Order parameter symmetry in ferromagnetic superconductors

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We analyze the symmetry and 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 *corepresentations* 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 superconductor, such as $ZrZn_2$, in the limit of weak spin-orbit coupling, thus complementing an earlier study by the authors¹ 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.² 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, $\Delta_{\perp \perp}$ 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 $ZrZn_2$ (Ref. 3), and UGe₂ (Ref. 4) have renewed interest in 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 UGe₂) are responsible for both the superconductivity and 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,⁵ or to the enhancement of the superconducting critical temperature T_c on the ferromagnetic side.⁶ 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 exchangetype interaction of the magnetic moments of the Cooper pairs with the magnetization density.⁷

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 nonmagnetic 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.8 In magnetic superconductors, timereversal 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 Minvariant.⁹ 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 antilinear and antiunitary, which brings about a number of novel features in the sym-

metry analysis compared to the nonmagnetic case. The symmetry properties of the superconducting state in ZrZn₂ assuming strong spin-orbit coupling have been studied in Ref. 1 (see also Refs. 10-12, where various aspects of the theory of ferromagnetic superconductors have been considered). However, a rather weak magnetic anisotropy in ZrZn₂ (Ref. 3) and also the results of the de Haas-van Alphen measurements¹³ point 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,¹⁴ 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 normalstate symmetry groups are derived assuming that spin-orbit coupling is neglibly small, focusing on the cubic crystal symmetry relevant for ZrZn₂. In Sec. III, the effect of the electromagnetic interaction on the symmetry of the spintriplet order parameters is analyzed, and 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. Section 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 $ZrZn_2$, 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., nonsuperconducting) state will be analyzed in terms of the effective single-particle Hamiltonian

$$H_{0} = \int d\boldsymbol{r} \psi_{\alpha}^{\dagger}(\boldsymbol{r}) \left\{ \frac{1}{2m} \left[-i\hbar \frac{\partial}{\partial \boldsymbol{r}} + \frac{e}{c} \boldsymbol{A}(\boldsymbol{r}) \right]^{2} \delta_{\alpha\beta} + U(\boldsymbol{r}) \delta_{\alpha\beta} - [\boldsymbol{h}_{ex}(\boldsymbol{r}) + g \mu_{B} \boldsymbol{B}] \cdot \boldsymbol{\sigma}_{\alpha\beta} \right\} \psi_{\beta}(\boldsymbol{r}).$$
(1)

Here *e* is the absolute value of the electron charge, $U(\mathbf{r})$ is the periodic crystal lattice potential, $\boldsymbol{\sigma} = (\sigma_1, \sigma_2, \sigma_3)$ are Pauli matrices, and $\boldsymbol{h}_{ex}(\mathbf{r})$ is the exchange field. The magnetic induction inside the ferromagnet (in the assumed long cylinder geometry) is $\boldsymbol{B} = \text{curl} \boldsymbol{A}(\mathbf{r}) = 4\pi \boldsymbol{M}$, and *g* is the Landé *g* factor for electrons, which determines the Zeeman splitting. In the case of a collinear ferromagnet, which is assumed here, $\boldsymbol{h}_{ex}(\mathbf{r}) = \boldsymbol{h}_0 f(\mathbf{r})$, where $f(\mathbf{r})$ has the same periodicity as $U(\mathbf{r})$, and \boldsymbol{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 $B = H_{ext} + 4 \pi M$), 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 G at zero pressure) is much smaller than the exchange field in ZrZn₂ 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 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

$$\mathcal{G} = \mathbf{G}_{orb} \times \mathbf{G}_{spin} \times U(1), \qquad (2)$$

where U(1) is the gauge group composed of phase rotations $\Phi \psi_{\alpha}(\mathbf{r}) \Phi^{-1} = e^{i\phi} \psi_{\alpha}(\mathbf{r})$. In the presence of the vector potential, the usual lattice translations should be replaced by magnetic translations,¹⁵ and Cooper pairing occurs between the eigenstates of the normal-state Hamiltonian (1), which are no longer Bloch functions characterized by the wave vector \mathbf{k} . We neglect these complications here and make a usual assumption that the \mathbf{k} dependence of the order parameter is determined by the point symmetry of the crystal lattice. Thus, \mathbf{G}_{orb} contains only orbital rotations R_{orb} ,

$$R_{orb}\psi_{\alpha}(\mathbf{r})R_{orb}^{-1} = \psi_{\alpha}(R_{orb}^{-1}\mathbf{r}), \qquad (3)$$

and inversion

$$I\psi_{\alpha}(\mathbf{r})I^{-1} = \psi_{\alpha}(-\mathbf{r}). \tag{4}$$

Also, the effects of time-reversal symmetry are included in \mathbf{G}_{orb} . Below we shall use the notation C_{kn} for the rotations by an angle $2\pi/k$ about the axis $\hat{\mathbf{n}}$ in orbital space. The group \mathbf{G}_{spin} contains spin rotations R_{spin} :

$$R_{spin}\psi_{\alpha}(\mathbf{r})R_{spin}^{-1} = [D^{(1/2)}(R_{spin})]_{\alpha\beta}\psi_{\beta}(\mathbf{r}), \qquad (5)$$

where $D^{(1/2)}(R)$ is the spinor (j=1/2) representation of rotations: for a rotation R by an angle θ around \hat{n} , $D^{(1/2)}(R)$ $= \exp[-i(\theta/2)(\boldsymbol{\sigma}\cdot\hat{\boldsymbol{n}})]$. It is convenient to introduce an orthogonal basis of unit vectors $\hat{\boldsymbol{e}}_1, \hat{\boldsymbol{e}}_2, \hat{\boldsymbol{e}}_3$ in spin space, such that $\hat{\boldsymbol{e}}_3 \| \boldsymbol{B}$. We shall use the notation C_{kn}^s for the rotations by an angle $2\pi/k$ about the axis $\hat{\boldsymbol{n}}$ in spin space.

A standard representation for the time-reversal operator *K* is $K = C_{2e_2}^s K_0$, where K_0 is the complex conjugation operator associated with the representation $\{r, s_z\}$.¹⁶ The antiunitary operator K_0 is defined more explicitly by the equation

$$K_0[c\psi_{\alpha}(\mathbf{r})]K_0 = c^*\psi_{\alpha}(\mathbf{r}), \qquad (6)$$

where *c* is an arbitrary *c* number. In the momentum representation, K_0 also reverses the sign of \mathbf{k} . It should be noted that, in the decomposition $K = C_{2e_2}^s K_0$, while $C_{2e_2}^s$ is an operator in spin space only, K_0 operates in both spin and orbital space [as indicated, for example, by the result $K_0 s_y K_0 = -s_y$, where $s_y = (\hbar/2)\sigma_2$ is the *y* component of the electron spin operator]. Nevertheless, in discussing the symmetry properties of the Hamiltonian H_0 given by Eq. (1) for the case where the common direction of \mathbf{h}_{ex} and \mathbf{B} is along $\hat{\mathbf{e}}_3$ (so that the Hamiltonian does not contain σ_2), it is useful to consider K_0 together with the symmetry operations in orbital space.

