Magnetic properties of superconductors with strong spin-orbit coupling

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We study the response of a superconductor with a strong spin-orbit coupling on an external magnetic field. The Ginzburg-Landau free energy functional is derived microscopically for a general crystal structure, both with and without an inversion center, and for an arbitrary symmetry of the superconducting order parameter. As a by-product, we obtain the general expressions for the intrinsic magnetic moment of the Cooper pairs. It is shown that the Ginzburg-Landau gradient energy in a superconductor lacking inversion symmetry has unusual structure. The general formalism is illustrated using as an example $CePt_3Si$, which is the first known heavy-fermion superconductor without an inversion center.

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I. INTRODUCTION

Superconductors with unconventional, or anisotropic, pairing have remained one of the favorite and most-studied systems in condensed matter physics for more than two decades. Any superconducting material in which the symmetry of the pair wave function is different from an *s*-wave spin singlet, predicted by the Bardeen-Cooper-Schrieffer (BCS) theory, can be called "unconventional." From the initial discoveries of superconductivity in the heavy-fermion compounds, the list of examples has grown to include the high-T_c cuprate superconductors, ruthenates, magnetic superconductors, and possibly organic materials. In contrast, such popular novel superconductor as MgB_2, in which the order parameter is an *s*-wave singlet, is still "conventional" despite its many unusual properties.

Although the pairing mechanism in most if not all unconventional superconductors is subject to much debate, their behavior can be well understood using the symmetry approach, pioneered in Refs. 1–3. The intrinsic anisotropy and the multicomponent nature of the order parameter lead to a variety of interesting magnetic properties, such as the internal magnetism of the Cooper pairs, multiple phases in the vortex state, and the upper critical field anisotropy near T_c not described by the effective mass tensor in the Ginzburg-Landau (GL) equations; for a review see, e.g., Refs. 4 and 5.

In most of the previous microscopic calculations of the magnetic properties of unconventional superconductors, the model of an isotropic band in a centrosymmetric crystal has been used. Historically, this has its origin in the fact that an unconventional Cooper pairing was first extensively studied in the context of the superfluid ^{3}He, which is indeed an isotropic Fermi liquid with a weak spin-orbit (SO) coupling.[6] Although taking into account a realistic Fermi surface anisotropy in a crystalline superconductor is not believed to cause any drastic qualitative effects, it might lead to some considerable quantitative changes compared to the parabolic band model. The SO coupling in crystals is usually taken care of by redefining the basis of the single-electron states: instead of the usual Bloch spinors, the Cooper pairs are now formed by pseudospin eigenstates.[2] Then the only significant change in the superconducting properties, compared to the case without SO coupling, is that the system is no longer invariant with respect to arbitrary SU(2) spin rotations, which alters the symmetry of the order parameter in the pseudospin-triplet channel.[1,2] A detailed analysis of the temperature dependence of the upper critical field, including the band anisotropy, impurity scattering, and sometimes the Fermi liquid corrections, has been done using the quasiclassical (Eilenberger) method, see, e.g., Ref. 7, and the references therein. A disadvantage of this approach is that it assumes a constant density of states of the normal electrons near the Fermi surface and therefore fails to capture some contributions to the intrinsic magnetism of the Cooper pairs. Additional complications arise when a superconductor with SO interaction lacks an inversion center. In a nutshell, the symmetry analysis of superconducting phases should be modified if the SO coupling is strong, because the twofold degeneracy of the single-electron bands is now lifted almost everywhere in the Brillouin zone, which makes it impossible to introduce pseudospin and also suppresses most of the pairing channels.[8]

Although most superconductors do have inversion symmetry, there are some exceptions. Early examples included such materials as V_3Si (Ref. 9) and HfV_2,[10] in which a possible loss of inversion symmetry is associated with a structural phase transition in the bulk of the crystal. The existence of superconductivity was later reported in ferroelectric perovskites $SrTiO_3$ (Ref. 11) and $BaPbO_3$-$BaBiO_3$.[12] It was pointed out in Ref. 13 that the surface superconductivity observed, e.g., in Na-doped WO_3,[14] is generically noncentrosymmetric simply because of the fact that the two sides of the surface layer are manifestly nonequivalent. Possible effects of the absence of inversion symmetry in the layered high-T_c cuprates were discussed in Ref. 15. Very recently, superconductivity was found in noncentrosymmetric compounds $CePt_3Si$ (Ref. 16) and UIr.[17]

