addition to the terms on the right-hand side of Eq. (32), the free energy should contain other invariants built from the components of \( (\eta_+, \eta_-) \). The magnetic group \( D_4 (C_4) \) generated by the rotations \( C_4 \) and the combined operations \( K C_2 z \). According to (29), \( C_4 d_{\pm}(k) = \pm i d_{\pm}(C_4 k) \), \( K C_2 d_{\pm}(k) = d_{\pm}^{-1}(C_2 k) \). In terms of \( \eta_\pm \), we have

\[
 C_4 \eta_{\pm,1} = \mp \eta_{\pm,1} \quad C_4 \eta_{\pm,2} = \pm \eta_{\pm,2} \quad C_4 \eta_{\pm,3} = \mp i \eta_{\pm,3} \quad K C_2 \eta_{\pm,1} = \eta_{\mp,1} \quad K C_2 \eta_{\pm,2} = \eta_{\mp,2} \quad K C_2 \eta_{\pm,3} = \eta_{\mp,3}. \quad (33)
\]

(Note that, because of our choice of the basis functions and the presence of the overall factors \( i \) on the right-hand side of Eq. (32), the action of \( K C_2 z \) on the order parameter components is equivalent to complex conjugation.) Using Eqs. (33), we obtain quadratic terms which are invariant under all transformations from \( D_4 (C_4) \) and should therefore be added to the free energy (32):

\[
 F_{\pm} = F_0 + \sum_{i=1}^{3} \left( \lambda_{\pm,i} |\eta_{\pm,i}|^2 + \lambda_{-i} |\eta_{-i}|^2 \right) + \gamma_1 (\eta^*_+ \eta_{+} + \eta^*_- \eta_{-}) + \gamma_2 (\eta^*_+ \eta_{-} + \eta^*_- \eta_{-}). \quad (34)
\]

The coefficients \( \lambda_{\pm,i} \) and \( \gamma_1, \gamma_2 \) are small at weak spin-orbit coupling. The model of Eqs. (32) and (34) can have a rich phase structure, depending on the relation between the “bare” critical temperatures \( T_{c,-} \) and \( T_{c,+} \) and other parameters. In order to work out the whole phase diagram and the structure of successive superconducting phases, one should include fourth-order terms in the free energy (32) and (34), which we shall not do here. Instead, we concentrate on finding the maximum critical temperature.

The components \( (\eta_{+,1}, \eta_{-,2}), (\eta_{+,2}, \eta_{-,1}), \eta_{+,3} \), and \( \eta_{-,3} \) can be considered separately. For example, the critical temperature for \( (\eta_{+,2}, \eta_{-,1}) \) is given by

\[
 T_c = \frac{T_{c,+} + T_{c,-} - 1}{2} + \frac{1}{2}\sqrt{\left( T_{c,+} - T_{c,-} \right)^2 + \frac{4 \gamma_1^2}{a_+ a_-}}, \quad (35)
\]

where \( T_{c,+} > T_{c,-} \). Both components \( \eta_{+,2} \) and \( \eta_{-,1} \) are non-zero below \( T_c \), so that superconductivity appears simultaneously on both sheets of the Fermi surface. The order parameter can be obtained from Eq. (34):

\[
 d(k) = i e^+ \frac{k_y + ik_x}{\sqrt{2}} \eta_{-,1} + i e^- \frac{k_y - ik_x}{\sqrt{2}} \eta_{+,2}. \quad (36)
\]

At weak spin-orbit coupling and \( T_{c,+} > T_{c,-} \), \( \eta_{+,2} \) is much smaller than \( \eta_{-,1} \). The critical temperature \( T_{c,-} \) has the form (35) with \( \Gamma = F_{1,1} \parallel [001] \). If one includes all representations of the cubic group in the free energy (34), then the spin-orbit coupling would lead to the appearance of a variety of quadratic terms which mix together different representations on different sheets, similar to Eq. (34). In this case, the order parameter will always be present on both sheets of the Fermi surface, and the results of Ref. [1] will be recovered.

Now we study how the nodal structure of the superconducting order parameter on a single sheet (say, the pseudospin-up sheet) evolves with spin-orbit coupling. We consider only the case \( M \parallel [001] \), neglect the electromagnetic interaction, and start from the representations \( A_1 \) and \( F_1 \) of the group \( O \) at zero spin-orbit coupling. The order parameters corresponding to \( A_1 \) is \( d_{A_1}(k, r) = i e^+ \xi(r) f_{A_1}(k) \). The order parameter corresponding to \( F_1 \) has the form (13) with \( \Gamma = F_{1,1} \parallel [001] \). The quadratic part of the Ginzburg-Landau functional is

\[
 F_0 = a_{A_1} (T - T_{A_1}) |\xi|^2 + a_{F_1} (T - T_{F_1}) |\eta|^2. \quad (37)
\]

There are no mixed terms in Eq. (37) because of the different transformation properties of \( \xi \) and \( \eta \) with respect to the elements of the cubic group. We assume
\( T_{A_1} > T_{F_1} \), so that only \( \xi \) is nonzero immediately below the critical temperature. From Table II, the order parameter \( d_{A_1} \) has six line nodes where the planes \( k_z = 0 \), \( k_y = 0, k_x = k_y, k_y = k_z \), and \( k_z = k_x \) cross the Fermi surface. However, according to Table \( \text{I} \), all these gap nodes, except from that on the plane \( k_z = 0 \), are incompatible with the magnetic symmetry \( D_4(C_4) \). Let us now see how the extra nodes disappear when the spin-orbit coupling is taken into account.