If R_{orb} leaves the periodic potential $U(\mathbf{r})$ and the exchange field $h_{ex}(r)$ invariant, then the transform of the Hamiltonian H_0 , namely, $R_{orb}H_0R_{orb}^{-1}$, is the same as H_0 except that the vector potential A(r) is replaced by A'(r) $=R_{orb}^{-1}A(R_{orb}r)$ ¹⁷ This means that the transformation rule for the magnetic induction under R_{orb} is $B(r) = \operatorname{curl} A(r)$ $\rightarrow \boldsymbol{B}'(\boldsymbol{r}) = \operatorname{curl} \boldsymbol{A}'(\boldsymbol{r}) = \boldsymbol{R}_{orb}^{-1} \boldsymbol{B}(\boldsymbol{R}_{orb}\boldsymbol{r}) = \boldsymbol{R}_{orb}^{-1} \boldsymbol{B}(\boldsymbol{r}).$ Also, $K_0H_0K_0$ is the same as H_0 except that $A(\mathbf{r})$ is replaced by $-A(\mathbf{r})$, so that the transformation rule for the magnetic induction under K_0 is simply $B \rightarrow -B$. Thus, if R_{orb} leaves $U(\mathbf{r})$ and $\mathbf{h}_{ex}(\mathbf{r})$ invariant and $R_{orb}\mathbf{B} = -\mathbf{B}$, then K_0R_{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 nonmagnetic case, i.e., at $h_{ex} = B = M = 0$, the orbital symmetry of H_0 is determined by the symmetry of the lattice potential $U(\mathbf{r})$. Since $ZrZn_2$ has a cubic Laves phase structure, $\mathbf{G}_{orb} = \mathbf{O}_h \times \mathbf{K}_0 = \mathbf{O} \times \mathbf{I} \times \mathbf{K}_0$, where $\mathbf{I} = \{E, I\}$ and $\mathbf{K}_0 = \{E, K_0\}$. In addition, H_0 is invariant under arbitrary rotations in spin space, so that $\mathbf{G}_{spin} = SU(2)$.

In the ferromagnetic case, where M, h_{ex} , and 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_0R_{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. (1) and (5) that H_0 is invariant under the operators of the group $C_{\infty e_3}^s$ 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 B. Therefore,

$$\mathbf{G}_{spin} = \mathbf{C}_{\infty e_3}^s. \tag{7}$$

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 orderparameter symmetries for each of the cases will be described later in Sec. III.

Case A. The orbital symmetry of the system is determined by the electromagnetic interaction of the conduction electrons with the induction **B** via the vector potential **A**. If this interaction can be neglected, which amounts to setting $e \rightarrow 0$ in Eq. (1), 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.,

$$\mathbf{G}_{orb} = \mathbf{O}_h \times \mathbf{K}_0 = \mathbf{O} \times \mathbf{I} \times \mathbf{K}_0. \tag{8}$$

In this case, which might be appropriate for a neutral Fermi system, such as the liquid ³He in magnetic field or the "cold" atomic gases, only the spin symmetry is influenced by the presence of ferromagnetic magnetization.

In ferromagnet metals, the electromagnetic interaction is always present, and the presence of 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 sufficiently 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

$$\mathbf{G}_{orb} = \mathbf{D}_{4}(\mathbf{C}_{4}) \times \mathbf{I}$$

= { $E, C_{4z}, C_{2z}, C_{4z}^{-1}, K_{0}C_{2x}, K_{0}C_{2y}, K_{0}C_{2a}, K_{0}C_{2b}$ }
× \mathbf{I} , (9)

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 $\mathbf{G}(\mathbf{H})$,¹⁸ where the subgroup **H** in parentheses (the unitary subgroup) includes all elements of **G** which are not multiplied by the antiunitary operation K_0 . A useful observation is that any magnetic group $\mathbf{G}(\mathbf{H})$ can be expressed in terms of left cosets with respect to the unitary subgroup **H**: $\mathbf{G}(\mathbf{H}) = \mathbf{H} + A\mathbf{H}$, where all elements of the coset $A\mathbf{H}$ are antiunitary. The choice of the antiunitary group element A is arbitrary and does not affect the final results, but once chosen it remains fixed. For the group $\mathbf{D}_4(\mathbf{C}_4)$, we choose $A = K_0 C_{2x}$.

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

$$\mathbf{G}_{orb} = \mathbf{D}_{3}(\mathbf{C}_{3}) \times \mathbf{I}$$

= { $E, C_{3\epsilon}, C_{3\epsilon}^{-1}, K_{0}C_{2b}, K_{0}C_{2b'}, K_{0}C_{2b''}$ } × \mathbf{I} , (10)

where $\hat{\boldsymbol{\epsilon}} = (\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}} + \hat{\boldsymbol{z}})/\sqrt{3}$, $\hat{\boldsymbol{b}}' = C_{3\epsilon}\hat{\boldsymbol{b}} = (\hat{\boldsymbol{y}} - \hat{\boldsymbol{z}})/\sqrt{2}$, and $\hat{\boldsymbol{b}}'' = C_{3\epsilon}^{-1}\hat{\boldsymbol{b}} = (\hat{\boldsymbol{z}} - \hat{\boldsymbol{x}})/\sqrt{2}$. For this magnetic group, we choose $A = K_0 C_{2b}$.

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

$$\mathbf{G}_{orb} = \mathbf{D}_2(\mathbf{C}_2) \times \mathbf{I} = \{E, C_{2a}, K_0 C_{2b}, K_0 C_{2z}\} \times \mathbf{I}.$$
(11)

In this case, we also choose $A = K_0 C_{2b}$.

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

$$\mathbf{G}_{orb} = \mathbf{C}_i = \mathbf{C}_1 \times \mathbf{I},\tag{12}$$

where C_1 consists of the unity operation *E*. This group is trivial and does not contain antiunitary elements.