This article is aimed at studying the magnetic properties of a clean superconductor with arbitrary pairing symmetry and band structure, with or without an inversion center. We focus on the strong SO coupling limit, which is believed to be the case in many unconventional superconductors, in particular the heavy-fermion compounds, because of the presence of elements with large atomic weights, such as U, Ce, etc. In contrast to the previous works, the starting point of

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our calculations is an effective band Hamiltonian, which describes the dynamics of the Bloch electrons in a magnetic field.[18] The superconducting pairing is introduced using a BCS-type weak-coupling model, generalized for the case of an unconventional pairing symmetry. We derive the GL free energy microscopically, which allows us not only to calculate the upper critical field, but also evaluate the intrinsic magnetic moment of the Cooper pairs in a crystalline superconductor. To the best of the author's knowledge, a microscopic derivation of the GL equations for a superconductor lacking an inversion center, in the presence of an arbitrary SO coupling, has never been done before, so we fill this gap here. On the other hand, although some of our results in the centrosymmetric case are not new and can be found scattered in the literature, we found it instructive to treat both cases within the same general framework, which also highlights the important differences between them.

The article is organized as follows. In Sec. II, we discuss the properties of the Bloch electrons in a magnetic field in the normal state, and introduce the single-band effective Hamiltonian. In Sec. III, we study the properties of a strong SO coupling superconductor in a magnetic field near T_c, derive the linearized GL equations in the lowest order in $\boldsymbol{B}$, and calculate the internal magnetic moment of the Cooper pairs, in both the centrosymmetric and noncentrosymmetric cases. In Sec. IV, we apply the general formalism to $CePt_3Si$. Section V concludes with a discussion of our results.

II. SINGLE-PARTICLE PROPERTIES

To develop the necessary framework for the analysis of the superconducting properties, we first need to understand how a uniform magnetic field affects the single-electron states in a normal crystal with SO coupling (with or without an inversion center). While for free electrons with a parabolic dispersion $\boldsymbol{p}^2/2m$ the magnetic Hamiltonian is obtained by simply replacing $\boldsymbol{p}$ with a gauge-invariant momentum operator $\boldsymbol{p}+(e/c)\boldsymbol{A}$ (e is the absolute value of the electron charge), the case of band electrons should be treated more carefully.

In zero field, the single-electron Hamiltonian has the form

$$H_0 = \sum_{\boldsymbol{k}\nu} \epsilon_\nu(\boldsymbol{k}) c^\dagger_{\boldsymbol{k}\nu} c_{\boldsymbol{k}\nu}, \tag{1}$$

where $c^\dagger$ and c are the creation and annihilation operators of band electrons with the wave vector $\boldsymbol{k}$, $\epsilon_\nu(\boldsymbol{k})$ is the quasiparticle dispersion in the ν th band, which takes into account all effects of the periodic lattice potential and the SO interaction, and $\Sigma_{\boldsymbol{k}}$ stands for the integration over the first Brillouin zone. We assume that there is no disorder in the crystal, so that $\boldsymbol{k}$ is a good quantum number in the absence of external fields. The Matsubara Green's function of electrons, defined in the standard fashion:

$$G_{\nu_1\nu_2}(\boldsymbol{k}_1,\tau_1;\boldsymbol{k}_2,\tau_2) = -\langle T_\tau c_{\boldsymbol{k}_1\nu_1}(\tau_1) c^\dagger_{\boldsymbol{k}_2\nu_2}(\tau_2)\rangle, \tag{2}$$

is diagonal with respect to both the band index and the wave vector:

$$G_\nu(\boldsymbol{k},\omega_n) = \frac{1}{i\omega_n - \epsilon_\nu(\boldsymbol{k})}, \tag{3}$$

where $\omega_n=(2n+1)\pi T$ is the fermionic Matsubara frequency (we use the units in which $k_B=1$).