The spin-orbit coupling reduces the cubic symmetry to \( D_4(C_4) \), whose action on the components \( \eta(= \eta_-) \) is given by Eqs. (33), and on \( \xi \) by

\[
C_{4z} \xi = -i \xi
\]

\[
K C_{2x} \xi = \xi^*
\]

where we used Eq. (29) and the identities \( f_{A_1}(C_{4z}^{-1} k) = f_{A_1}(k) \) and \( f_{A_1}(-C_{2x} k) = -f_{A_1}(k) \). Since the components \( \xi \) and \( \eta \) have the same transformation properties under all operations from \( D_4(C_4) \), the free energy, which is invariant with respect to the magnetic group, should contain mixed terms in addition to (37):

\[
F_{so} = F_0 + \gamma (\xi^* \eta_3 + \eta_3^* \xi),
\]

where \( \gamma \) is small at weak spin-orbit coupling. The critical temperature is changed compared to \( T_{A_1} \):

\[
T_c = \frac{T_{A_1} + T_{F_1}}{2} + \frac{1}{2} \sqrt{(T_{A_1} - T_{F_1})^2 + \frac{4\gamma^2}{\alpha A_1 \alpha F_1}}
\]

and the order parameter on the pseudospin-up sheet now has the form

\[
d(k) = i \hat{e}_+ [\xi f_{A_1}(k) + \eta_3 f_{F_1,3}(k)] \propto \hat{e}_+ k_2.
\]

This order parameter corresponds to the co-representation \( A \) of \( D_4(C_4) \). Thus, the only line node that survives the presence of the spin-orbit coupling is located on the plane \( k_z = 0 \). However, if the spin-orbit coupling is weak, then the subdominant component \( \eta_3 \) is small, and the other five line nodes of \( f_{A_1}(k) \) are just slightly filled, so that we shall have deep minima in the gap. At not very low temperatures, these “quasi-nodes” cannot be distinguished experimentally from true line nodes.

V. GINZBURG-LANDAU THEORY FOR FERROMAGNETIC SUPERCONDUCTORS

We have seen in the previous sections that both the electromagnetic interaction and the spin-orbit coupling break the cubic symmetry, lift the degeneracy of the order parameter, and change the gap structure. In addition, the spin-orbit coupling induces non-zero order parameters on both sheets of the Fermi surface. The symmetry is reduced to a magnetic group \( D_{n}(C_n) \) \( (n = 2, 3, 4) \), or \( C_1 \). All co-representations of these groups are one-dimensional, so that the general form of the order parameter is given by

\[
d(k, r) = i e_+ f_{\Gamma_+}(k) \eta_-(r) + i e_- f_{\Gamma_-}(k) \eta_+(r).
\]

The order parameter symmetry should be the same on both sheets, which means that (i) both components \( \eta_- \) and \( \eta_+ \) have the same transformation properties under the action of the magnetic group elements, and (ii) there are some restrictions as to the choice of \( \Gamma_+ \) and \( \Gamma_- \), stemming from the different transformation properties of the spin vectors \( \hat{e}_+ \) and \( \hat{e}_- \). In Table III, the pairs of orbital co-representations giving rise to the same symmetry of \( d \) are listed for all three relevant magnetic groups. For instance, the order parameter (36) corresponds to \( (\Gamma_+, \Gamma_-) = (2E, 3E) \). The examples of the basis functions \( f_{\Gamma \pm}(k) \), which have only the zeros imposed by symmetry, can be found in Tables III and IV. It is easy to see that the order parameter always has nodes, at least on one of the sheets of the Fermi surface.

The Ginzburg-Landau functional contains all possible uniform and gradient terms which are (i) invariant with respect to \( G(H) \), and (ii) gauge invariant. The uniform terms have the same form for all three magnetic groups:

\[
F_{\text{uniform}} = a_+(T - T_+) |\eta_+|^2 + a_-(T - T_-) |\eta_-|^2 + \gamma (\eta_+^* \eta_- + \eta_-^* \eta_+) + F_4,
\]

where \( F_4 \) is given by

\[
F_4 = \beta_1 |\eta_+|^4 + \beta_2 |\eta_-|^4 + \beta_3 |\eta_+|^2 |\eta_-|^2 + \beta_4 (\eta_+^* \eta_-^2 + \eta_-^* \eta_+^2)
+ (\beta_5 |\eta_+|^2 + \beta_6 |\eta_-|^2)(\eta_+^* \eta_- + \eta_-^* \eta_+).
\]

The coefficients \( \gamma, \beta_3, \beta_5, \beta_6 \) vanish at zero spin-orbit coupling, due to the spin rotation symmetry.