In the next section, we study the symmetry properties of the superconducting order parameter at $M \neq 0$ using \mathbf{G}_{spin} from Eq. (7), and \mathbf{G}_{orb} from Eqs. (8)–(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 ZrZn₂, the exchange band splitting is $E_{ex} \approx 5$ mRy ≈ 800 K,¹⁹ which greatly exceeds the superconducting critical temperature $T_c \approx 0.2$ K. In these conditions, the usual Chandrasekhar-Clogston arguments² make any pairing of electrons with opposite spins, in particular in the singlet channel, strongly suppressed. The general form of a spintriplet superconducting order parameter is $\Delta_{\alpha\beta}(\mathbf{k},\mathbf{r}) = (i\boldsymbol{\sigma}\boldsymbol{\sigma}_2)_{\alpha\beta}d(\mathbf{k},\mathbf{r})$.⁸ It is convenient to use the following representation: $d(\mathbf{k}) = \hat{\mathbf{e}}_+ d_-(\mathbf{k}) + \hat{\mathbf{e}}_- d_+(\mathbf{k}) + \hat{\mathbf{e}}_3 d_3(\mathbf{k})$, where $\hat{\mathbf{e}}_{\pm} = (\hat{\mathbf{e}}_1 \pm i\hat{\mathbf{e}}_2)/\sqrt{2}$ 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 \mathcal{G} . The easiest way to obtain the transformation properties of the order parameter under the operations from \mathcal{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:

$$H_{sc} = \frac{1}{2} \sum_{\boldsymbol{k}} \sum_{\alpha,\beta=\uparrow,\downarrow} \left[\Delta_{\alpha\beta}(\boldsymbol{k}) c^{\dagger}_{\boldsymbol{k}\alpha} c^{\dagger}_{-\boldsymbol{k},\beta} + \text{H.c.} \right].$$
(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(-k) = -d(k). From Eqs. (13), (3), (5), and (6), we obtain

$$R_{orb}d_{\alpha}(\boldsymbol{k}) = d_{\alpha}(R_{orb}^{-1}\boldsymbol{k}),$$

$$R_{spin}d_{\alpha}(\boldsymbol{k}) = [D^{(1)}(R_{spin})]_{\alpha\beta}d_{\beta}(\boldsymbol{k}), \qquad (14)$$

$$K_{0}d_{\alpha}(\boldsymbol{k}) = d_{\alpha}^{*}(-\boldsymbol{k}),$$

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 (2), the basis functions of the irreducible representations of G are given by products of the basis functions of \mathbf{G}_{orb} and \mathbf{G}_{spin} . An important point here is that, because of the presence of the antiunitary operations K_0R_{orb} in \mathbf{G}_{orb} , the symmetry analysis should be modified. The order parameter should transform according to one of the irreducible *corepresentations* of $\mathbf{G}_{orb} = \mathbf{G}(\mathbf{H})$, which can be derived from the irreducible representations of the unitary subgroup \mathbf{H} .¹⁸

At M=0, $\mathbf{G}_{spin} = SU(2)$, and d transforms according to the three-dimensional vector representation of SU(2), whose basis functions are \hat{e}_{\pm} and \hat{e}_3 . All three spin components d_{\pm} and d_3 have the same critical temperature. At $M \neq 0$, the spin symmetry is reduced to $\mathbf{G}_{spin} = \mathbf{C}_{\infty e_3}^s$ [see Eq. (7)], and the vector representation is split into three onedimensional representations of the group $\mathbf{C}_{\infty e_3}^s$. The spin components d_{\pm} 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

$$\boldsymbol{d}_{\Gamma}(\boldsymbol{k},\boldsymbol{r}) = i \hat{\boldsymbol{e}}_{+} \sum_{i=1}^{n_{\Gamma}} \eta_{i}(\boldsymbol{r}) \boldsymbol{f}_{\Gamma,i}(\boldsymbol{k}). \tag{15}$$

Here $f_{\Gamma,i}(\mathbf{k})$ are the odd basis functions of a n_{Γ} -dimensional irreducible corepresentation Γ of \mathbf{G}_{orb} (the parity of the spintriplet order parameter is fixed, and the inversion operation can be omitted from \mathbf{G}_{orb}). The action of the orbital symmetry elements on the functions $f_{\Gamma,i}(\mathbf{k})$ in the momentum space is defined as follows: under the crystal rotations, $R_{orb}f(\mathbf{k}) = f(R_{orb}^{-1}\mathbf{k})$, under the combined operations, $K_0R_{orb}f(\mathbf{k}) = f^*(-R_{orb}^{-1}\mathbf{k})$. The expansion coefficients $\eta_i(\mathbf{r})$ 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 antiunitary 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 $d_{\pm} \neq 0$, i.e., $d \propto \hat{e}_{-}$). It should be mentioned here that the band structure of ZrZn₂ is quite complex,^{19,20} but we neglect such a complication here and assume that there are only two exchangesplit bands. This assumption should not affect the essence of our results. Experimentally, the absence of a clear specific heat anomaly at T_c in ZrZn₂ (Ref. 3) might be due to the fact that a large portion, e.g., one of the sheets, of the Fermi surface is not paired. This, together with the magnetic anisotropy and de Haas-van Alphen data mentioned in the Introduction, points out that the spin-orbit coupling in this material is indeed quite small. In contrast to the strong spin-orbit coupling case considered in Ref. 1, the interband interactions $c_{k\uparrow}^{\dagger}c_{-k,\uparrow}^{\dagger}c_{k'\downarrow}c_{-k',\downarrow}$, which could induce order parameters of the same symmetry on both sheets of the Fermi surface, are

TABLE I. The examples of the basis functions for the odd irreducible representations of the point group **O** from Ref. 22, $\omega = e^{2\pi i/3}$.

Г	$f_{\Gamma}(\pmb{k})$
A_1	$k_x k_y k_z (k_x^2 - k_y^2) (k_y^2 - k_z^2) (k_z^2 - k_x^2)$
A_2	$k_x k_y k_z$
Ε	$k_{x}k_{y}k_{z}(k_{x}^{2}+\omega k_{y}^{2}+\omega^{*}k_{z}^{2}), k_{x}k_{y}k_{z}(k_{x}^{2}+\omega^{*}k_{y}^{2}+\omega k_{z}^{2})$
F_1	k_x, k_y, k_z
F_2	$k_x(k_y^2 - k_z^2), k_y(k_z^2 - k_x^2), k_z(k_x^2 - k_y^2)$

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_{\pm} , because of the large value of the exchange splitting in ZrZn₂, mentioned in the beginning of this section. For the same reason, we also neglect the possibility of a superconducting state with a nonzero momentum, i.e., with $\langle c_{k+q,\uparrow}^{\dagger} c_{-k,\downarrow}^{\dagger} \rangle \neq 0$ (Larkin-Ovchinnikov-Fulde-Ferrell state).²¹

When the symmetry is described by one of the magnetic point groups (9), (10), (11), or (12), \mathbf{G}_{orb} has only onedimensional corepresentations (see below); therefore Eq. (15) reduces to the form

$$\boldsymbol{d}_{\Gamma}(\boldsymbol{k},\boldsymbol{r}) = i\hat{\boldsymbol{e}}_{+} \,\boldsymbol{\eta}(\boldsymbol{r})f_{\Gamma}(\boldsymbol{k}). \tag{16}$$

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 nontrivial; in particular, there are zeros in the spectrum of elementary excitations where $f_{\Gamma}(\mathbf{k}) = 0$. Below we examine the order parameter symmetry for different cases and determine the positions of the gap zeros dictated by the magnetic symmetry.