In the presence of a nonzero uniform magnetic field $\boldsymbol{B}$, Eq. (1) is replaced by

$$H_0 = \sum_{\boldsymbol{k}\nu} c^\dagger_{\boldsymbol{k}\nu} \mathcal{E}_\nu(\boldsymbol{k},\boldsymbol{B}) c_{\boldsymbol{k}\nu}, \tag{4}$$

where $\mathcal{E}$ is the effective one-band Hamiltonian in the $\boldsymbol{k}$-space.[18] The main technical difficulty in the derivation of Eq. (4) is that the corresponding vector potential $\boldsymbol{A}$ grows linearly as a function of $\boldsymbol{r}$, leading to divergent matrix elements of the Hamiltonian with respect to the zero-field Bloch waves. As was first pointed out by Peierls,[19] these nonperturbative features can be taken into account by simply replacing the wave vector $\boldsymbol{k}$ in the zero-field band dispersion $\epsilon_\nu(\boldsymbol{k})$ by the gauge-invariant combination $\boldsymbol{k}+(e/\hbar c)\boldsymbol{A}(\hat{\boldsymbol{r}})$, where $\hat{\boldsymbol{r}} = i\nabla_{\boldsymbol{k}}$ is the position operator in the $\boldsymbol{k}$-representation. Later, this idea was elaborated in Refs. 20 and 21, where it was shown that the Peierls Hamiltonian corresponds in fact to the zero-order term in the expansion of the general effective one-band Hamiltonian in powers of $\boldsymbol{B}$:

$$\mathcal{E}_\nu(\boldsymbol{k},\boldsymbol{B}) = \epsilon_\nu(\boldsymbol{K}) + B_i \epsilon^{(1)}_{\nu,i}(\boldsymbol{K}) + B_i B_j \epsilon^{(2)}_{\nu,ij}(\boldsymbol{K}) + \ldots, \tag{5}$$

where $\boldsymbol{K}$ is an operator in the $\boldsymbol{k}$-space:

$$\boldsymbol{K} = \boldsymbol{k} + \frac{e}{\hbar c}\boldsymbol{A}(\hat{\boldsymbol{r}}) = \boldsymbol{k} + i\frac{e}{2\hbar c}\left(\boldsymbol{B}\times\frac{\partial}{\partial \boldsymbol{k}}\right)$$

[here and below we use the symmetric gauge: $\boldsymbol{A}=(\boldsymbol{B}\times\boldsymbol{r})/2$]. Since the components of $\boldsymbol{K}$ do not commute: $[K_i,K_j] = -i(e/\hbar c)e_{ijk}B_k$, the order of application is important, so that $\mathcal{E}$ is assumed to be a completely symmetrized function of K_i. This can be achieved, e.g., by representing the expansion coefficients in Eq. (5), which are periodic in $\boldsymbol{k}$, in the form of a Fourier series over the lattice vectors $\boldsymbol{R}$, and then replacing $\boldsymbol{k}\to\boldsymbol{K}$ to obtain the operators $\epsilon_\nu(\boldsymbol{K})=\Sigma_{\boldsymbol{R}}\epsilon_\nu(\boldsymbol{R})e^{-i\boldsymbol{R}\boldsymbol{K}}$, etc.

If the electron bands are degenerate in zero field due to spin or pseudospin (see Sec. II A below), then the effective Hamiltonian $\mathcal{E}$ and all the expansion coefficients are 2×2 matrices. The Green's function corresponding to the Hamiltonian (4) is not diagonal with respect to $\boldsymbol{k}$, because the system is no longer invariant under lattice translations (it is still invariant though under the magnetic translations which combine the lattice translations with gauge transformations).

Although the explicit expressions for the expansion coefficients in Eq. (5) can be derived, at least in principle, using the procedure described in detail in Ref. 21, some important information can be obtained from general symmetry considerations. The full symmetry group $\mathcal{G}$ of the system in the normal state is given by a product of the space group and the gauge group U(1). Assuming that there is no magnetic order in zero field and omitting the lattice translations, we can write $\mathcal{G}=G\times K\times \mathrm{U}(1)$, where $\mathcal{G}$ is the point group of the crystal, which may or may not include the inversion operation I, and K is the time reversal operation. At nonzero $\boldsymbol{B}$, the Hamiltonian (4) is invariant with respect to time reversal

only if the sign of $\boldsymbol{B}$ (and of $\boldsymbol{A}$) is also changed, which imposes the following constraint on the function $\mathcal{E}$: $K^{\dagger}\mathcal{E}_{\nu}(-\boldsymbol{B})K=\mathcal{E}_{\nu}(\boldsymbol{B})$. In addition, the expansion coefficients must have certain transformation properties under the action of the point group elements, in particular, the band dispersion $\epsilon(\boldsymbol{k})$ must be invariant under all operations from G.