The gradient terms are different for different magnetic groups. For \( G(H) = D_4(C_4) \),

\[
F_{\text{grad}} = K_1 |D_{\pm} \eta_+|^2 + K_3 |D_{\pm} \eta_-|^2 + K_4 (|D_{\pm} \eta_+|^2 + |D_{\pm} \eta_-|^2) + K_6 (|D_{\pm} \eta_+|^2 + |D_{\pm} \eta_-|^2 + c.c.),
\]

where \( D_{\pm} = (D_x, D_y) \). The coefficients \( K_4 \) and \( K_6 \) vanish in the absence of spin-orbit coupling.
In the case of \( \mathbf{G}(\mathbf{H}) = \mathbf{D}_3(\mathbf{C}_3) \), it is convenient to make a change of coordinates after which \( \hat{\mathbf{z}} \) is directed along [111]: \( \mathbf{r} \to \mathbf{r}' = \mathbf{R}\mathbf{r} \), where \( \mathbf{R} \) is the matrix of a three-dimensional rotation by an angle \( \theta = \arccos(1/\sqrt{3}) \) about the axis \( \mathbf{B} \). Omitting the primes, the gradient terms in the new coordinates have the same form as Eq. (42).

Finally, for \( \mathbf{G}(\mathbf{H}) = \mathbf{D}_2(\mathbf{C}_2) \), it is convenient to rotate the coordinates in such a way that \( \hat{\mathbf{z}} \) is directed along [110]: \( \mathbf{r} \to \mathbf{r}' = \mathbf{R}\mathbf{r} \), where \( \mathbf{R} \) is the matrix of a three-dimensional rotation by an angle \( \theta = \pi/2 \) about the axis \( \mathbf{B} \). In this case, the gradient terms have the following form:

\[
F_{\text{grad}} = K_1^+ |D_x\eta_+|^2 + K_2^+ |D_y\eta_+|^2 + K_3^+ |D_z\eta_+|^2 \\
+ K_1^- |D_x\eta_-|^2 + K_2^- |D_y\eta_-|^2 + K_3^- |D_z\eta_-|^2 \\
+ [K_4(D_x\eta_+)^*(D_x\eta_-) + K_5(D_y\eta_+)^*(D_y\eta_-) \nonumber \\
+ K_6(D_z\eta_+)^*(D_z\eta_-) + \text{c.c.}]].
\]

Because of the choice of coordinates, \( \mathbf{M} = \mathbf{M}\hat{\mathbf{z}} \) and \( \mathbf{B} = \mathbf{B}\hat{\mathbf{z}} \) in all three cases. The coefficients \( K_4, K_5, K_6 \) vanish in the absence of spin-orbit coupling.

If the ferromagnetic magnetization is not directed along a high symmetry axis, then \( \mathbf{G}(\mathbf{H}) = \mathbf{C}_1 \). In this case, the only symmetry element is the unity operation, and the gradient terms contain all possible real combinations of the components of \( \mathbf{D} \) and \( \eta_\pm \). We shall not give these (rather cumbersome) expressions here.

The Ginzburg-Landau functionals listed above can be used for deriving the phase diagram of a cubic ferromagnetic superconductor, which can be quite complex. In particular, one cannot exclude the possibility of extra phase transitions in the superconducting state.

VI. CONCLUSIONS

We have studied the symmetry of the superconducting order parameter in a cubic ferromagnetic superconductor. An experimental example is provided by \( \text{ZrZn}_2 \). Because of the anti-unitarity of time reversal, the usual symmetry analysis of possible superconducting states (see Refs. [13], [2], and [3]) is not applicable. In a metallic ferromagnet, when both the electromagnetic interaction and the spin-orbit coupling are present, the order parameter symmetry evolves from that appropriate for the cubic group \( \mathbf{O}_h \) to one of the magnetic point groups, which is studied here using the phenomenological Ginzburg-Landau theory. It is shown that the order parameter corresponds to one of the irreducible co-representations of the magnetic group, and has two components, which describe pairing on the exchange-split sheets of the Fermi surface, see Eq. (42). It should be noted that our results would manifest themselves as deep minima of the gap, which would also have to be taken into account when analyzing the experimental data.

The situation might be complicated by the presence of additional phase transitions in the superconducting state, which is a common feature of the systems with multi-component order parameters. Because of the complexity of the Ginzburg-Landau functionals derived in Sec. IV the number of possible scenarios with different predictions for experiment is quite large. In our view, it is still premature to discuss specific models, because of the lack of experimental data in the superconducting phase of \( \text{ZrZn}_2 \).

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