A: $G_{orb} = O \times I \times K_0$

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 nonzero M. The order parameter is given by Eq. (15). The group **O** has 2 onedimensional (A_1 and A_2), 1 two- dimensional (E), and 2 three-dimensional (F_1 and F_2) representations. The examples of the basis functions are given in Table I. The onecomponent 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 multicomponent 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-

TABLE II. The character table and the examples of the basis functions for the odd irreducible corepresentations of the magnetic point group $\mathbf{D}_4(\mathbf{C}_4)$. The overall phases of the basis functions are chosen so that $K_0C_{2x}f_{\Gamma}(\mathbf{k}) = f_{\Gamma}(\mathbf{k})$. $\lambda_{1,2}$ are arbitrary real constants.

Г	Ε	C_{4z}	$f_{\Gamma}(\boldsymbol{k})$
Α	1	1	k_z
В	1	-1	$k_{z}[\lambda_{1}(k_{y}+ik_{x})^{2}+\lambda_{2}(k_{y}-ik_{x})^{2}]$
^{1}E	1	i	$k_y + ik_x$
^{2}E	1	-i	$k_y - ik_x$

electron wave functions, the cubic symmetry is reduced to one of the magnetic groups (9), (10), or (11), 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 onedimensional corepresentations. If $M \parallel [001]$ and **O** $\rightarrow \mathbf{D}_4(\mathbf{C}_4)$, then it is easy to check, using Table II, that

$$A_{1} \rightarrow A,$$

$$A_{2} \rightarrow B,$$

$$E \rightarrow A + B,$$

$$F_{1} \rightarrow A + {}^{1}E + {}^{2}E,$$

$$F_{2} \rightarrow B + {}^{1}E + {}^{2}E.$$
(17)

We also gave here the correspondence between the onedimensional representations of **O** and the corepresentations of $\mathbf{D}_4(\mathbf{C}_4)$. If $M \| [111]$ and $\mathbf{O} \rightarrow \mathbf{D}_3(\mathbf{C}_3)$, then, using Table III,

$$A_{1} \rightarrow A,$$

$$A_{2} \rightarrow A,$$

$$E \rightarrow {}^{1}E + {}^{2}E,$$

$$F_{1} \rightarrow A + {}^{1}E + {}^{2}E,$$

$$F_{2} \rightarrow A + {}^{1}E + {}^{2}E.$$
(18)

If M | [110] and $\mathbf{O} \rightarrow \mathbf{D}_2(\mathbf{C}_2)$, then, using Table IV,

$$A_1 \rightarrow A,$$

 $A_2 \rightarrow B,$

TABLE III. The character table and the examples of the basis functions for the odd irreducible corepresentations of the magnetic point group $\mathbf{D}_3(\mathbf{C}_3)$. The overall phases of the basis functions are chosen so that $K_0C_{2b}f_{\Gamma}(\mathbf{k}) = f_{\Gamma}(\mathbf{k})$.

Γ	Ε	$C_{3\epsilon}$	$C_{3\epsilon}^{-1}$	$f_{\Gamma}(\mathbf{k})$
$A^{1}E^{2}E$	1 1 1	1 ω ω*	1 ω* ω	$k_{x}+k_{y}+k_{z}$ $e^{-i\pi/3}k_{x}-k_{y}+e^{i\pi/3}k_{z}$ $e^{i\pi/3}k_{x}-k_{y}+e^{-i\pi/3}k_{z}$

TABLE IV. The character table and the examples of the basis functions for the odd irreducible corepresentations of the magnetic point group $\mathbf{D}_2(\mathbf{C}_2)$. The overall phases of the basis functions are chosen so that $K_0C_{2b}f_{\Gamma}(\mathbf{k})=f_{\Gamma}(\mathbf{k})$. λ is an arbitrary real constant.

Г	Ε	C_{2a}	$f_{\Gamma}(\boldsymbol{k})$
Α	1	1	$k_x + k_y$
В	1	-1	$k_z + i\lambda(k_x - k_y)$
		$E \rightarrow A + B$,	(19)

$$F_1 \rightarrow A + B + B,$$

$$F_2 \rightarrow A + A + B.$$

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 $\mathbf{G}_{orb} = \mathbf{O} \times \mathbf{I} \times \mathbf{K}_0$ and corresponding to a gap function on the spin-up Fermi surface. Then the Ginzburg-Landau free energy describing a homogeous phase is

$$F = \alpha \, \boldsymbol{\eta}^* \cdot \boldsymbol{\eta} + \beta_1 (\, \boldsymbol{\eta}^* \cdot \boldsymbol{\eta})^2 + \beta_2 |\, \boldsymbol{\eta} \cdot \boldsymbol{\eta}|^2 + \beta_3 (|\, \boldsymbol{\eta}_x|^4 + |\, \boldsymbol{\eta}_y|^4 + |\, \boldsymbol{\eta}_z|^4), \qquad (20)$$

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;²² 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 become²³

$$F = a(T - T_{c,0}) | \boldsymbol{\eta} |^{2} + K_{1}(D_{i}\eta_{j})^{*}(D_{i}\eta_{j}) + K_{2}(D_{i}\eta_{i})^{*}(D_{j}\eta_{j}) + K_{3}(D_{i}\eta_{j})^{*}(D_{j}\eta_{i}) + K_{4}(D_{i}\eta_{i})^{*}(D_{i}\eta_{i}) = a(T - T_{c,0}) | \boldsymbol{\eta} |^{2} + i \gamma [\boldsymbol{\eta}^{*} \times \boldsymbol{\eta}] \boldsymbol{B} + K_{1}(D_{i}\eta_{j})^{*}(D_{i}\eta_{j}) + K_{23} [(D_{i}\eta_{i})^{*}(D_{j}\eta_{j}) + (D_{i}\eta_{j})^{*}(D_{j}\eta_{i})] + K_{4}(D_{i}\eta_{i})^{*}(D_{i}\eta_{i}).$$
(21)

Here $D = \nabla + i(2\pi/\Phi_0)A$, $\Phi_0 = \pi\hbar c/e$ 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 $i[\eta^* \times \eta]$ 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 $M \| [001]$, so that $\mathbf{G}_{orb} = \mathbf{D}_4(\mathbf{C}_4)$. The critical temperature for the order parameter component η_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. 24, with the result

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

$$T_{c,-} = T_{c,0} - \frac{8\pi^2}{a\Phi_0} \left(K_1 + K_2 + \frac{K_4}{2} \right) M,$$
 (22)

$$T_{c,z} = T_{c,0} - \frac{8\pi^2}{a\Phi_0} K_1 M.$$

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 γ , and is entirely due to the interaction of the orbital pair magnetization with **B**. It is easy to see, using Table II, that the order parameter components η_+ , η_- , and η_z correspond to the following one-dimensional corepresentations of $\mathbf{D}_4(\mathbf{C}_4)$: $\eta_z \sim A$, η_+ $\sim {}^1E$, $\eta_- \sim {}^2E$. 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 that into a state that does a better job of minimizing the fourth-order contributions to the free energy.