Further steps depend crucially on whether or not there is an inversion center in the crystal lattice, which determines the degeneracy of the zero-field bands.

A. Crystals with inversion center

If the crystal has an inversion center, then the bands are twofold degenerate at each $\boldsymbol{k}$, because the Bloch states $\psi_{\boldsymbol{k}+}=\psi_{\boldsymbol{k}\nu}$ and $\psi_{\boldsymbol{k}-}=KI\psi_{\boldsymbol{k}\nu}$ have the same energy, belong to the same wave vector, and are orthogonal. These states can be chosen to transform under the action of the space group operations similar to the spin eigenstates, in which case they are referred to as the pseudospin states.[2] Thus the bands can be labeled by $\nu=(n,\alpha)$, where $\alpha=\pm$ is the pseudospin projection. Focussing on a single band, we can omit the index n, and the effective band Hamiltonian (5) becomes

$$\mathcal{E}_{\alpha\beta}(\boldsymbol{k},\boldsymbol{B})=\epsilon(\boldsymbol{K})\delta_{\alpha\beta}-B_i\mu_{ij}(\boldsymbol{K})\sigma_{j,\alpha\beta}+\cdots, \tag{6}$$

where σ_j are the Pauli matrices, and both the zero-field band dispersion $\epsilon(\boldsymbol{k})$ and the tensor $\mu_{ij}(\boldsymbol{k})$ are invariant under all point group operations. It is easy to see that this form of the effective Hamiltonian is compatible with all the symmetry requirements, in particular that $\mathcal{E}$ should be Hermitian and K- and I-invariant. Indeed, the time reversal operator is $K=(i\sigma_2)K_0$, where K_0 is the operation of complex conjugation, which changes $\boldsymbol{k}\to-\boldsymbol{k}$. Therefore, we have $[\sigma_2\mathcal{E}(-\boldsymbol{k},-\boldsymbol{B})\sigma_2]^{*}=\mathcal{E}(\boldsymbol{k},\boldsymbol{B})$. Also, $\mathcal{E}(-\boldsymbol{k},\boldsymbol{B})=\mathcal{E}(\boldsymbol{k},\boldsymbol{B})$, because of inversion symmetry. In the limit of zero SO coupling, the usual Zeeman interaction term is recovered: $\mu_{ij}(\boldsymbol{k})\to\mu_B\delta_{ij}$, where μ_B is the Bohr magneton.

The Green's function (2) is a 2×2 matrix in the pseudospin space, which satisfies the following equation in the frequency representation:

$$(i\omega_n-\mathcal{E}_1)_{\alpha\gamma}G_{\gamma\beta}(\boldsymbol{k}_1,\boldsymbol{k}_2;\omega_n)=\delta_{\alpha\beta}\delta(\boldsymbol{k}_1-\boldsymbol{k}_2). \tag{7}$$

The Fourier transform of the Green's function, defined as

$$G_{\alpha\beta}(\boldsymbol{r}_1,\boldsymbol{r}_2;\omega_n)=\sum_{\boldsymbol{k}_1,\boldsymbol{k}_2}e^{i\boldsymbol{k}_1\boldsymbol{r}_1-i\boldsymbol{k}_2\boldsymbol{r}_2}G_{\alpha\beta}(\boldsymbol{k}_1,\boldsymbol{k}_2;\omega_n), \tag{8}$$

satisfies the equation

$$(i\omega_n-\hat{\mathcal{E}}_1)_{\alpha\gamma}G_{\gamma\beta}(\boldsymbol{r}_1,\boldsymbol{r}_2;\omega_n)=\delta_{\alpha\beta}\delta(\boldsymbol{r}_1-\boldsymbol{r}_2), \tag{9}$$

where $\hat{\mathcal{E}}$ is the Fourier transform of the effective band Hamiltonian (6), which is obtained by replacing $\boldsymbol{K}$ by the operator

$$\hat{\boldsymbol{K}}=-i\frac{\partial}{\partial\boldsymbol{r}}+\frac{e}{\hbar c}\boldsymbol{A}(\boldsymbol{r})=-i\frac{\partial}{\partial\boldsymbol{r}}+\frac{e}{2\hbar c}(\boldsymbol{B}\times\boldsymbol{r}).$$

The subscript 1 in $\mathcal{E}_1$ or $\hat{\mathcal{E}}_1$ means that the operator acts on the first argument of G. It should be noted that the Green's function (8) is not the same as the Green's function of the band electrons in the coordinate representation. The latter is defined as $\langle\boldsymbol{r}_1\sigma|(i\omega_n-H_0)^{-1}|\boldsymbol{r}_2\sigma'\rangle=\langle\boldsymbol{r}_1\sigma|\boldsymbol{k}_1\alpha\rangle G_{\alpha\beta}(\boldsymbol{k}_1,\boldsymbol{k}_2;\omega_n)\langle\boldsymbol{k}_2\beta|\boldsymbol{r}_2\sigma'\rangle$ (the summation over repeated indices is implied), where $\langle\boldsymbol{r}\sigma|\boldsymbol{k}\alpha\rangle=\psi_{\boldsymbol{k}\alpha}(\boldsymbol{r}\sigma)$ is the Bloch spinor, with $\sigma=\uparrow,\downarrow$ being the z-projection of spin.

The second term in $\hat{\boldsymbol{K}}$ presents some difficulty because it grows linearly as a function of $\boldsymbol{r}$ and therefore cannot be treated as a small perturbation. To handle this problem, we seek solution of Eq. (9) in a factorized form

$$G_{\alpha\beta}(\boldsymbol{r}_1,\boldsymbol{r}_2;\omega_n)=\overline{G}_{\alpha\beta}(\boldsymbol{r}_1-\boldsymbol{r}_2,\omega_n)e^{i\varphi(\boldsymbol{r}_1,\boldsymbol{r}_2)}, \tag{10}$$

where $\varphi(\boldsymbol{r}_1,\boldsymbol{r}_2)=(e/\hbar c)\int_{\boldsymbol{r}_1}^{\boldsymbol{r}_2}\boldsymbol{A}(\boldsymbol{r})d\boldsymbol{r}$, and the integration goes along a straight line connecting $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$.[22] Using the identities

$$\frac{\partial}{\partial\boldsymbol{r}_{1,2}}\int_{\boldsymbol{r}_1}^{\boldsymbol{r}_2}\boldsymbol{A}(\boldsymbol{r})d\boldsymbol{r}=\mp\boldsymbol{A}(\boldsymbol{r}_{1,2})+\frac{1}{2}[\boldsymbol{B}\times(\boldsymbol{r}_1-\boldsymbol{r}_2)], \tag{11}$$

one can show that the translationally-invariant function $\overline{G}(\boldsymbol{r}_1-\boldsymbol{r}_2)=\overline{G}(\boldsymbol{R})$ obeys the equation

$$(i\omega_n-\overline{\mathcal{E}})_{\alpha\gamma}\overline{G}_{\gamma\beta}(\boldsymbol{R},\omega_n)=\delta_{\alpha\beta}\delta(\boldsymbol{R}), \tag{12}$$

where the operator $\overline{\mathcal{E}}$ is obtained by replacing $\hat{\boldsymbol{K}}$ in the argument of $\hat{\mathcal{E}}$ in Eq. (9) by $\hat{\boldsymbol{K}}_{\boldsymbol{R}}=-i\partial/\partial\boldsymbol{R}+(e/2\hbar c)(\boldsymbol{B}\times\boldsymbol{R})$.

The advantage of introducing the function $\overline{G}$ is that, in contrast to Eq. (9), the magnetic field term in Eq. (12) can be treated as a perturbation at small enough $\boldsymbol{B}$. The precise condition can be easily obtained in the case of an isotropic parabolic band $\epsilon(\boldsymbol{k})=\hbar^2(k^2-k_F^2)/2m$, when the solution of Eq. (12) in zero field is $\overline{G}_{\alpha\beta}(\boldsymbol{R},\omega_n)\sim\delta_{\alpha\beta}e^{ik_FR\ \mathrm{sign}\ \omega_n}e^{-|\omega_n|R/v_F}$, where $v_F=\hbar k_F/m$ is the Fermi velocity. Because of the fast oscillations of the exponential, the characteristic scale of the derivative $\partial/\partial\boldsymbol{R}$ is k_F. On the other hand, the scale of R is given by $\hbar v_F/k_BT$, so that the field-dependent term in $\hat{\boldsymbol{K}}_{\boldsymbol{R}}\overline{G}$ is small compared with the gradient term if $\hbar\omega_c\ll k_BT$, where $\omega_c=eB/mc$ is the cyclotron frequency. Although this condition does not have a simple form for a realistic band structure, it is usually assumed that the perturbative treatment of $\boldsymbol{B}$ in Eq. (12) is legitimate at all but very low temperatures, where the Landau level quantization effects become important.