B: $G_{orb} = D_4(C_4) \times I(M | [001])$

The order parameter is given by Eq. (16) and the irreducible corepresentations are listed in Table II. We see that the order parameters $d_A(k)$ and $d_B(k)$ vanish on the line $k_z=0$ at the Fermi surface, while $d_{1E}(k)$ and $d_{2E}(k)$ vanish at the points $k_z=k_y=0$ [note that here the label Γ refers to the orbital symmetry, whereas in Ref. 1 we labeled the corepresentations 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 twofold rotation C_{2z} . Therefore,

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

= $f_{A,B}(\mathbf{k}),$ (23)

so that $f_{A,B}(k_x, k_y, 0) = 0$. Similarly, under a fourfold rotation around the *z* axis,

$$C_{4z}f_B(\mathbf{k}) = f_B(k_y, -k_x, k_z) = -f_B(\mathbf{k});$$

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

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

hence $f_{1_E, 2_E}(0, 0, k_z) = 0$.

It also follows from Eq. (23) that $f_A(\mathbf{k})$ and $f_B(\mathbf{k})$ 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 $f(\mathbf{k}) = \sum_{n} f_{n} e^{i\mathbf{k}\cdot\mathbf{R}_{n}}$, 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

$$f(\boldsymbol{k}) = \sum_{n} c_{n} \sin \boldsymbol{k} \cdot \boldsymbol{R}_{n}, \qquad (24)$$

where \mathbf{R}_n are the sites of a fcc cubic lattice, which cannot be transformed one into another by inversion. In the nearestneighbor approximation, we choose the following set of \mathbf{R}_{n} 's: $\{\mathbf{R}_{n}\} = (a/2)\{(101), (\overline{1}01), (011), (0\overline{1}1), (110), (\overline{1}10)\}.$ Using Table II, we obtain the basis functions which have symmetry-imposed zeros at the surface of the Brillouin zone:

$$\begin{split} f_A(\mathbf{k}) &= \sin \frac{k_z a}{2} \left(\cos \frac{k_x a}{2} + \cos \frac{k_y a}{2} \right), \\ f_B(\mathbf{k}) &= \sin \frac{k_z a}{2} \left(\cos \frac{k_x a}{2} - \cos \frac{k_y a}{2} \right), \\ f_1(\mathbf{k}) &= \cos \frac{k_z a}{2} \left(\sin \frac{k_y a}{2} + i \sin \frac{k_x a}{2} \right) \\ &+ \lambda_1 \left[e^{i \pi/4} \sin \left(\frac{k_x a}{2} + \frac{k_y a}{2} \right) \right. \\ &- e^{-i \pi/4} \sin \left(\frac{k_x a}{2} - \frac{k_y a}{2} \right) \right], \\ f_{2E}(\mathbf{k}) &= \cos \frac{k_z a}{2} \left(\sin \frac{k_y a}{2} - i \sin \frac{k_x a}{2} \right) \\ &+ \lambda_2 \left[e^{-i \pi/4} \sin \left(\frac{k_x a}{2} + \frac{k_y a}{2} \right) \right] . \end{split}$$

Here $\lambda_{1,2}$ are arbitrary real constants. The polynomial expressions for the basis functions from Table II are recovered in the limit of a "small" Fermi surface $k \rightarrow 0$ [note that $f_B(k)$] from Table II 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., $f_B(\mathbf{k}) = 0$ 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.

C: $G_{arb} = D_3(C_3) \times I(M \| [111])$

The order parameter is given by Eq. (16), and the irreducible corepresentations 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 threefold rotation about the axis $\hat{\boldsymbol{\epsilon}}$,

$$C_{3\epsilon}f_{1E,2E}(\mathbf{k}) = f_{1E,2E}(k_z,k_x,k_y) = e^{\pm 2\pi i/3}f_{1E,2E}(\mathbf{k}),$$

so that $f_{1_{E_1}2_E}(k_x = k_y = k_z) = 0$.

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We also give 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:

$$f_A(\mathbf{k}) = S_1^+ + S_2^+ + S_3^+ + i\lambda_1(S_1^- + S_2^- + S_3^-),$$

$$f_{1E}(\mathbf{k}) = \omega^* S_1^+ + \omega S_2^+ + S_3^+ + i\lambda_2(\omega^* S_1^- + \omega S_2^- + S_3^-),$$

$$f_{2E}(\mathbf{k}) = \omega S_1^+ + \omega^* S_2^+ + S_3^+ + i\lambda_3(\omega S_1^- + \omega^* S_2^- + S_3^-),$$

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

D: $G_{arb} = D_2(C_2) \times I(M \| [110])$

The order parameter is given by Eq. (16), and the irreducible corepresentations are listed in Table IV. The order parameter $d_B(k)$ does not have zeros, but $d_A(k)$ has the symmetry-imposed lines of zeros where the plane $k_x = -k_y$ crosses the Fermi surface, because under a twofold rotation about the axis \hat{a} .

$$C_{2a}f_A(\mathbf{k}) = f_A(k_y, k_x, -k_z) = -f_A(-k_y, -k_x, k_z) = f_A(\mathbf{k}),$$

so that $f_A(k_x = -k_y) = 0$.

The basis functions of the magnetic point group $D_3(C_3)$ in terms of the lattice Fourier series in the nearest-neighbor approximation:

$$f_A(\mathbf{k}) = \cos\frac{k_z a}{2} \left(\sin\frac{k_x a}{2} + \sin\frac{k_y a}{2} \right) + \lambda_1 \sin\left(\frac{k_x a}{2} + \frac{k_y a}{2}\right),$$
$$f_B(\mathbf{k}) = \sin\frac{k_z a}{2} \left(\cos\frac{k_x a}{2} + \cos\frac{k_y a}{2} \right) + i\lambda_2 \sin\left(\frac{k_x a}{2} - \frac{k_y a}{2}\right),$$

where $\lambda_{1,2}$ are arbitrary real constants.