The Fourier transform of $\overline{G}$ satisfies the equation

$$[i\omega_n-\overline{\mathcal{E}}(\boldsymbol{k},\boldsymbol{B})]_{\alpha\gamma}\overline{G}_{\gamma\beta}(\boldsymbol{k},\omega_n)=\delta_{\alpha\beta}, \tag{13}$$

which is solved perturbatively in $\boldsymbol{B}$. The expansion of the effective band Hamiltonian has the form

$$\overline{\mathcal{E}}_{\alpha\beta}(\boldsymbol{k},\boldsymbol{B})=\epsilon(\boldsymbol{k})\delta_{\alpha\beta}-\boldsymbol{B}\boldsymbol{m}_{\alpha\beta}(\boldsymbol{k})+O(B^2), \tag{14}$$

where

$$m_{i,\alpha\beta}(\boldsymbol{k})=i\frac{e}{2c}\left[\boldsymbol{v}(\boldsymbol{k})\times\frac{\partial}{\partial\boldsymbol{k}}\right]_i\delta_{\alpha\beta}+\mu_{ij}(\boldsymbol{k})\sigma_{j,\alpha\beta}. \tag{15}$$

The first term comes from the expansion of $\epsilon(\boldsymbol{K})$, with $\boldsymbol{v}(\boldsymbol{k})=(1/\hbar)\partial\epsilon(\boldsymbol{k})/\partial\boldsymbol{k}$ being the band velocity, while the second one is obtained by replacing $\boldsymbol{K}$ with $\boldsymbol{k}$ in μ_{ij}. As obvious from Eq. (14), $\boldsymbol{m}$ can be interpreted as the magnetic moment

operator of the band electrons, although one cannot say that the first and the second terms correspond to the orbital and the spin magnetic moments respectively, because both $\boldsymbol{v}(\boldsymbol{k})$ and $\mu_{ij}(\boldsymbol{k})$ include the effects of SO coupling. The solution of Eq. (13) can be written as $\overline{G}=\overline{G_0}-\boldsymbol{B}\overline{G_0}\boldsymbol{m}\overline{G_0}+O(B^2)$. Inserting expression (15) here and keeping only the corrections of the first order in $\boldsymbol{B}$, we have

$$\overline{G}_{\alpha\beta}(\boldsymbol{k},\omega_n)=\frac{\delta_{\alpha\beta}}{i\omega_n-\epsilon(\boldsymbol{k})}-B_i\mu_{ij}(\boldsymbol{k})\frac{\sigma_{j,\alpha\beta}}{[i\omega_n-\epsilon(\boldsymbol{k})]^2}. \quad (16)$$

Note that because of inversion symmetry, $\overline{G}_{\alpha\beta}(-\boldsymbol{k},\omega_n)=\overline{G}_{\alpha\beta}(\boldsymbol{k},\omega_n)$.

B. Crystals without inversion center

In the absence of inversion center in the crystal lattice, the electron bands are nondegenerate almost everywhere, except from some high-symmetry lines in the Brillouin zone. The formal reason for this is that without the inversion operation I, one cannot in general construct two orthogonal degenerate Bloch states at the same $\boldsymbol{k}$ (note that the Kramers theorem still holds: there is a degeneracy between the time reversed states $\psi_{\boldsymbol{k}\nu}$ and $K\psi_{\boldsymbol{k}\nu}$ belonging to $\boldsymbol{k}$ and $-\boldsymbol{k}$ respectively). The above is not valid at zero SO coupling. In that case, there is an additional symmetry in the system—the invariance with respect to arbitrary spin rotations, which leads to the bands being twofold degenerate because of spin, so that the results of the previous section apply.

Assuming that the SO coupling is strong and the bands are well split [which is the case in $CePt_3Si$ (Ref. 23)], the effective single-band Hamiltonian (5) can be written in the following form:

$$\mathcal{E}(\boldsymbol{k},\boldsymbol{B})=\epsilon(\boldsymbol{K})-\boldsymbol{B}\boldsymbol{\lambda}(\boldsymbol{K})+\ \ldots, \quad (17)$$

where the band dispersion $\epsilon(\boldsymbol{k})$ is invariant with respect to all point group operations, and $\boldsymbol{\lambda}(\boldsymbol{k})$ is a pseudovector, which, being a property of the crystal in zero field, satisfies the conditions $(g\boldsymbol{\lambda})(g^{-1}\boldsymbol{k})=\boldsymbol{\lambda}(\boldsymbol{k})$, where g is any operation from the point group. Because of the time-reversal symmetry, we also have $\epsilon(-\boldsymbol{k})=\epsilon(\boldsymbol{k})$ and $\boldsymbol{\lambda}(-\boldsymbol{k})=-\boldsymbol{\lambda}(\boldsymbol{k})$. At a nonzero $\boldsymbol{B}$ we have $\mathcal{E}(-\boldsymbol{k},-\boldsymbol{B})=\mathcal{E}(\boldsymbol{k},\boldsymbol{B})$, but $\mathcal{E}(-\boldsymbol{k},\boldsymbol{B})\neq\mathcal{E}(\boldsymbol{k},\boldsymbol{B})$ in general, because of the lack of inversion symmetry. An example of the microscopic calculation of $\boldsymbol{\lambda}(\boldsymbol{k})$ using a simple two-dimensional model is given at the end of this subsection. Also, in Sec. IV below, we discuss how to find the momentum dependence of $\boldsymbol{\lambda}$ in a noncentrosymmetric tetragonal crystal.

The only modification to the analysis of Sec. IIA is that both the effective Hamiltonian (5) and the Green's function (2) become scalar functions. The Green's function is factorized:

$$G(\boldsymbol{r}_1,\boldsymbol{r}_2;\omega_n)=\overline{G}(\boldsymbol{r}_1-\boldsymbol{r}_2,\omega_n)e^{i\varphi(\boldsymbol{r}_1,\boldsymbol{r}_2)}, \quad (18)$$

where the Fourier transform of $\overline{G}$ satisfies the equation

$$[i\omega_n-\overline{\mathcal{E}}(\boldsymbol{k},\boldsymbol{B})]\overline{G}(\boldsymbol{k},\omega_n)=1. \quad (19)$$

As in the centrosymmetric case, at low fields we solve this equation perturbatively in $\boldsymbol{B}$, using

$$\overline{\mathcal{E}}(\boldsymbol{k},\boldsymbol{B})=\epsilon(\boldsymbol{k})-\boldsymbol{B}\boldsymbol{m}(\boldsymbol{k})+O(B^2), \quad (20)$$

where

$$\boldsymbol{m}(\boldsymbol{k})=i\frac{e}{2c}\left[\boldsymbol{v}(\boldsymbol{k})\times\frac{\partial}{\partial\boldsymbol{k}}\right]+\boldsymbol{\lambda}(\boldsymbol{k}) \quad (21)$$

has the meaning of the magnetic moment operator of the band electrons. The contribution from the first term in $\boldsymbol{m}$ to $\overline{G}$ vanishes, and we finally have, in the first order in $\boldsymbol{B}$,

$$\overline{G}(\boldsymbol{k},\omega_n)=\frac{1}{i\omega_n-\epsilon(\boldsymbol{k})}-B_i\lambda_i(\boldsymbol{k})\frac{1}{[i\omega_n-\epsilon(\boldsymbol{k})]^2}. \quad (22)$$

Most of the previous works on noncentrosymmetric superconductors, both two-dimensional,[13,15,24] and three-dimensional,[25] have been based on the Rashba model (we would like to mention, in particular, Ref. 26, in which the GL functional was derived for a one-component s-wave order parameter in a Rashba superconductor). In this model, the combined effect of the SO coupling and the lack of inversion symmetry is mimicked by an additional term in the single-particle Hamiltonian:

$$H_0=\sum_{\boldsymbol{k}}\epsilon_0(\boldsymbol{k})a^\dagger_{\boldsymbol{k}\sigma}a_{\boldsymbol{k}\sigma}+\gamma\sum_{\boldsymbol{k}}\boldsymbol{n}\cdot(\boldsymbol{\sigma}_{\sigma\sigma'}\times\boldsymbol{k})a^\dagger_{\boldsymbol{k}\sigma}a_{\boldsymbol{k}\sigma'}. \quad (23)$$