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 twofold. 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 (1) contains an extra term:

$$H_{0,s-o} = H_0 + \frac{\hbar}{4m^2c^2} \left[\nabla U(\mathbf{r}) \times \left(\mathbf{p} + \frac{e}{c} \mathbf{A} \right) \right] \cdot \boldsymbol{\sigma}.$$
 (25)

Spin is no longer a good quantum number and should be replaced by pseudospin.²⁵ In contrast to Eq. (2), the symmetry group of Eq. (25) cannot be represented as a product of independent orbital and spin groups. Instead, we have, neglecting the translations,

$$\mathcal{G} = \mathbf{G}_{s-o} \times U(1), \tag{26}$$

where \mathbf{G}_{s-o} consist of rotations which affect both the orbital and the pseudospin degrees of freedom,

$$R\psi_{\alpha}(\mathbf{r})R^{-1} = [D^{(1/2)}(R)]_{\alpha\beta}\psi_{\beta}(R^{-1}\mathbf{r}), \qquad (27)$$

and also the combined operations *KR*, where $K = C_{2e_2}^s K_0$, so that

$$K[c\psi_{\alpha}(\mathbf{r})]K^{-1} = c^{*}(i\sigma_{2})_{\alpha\beta}\psi_{\beta}(\mathbf{r}), \qquad (28)$$

where *c* is an arbitrary *c* number (note that $K^2 = -1$). The transformation rules for the order parameter become [cf. Eq. (14)]

$$Rd_{\alpha}(\boldsymbol{k}) = [D^{(1)}(R)]_{\alpha\beta}d_{\beta}(R^{-1}\boldsymbol{k}),$$

$$Kd_{\alpha}(\boldsymbol{k}) = -d^{*}_{\alpha}(-\boldsymbol{k}) = d^{*}_{\alpha}(\boldsymbol{k}).$$
(29)

In this case, as shown in Ref. 1, the symmetry of the system is reduced to a magnetic point group $\mathbf{G}(\mathbf{H})$, and the superconducting order parameter transforms according to one of the one-dimensional irreducible corepresentations. Depending on the direction of the magnetization, $\mathbf{G}(\mathbf{H}) = \mathbf{D}_4(\mathbf{C}_4)$, $\mathbf{D}_3(\mathbf{C}_3)$, $\mathbf{D}_2(\mathbf{C}_2)$, or \mathbf{C}_1 (in Ref. 1, only the first two cases were studied). The only difference from the previous section is that the elements of the magnetic groups now act simultaneously on the orbital and the spin coordinates, see [Eqs. (27) and (28], and one should replace K_0R with KR in the definitions (9), (10), and (11).

Because of the possibility of the interband pairing interactions of the form $c_{k\uparrow}^{\dagger}c_{-k,\uparrow}^{\dagger}c_{k'\downarrow}c_{-k',\downarrow}$, the superconductivity is present on both sheets of the Fermi surface. Instead of Eq. (15), we have the following general expression for the order parameter:

$$d(\mathbf{k}) = \hat{\mathbf{e}}_{+} d_{-}(\mathbf{k}) + \hat{\mathbf{e}}_{-} d_{+}(\mathbf{k}) + \hat{\mathbf{e}}_{3} d_{3}(\mathbf{k})$$

$$\approx i \hat{\mathbf{e}}_{+} \sum_{i=1}^{n_{\Gamma_{-}}} \eta_{-,i} f_{\Gamma_{-},i}(\mathbf{k}) + i \hat{\mathbf{e}}_{-} \sum_{i=1}^{n_{\Gamma_{+}}} \eta_{+,i} f_{\Gamma_{+},i}(\mathbf{k}).$$
(30)

Here $\Gamma_{-}(\Gamma_{+})$ label the irreducible corepresentations of **G**(**H**) describing the orbital symmetry of the order parameter at the pseudospin-up (pseudospin-down) sheets of the Fermi surface. The choice of these representations is not arbitrary, because $\hat{e}_{+}d_{-}$ and $\hat{e}_{-}d_{+}$ should have the same symmetry properties. Thus, the order parameter has $n_{\Gamma_{+}} + n_{\Gamma_{-}}$ components: (η_{+}, η_{-}) , where $\eta_{+} = (\eta_{+,1}, \dots, \eta_{+,n_{\Gamma_{+}}})$ and $\eta_{-} = (\eta_{-,1}, \dots, \eta_{-,n_{\Gamma_{+}}})$. For the magnetic groups of interest

to us, all corepresentations are one dimensional, so that $n_{\Gamma_+} = n_{\Gamma_-} = 1$. As discussed in Sec. III, the contribution proportional to \hat{e}_3 is small because of the large exchange band splitting, and is neglected in the second line of Eq. (30).

It is instructive to study the evolution of the order parameter symmetry in the presence of spin-orbit coupling using the Ginzburg-Landau theory. Let us start by looking at the first of the effects mentioned in the beginning of this section (i.e., the order parameter mixing), using as an example the vector representation F_1 of **O** and assuming M || [001]. 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 :

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

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

$$F_0 = a_+ (T - T_{c,+}) |\boldsymbol{\eta}_+|^2 + a_- (T - T_{c,-}) |\boldsymbol{\eta}_-|^2.$$
(32)

The critical temperatures $T_{c,-}$ and $T_{c,+}$ for the spin-up and spin-down order parameters are different, in general (we assume that $T_{c,-} > T_{c,+}$). There are no mixed terms of the form $\eta_{+,i}^* \eta_{-,j}$ in Eq. (32), because of the spin rotation symmetry U(1). Indeed, under a spin rotation by an angle θ about \hat{e}_3 , we have $d_{\pm} \rightarrow e^{\pm i\theta} d_{\pm}$, which can be interpreted as an operation acting on the order parameter components: η_{\pm} $\rightarrow e^{\pm i\theta} \eta_{\pm}$. 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, the symmetry is lowered from **O** to $\mathbf{D}_4(\mathbf{C}_4)$, 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 $(\boldsymbol{\eta}_+, \boldsymbol{\eta}_-)$. The magnetic group $\mathbf{D}_4(\mathbf{C}_4)$ is generated by the rotations C_{4z} and the combined operations KC_{2x} . According to Eqs. (29), $C_{4z}d_{\pm}(k) = \pm id_{\pm}(C_{4z}^{-1}k)$, $KC_{2x}d_{\pm}(k) = d_{\pm}^*(C_{2x}^{-1}k)$. In terms of $\boldsymbol{\eta}_{\pm}$, we have

$$C_{4z} \eta_{\pm,1} = \mp \eta_{\pm,1},$$

$$C_{4z} \eta_{\pm,2} = \pm \eta_{\pm,2},$$

$$C_{4z} \eta_{\pm,3} = \pm i \eta_{\pm,3},$$

$$KC_{2x} \eta_{\pm} = \eta_{\pm}^{*}.$$
(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. (29), the action of KC_{2x} 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):

$$F_{s-o} = F_0 + \sum_{i=1}^{3} (\lambda_{+,i} | \eta_{+,i} |^2 + \lambda_{-,i} | \eta_{-,i} |^2) + \gamma_1 (\eta_{-,1}^* \eta_{+,2} + \eta_{+,2}^* \eta_{-,1}) + \gamma_2 (\eta_{-,2}^* \eta_{+,1} + \eta_{+,1}^* \eta_{-,2}).$$
(34)

The coefficients $\lambda_{\pm,i}$ and $\gamma_{1,2}$ 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

$$T_{c} = \frac{T_{+,2} + T_{-,1}}{2} + \frac{1}{2}\sqrt{(T_{+,2} - T_{-,1})^{2} + \frac{4\gamma_{1}^{2}}{a_{+}a_{-}}},$$
 (35)

where $T_{\pm,i} = T_{c,\pm} - \lambda_{\pm,i}/a_{\pm}$. Both components $\eta_{+,2}$ and $\eta_{-,1}$ are nonzero below T_c , so that superconductivity appears simultaneously on both sheets of the Fermi surface. The order parameter can be obtained from Eq. (30):

$$d(\mathbf{k}) = i\hat{\mathbf{e}}_{+} \frac{k_{y} + ik_{x}}{\sqrt{2}} \eta_{-,1} + i\hat{\mathbf{e}}_{-} \frac{k_{y} - ik_{x}}{\sqrt{2}} \eta_{+,2}.$$
 (36)

At weak spin-orbit coupling and $T_{c,-} > T_{c,+}$, $\eta_{+,2}$ is much smaller than $\eta_{-,1}$: $\eta_{+,2}/\eta_{-,1} \propto \gamma_1$. The order parameter (36) has point nodes at the poles of the Fermi surfaces and, according to the classification of Ref. 1, corresponds to the irreducible corepresentation *A* of $\mathbf{D}_4(\mathbf{C}_4)$. Similarly, one can derive T_c for the order parameter ($\eta_{+,1}, \eta_{-,2}$) and check that it corresponds to the corepresentation *B*.

The critical temperatures for $\eta_{\pm,3}$ are $T_{\pm,3}=T_{c,\pm}$ $-\lambda_{\pm,3}/a_{\pm}$. The corresponding order parameter d still vanishes on one of the sheets of the Fermi surface, which is an artifact of our model, based on the representation F_1 of **O**. If one includes *all* representations of the cubic group in the free energy (32), 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 $d_{A_1}(k,r) = i\hat{e}_+\xi(r)f_{A_1}(k)$ [see Eq. (16)]. The order parameter corresponding to F_1 has the form (15) with $\Gamma = F_1$, $n_{\Gamma} = 3$, and the basis functions given by Eqs. (31). The quadratic part of the Ginzburg-Landau functional is

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

There are no mixed terms in Eq. (37) because of the different transformation properties of ξ and η with respect to the elements of the cubic group. We assume $T_{A_1} > T_{F_1}$, so that only ξ is nonzero immediately below the critical temperature. From Table I, the order parameter d_{A_1} has six line nodes where the planes $k_x=0$, $k_y=0$, $k_z=0$, $k_x=k_y$, $k_y=k_z$, and $k_z=k_x$ cross the Fermi surface. However, according to Table II, all these gap nodes, except from that on the plane $k_z=0$, are incompatible with the magnetic symmetry $\mathbf{D}_4(\mathbf{C}_4)$. 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 $\mathbf{D}_4(\mathbf{C}_4)$, whose action on the components $\boldsymbol{\eta}(=\boldsymbol{\eta}_-)$ is given by Eqs. (33), and on $\boldsymbol{\xi}$ by

$$C_{4z}\xi = -i\xi,$$

$$KC_{2z}\xi = \xi^*$$
(38)

[here we used Eq. (29) and the identities $f_{A_1}(C_{4z}^{-1}\mathbf{k}) = f_{A_1}(\mathbf{k})$ and $f_{A_1}^*(-C_{2x}^{-1}\mathbf{k}) = -f_{A_1}(\mathbf{k})$]. Since the components ξ and η_3 have the same transformation properties under all operations from $\mathbf{D}_4(\mathbf{C}_4)$, the free energy, which is invariant with respect to the magnetic group, should contain mixed terms in addition to Eq. (37):

$$F_{s-o} = F_0 + \gamma(\xi^* \eta_3 + \eta_3^* \xi), \tag{39}$$

where γ is small at weak spin-orbit coupling. The critical temperature is changed compared to T_{A_1} ,

$$T_{c} = \frac{T_{A_{1}} + T_{F_{1}}}{2} + \frac{1}{2}\sqrt{(T_{A_{1}} - T_{F_{1}})^{2} + \frac{4\gamma^{2}}{a_{A_{1}}a_{F_{1}}}},$$
 (40)

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

$$\boldsymbol{d}(\boldsymbol{k}) = i\hat{\boldsymbol{e}}_{+} [\xi f_{A_{1}}(\boldsymbol{k}) + \eta_{3} f_{F_{1},3}(\boldsymbol{k})] \propto \hat{\boldsymbol{e}}_{+} k_{z}.$$
(41)

This order parameter corresponds to the corepresentation A of $\mathbf{D}_4(\mathbf{C}_4)$. 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 η_3 is small, and the other five line nodes of $f_{A_1}(\mathbf{k})$ are just slightly filled, so that we shall have deep minima in the gap. At not very low temperatures, these "quasinodes" 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

TABLE V. The pairs of orbital corepresentations corresponding to the same symmetry of the order parameter (42) on both sheets of the Fermi surface.

G(H)	(Γ_+,Γ)
$D_4(C_4)$ $D_3(C_3)$ $D_2(C_2)$	$ \begin{array}{c} (A,B), \ (B,A), \ ({}^{1}E,{}^{2}E), \ ({}^{2}E,{}^{1}E) \\ (A,{}^{2}E), \ ({}^{1}E,A), \ ({}^{2}E,{}^{1}E) \\ (A,B), \ (B,A) \end{array} $

cubic symmetry, lift the degeneracy of the order parameter, and change the gap structure. In addition, the spin-orbit coupling induces nonzero order parameters on both sheets of the Fermi surface. The symmetry is reduced to a magnetic group $\mathbf{D}_n(\mathbf{C}_n)(n=2,3,4)$ or \mathbf{C}_1 . All corepresentations of these groups are one dimensional, so that the general form of the order parameter is given by

$$\boldsymbol{d}(\boldsymbol{k},\boldsymbol{r}) = i\hat{\boldsymbol{e}}_{+}f_{\Gamma} (\boldsymbol{k}) \eta_{-}(\boldsymbol{r}) + i\hat{\boldsymbol{e}}_{-}f_{\Gamma_{+}}(\boldsymbol{k}) \eta_{+}(\boldsymbol{r}). \quad (42)$$

The order parameter symmetry should be the same on both sheets, which means that (i) both components η_{-} and η_{+} have the same transformation properties under the action of the magnetic group elements and (ii) there are some restrictions as to the choice of Γ_{+} and Γ_{-} , stemming from the different transformation properties of the spin vectors \hat{e}_{+} and \hat{e}_{-} . In Table V, the pairs of orbital corepresentations giving rise to the same symmetry of *d* are listed for all three relevant magnetic groups. For instance, the order parameter (36) corresponds to $(\Gamma_{+}, \Gamma_{-}) = ({}^{2}E, {}^{1}E)$. The examples of the basis functions $f_{\Gamma_{\pm}}(k)$, which have only the zeros imposed by symmetry, can be found in Tables II, 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:

$$F_{uniform} = \sum_{i,j=\pm} A_{ij}(T) \eta_i^* \eta_j + F_4, \qquad (43)$$

where A_{ij} is a real symmetric matrix. Above the critical temperature T_c , A is positive definite, and $\eta_+ = \eta_- = 0$. Below T_c , both components of η are nonzero, in general. The coefficients A_{+-} vanish at zero spin-orbit coupling, due to the spin rotation symmetry. The fourth order terms in Eq. (43) are given by

$$F_4 = \sum_{ijkl=\pm} B_{ij,kl} \eta_i^* \eta_j^* \eta_k \eta_l, \qquad (44)$$

where the matrix *B* is real and symmetric with respect to $i \leftrightarrow j$ and $k \leftrightarrow l$, and satisfies the following condition: $B_{ij,kl} = B_{kl,ij}$.

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

$$F_{grad} = \sum_{i,j=\pm} \left[K_{ij}^{\perp} (\boldsymbol{D}_{\perp} \, \boldsymbol{\eta}_i)^* (\boldsymbol{D}_{\perp} \, \boldsymbol{\eta}_j) + K_{ij}^z (\boldsymbol{D}_z \, \boldsymbol{\eta}_i)^* (\boldsymbol{D}_z \, \boldsymbol{\eta}_j) \right],$$
(45)

where D_{\perp} stands for (D_x, D_y) , and K_{ij}^{\perp} and K_{ij}^{z} are real symmetric matrices, whose off-diagonal elements vanish in the absence of spin-orbit coupling.

In the case of $\mathbf{G}(\mathbf{H}) = \mathbf{D}_3(\mathbf{C}_3)$, we can make a change of coordinates after which \hat{z} is directed along [111]: $\mathbf{r} \rightarrow \mathbf{r}' = R\mathbf{r}$, where *R* is the matrix of a three-dimensional rotation by an angle $\theta = \arccos(1/\sqrt{3})$ about the axis *B*. Omitting the primes, the gradient terms in the new coordinates have the same form as Eq. (45).

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{z} is directed along [110]: $\mathbf{r} \rightarrow \mathbf{r}' = R\mathbf{r}$, where *R* is the matrix of a three-dimensional rotation by an angle $\theta = \pi/2$ about the axis *B*. In this case, the gradient terms have the following form:

$$F_{grad} = \sum_{i,j=\pm} \left[K_{ij}^{x} (\boldsymbol{D}_{x} \boldsymbol{\eta}_{i})^{*} (\boldsymbol{D}_{x} \boldsymbol{\eta}_{j}) + K_{ij}^{y} (\boldsymbol{D}_{y} \boldsymbol{\eta}_{i})^{*} (\boldsymbol{D}_{y} \boldsymbol{\eta}_{j}) + K_{ij}^{z} (\boldsymbol{D}_{z} \boldsymbol{\eta}_{i})^{*} (\boldsymbol{D}_{z} \boldsymbol{\eta}_{j}) \right],$$

$$(46)$$

where $K_{ij}^{x,y,z}$ are real symmetric matrices which are diagonal in the absence of spin-orbit coupling. Because of the choice of coordinates, $M = M\hat{z}$ and $B = B\hat{z}$ in all three cases.

If the ferromagnetic magnetization is not directed along a high-symmetry axis, then $G(H) = C_1$. In this case, the only symmetry element is the unity operation, and the gradient terms contain all possible real combinations of the components of D and η_{\pm} . We shall not give these rather cumbersome expressions here.

The expressions for the free energy given 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. Also, from Eqs. (43), (44) and (45) or (46), we see that the Ginzburg-Landau theory for ferromagnetic superconductors with large exchange band splitting is formally equivalent to a model of a two-band superconductor with two scalar order parameters of the same symmetry.²⁶ Interest in this model has been revived recently in the context of a "high-temperature" superconductivity in MgB₂; see e.g., Ref. 27.

VI. CONCLUSIONS

We have studied the symmetry of the superconducting order parameter in a cubic ferromagnetic superconductor. An experimental example is provided by $ZrZn_2$. Because of the antiunitarity of time reversal, the usual symmetry analysis of possible superconducting states (see Refs. 22, 23, and 8) 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 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 corepresentations 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 follow from general symmetry considerations and do not depend on the nature of ferromagnetism in the normal state (itinerant versus localized moments) or the mechanism of superconducting pairing.

We have determined the k dependence of the order parameter imposed by the magnetic symmetry for all possible directions of the ferromagnetic magnetization; see Table V. The most remarkable result is that there should always be zeros in the energy gap, either point nodes or line nodes or both, at least on one of the sheets of the Fermi surface, when M is directed along any of the high-symmetry axis of the cubic lattice. These nodes should give rise to a power-law behavior of the thermodynamic and kinetic characteristics at low temperatures.⁸ It is expected that such experimental techniques as ultrasonic attenuation measurements in the superconducting state might be especially useful in determining the detailed structure of the order parameter (a discussion

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of this can be found in Ref. 1). It should be noted that, if the electromagnetic and spin-orbit interactions are weak, then the gap nodes appropriate for the underlying cubic symmetry 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 multicomponent order parameters. Because of the complexity of the Ginzburg-Landau functionals derived in Sec. V, 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 ZrZn₂.

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