Here $\sigma,\sigma'=\uparrow,\downarrow$ is the z-axis spin projection, the operator $a_{\boldsymbol{k}\sigma}$ destroys an electron in a Bloch state of energy $\epsilon_0(\boldsymbol{k})$ corresponding to zero SO coupling, and $\boldsymbol{n}$ is a unit vector allowed by symmetry (in a 2D system, $\boldsymbol{n}$ is simply the normal vector to the plane). Choosing $\boldsymbol{n}=\hat{z}$, we diagonalize the Hamiltonian (23) by a unitary transformation $a_{\boldsymbol{k}\sigma}=U_{\boldsymbol{k},\sigma n}c_{\boldsymbol{k}n}$ $(n=1,2)$, which gives two Rashba bands:

$$\epsilon_{1(2)}(\boldsymbol{k})=\epsilon_0(\boldsymbol{k})\pm|\gamma|k_\perp \quad (24)$$

$(k_\perp=\sqrt{k_x^2+k_y^2})$, with the eigenfunctions

$$\psi_{\boldsymbol{k},1(2)}(r)=\frac{1}{\sqrt{2}}\begin{pmatrix}1\\ \mp ie^{i\varphi_{\boldsymbol{k}}}\end{pmatrix}e^{i\boldsymbol{k}\boldsymbol{r}}, \quad (25)$$

where $\tan\varphi_{\boldsymbol{k}}=k_y/k_x$. The bands (24) are nondegenerate almost everywhere, touching only at the two poles of the Fermi surface along the z axis. We would like to emphasize that the band indices $n=1,2$ cannot be interpreted as the pseudospin projections. Indeed, under time reversal the pseudospin eigenstates would transform similar to the spin eigenstates, i.e., into one another. However, being a symmetry of the Hamiltonian time reversal transforms the Rashba bands into themselves, which can be directly verified for the eigenstates (25),

$$K\psi_{\mathbf{k},1} = (i\sigma_2)K_0\psi_{\mathbf{k},1} = \frac{ie^{-i\varphi_{\mathbf{k}}}}{\sqrt{2}}\begin{pmatrix} 1 \\ ie^{i\varphi_{\mathbf{k}}} \end{pmatrix} e^{-i\mathbf{kr}}$$

$$= \frac{ie^{-i\varphi_{\mathbf{k}}}}{\sqrt{2}}\begin{pmatrix} 1 \\ -ie^{i\varphi_{-\mathbf{k}}} \end{pmatrix} e^{-i\mathbf{kr}} \propto \psi_{-\mathbf{k},1},$$

and similarly for $\psi_{\mathbf{k},2}$ (we used $\varphi_{-\mathbf{k}} = \varphi_{\mathbf{k}} + \pi$).

It is easy to show that in the presence of a nonzero magnetic field the effective Hamiltonian for the Rashba model can be cast in the form (17). To obtain the pseudovector $\boldsymbol{\lambda}(\boldsymbol{k})$, let us consider a two-dimensional system in a field parallel to the xy plane. Then the Hamiltonian (23) is modified by the Zeeman term: $H_B = H_0 - \mu_B \boldsymbol{\sigma B}$. The diagonalization of H_B, followed by an expansion in powers of B, gives

$$\mathcal{E}_{1(2)}(\boldsymbol{k},\boldsymbol{B}) = \epsilon_0(\boldsymbol{k}) \pm \sqrt{\gamma^2 k_\perp^2 + 2\gamma\mu_B(\boldsymbol{k}\times\boldsymbol{B})_x + \mu_B^2 B^2}$$

$$\simeq \epsilon_{1(2)}(\boldsymbol{k}) - \boldsymbol{\lambda}_{1(2)}(\boldsymbol{k})\boldsymbol{B},$$

where

$$\boldsymbol{\lambda}_{1(2)}(\boldsymbol{k}) = \pm\mu_B \frac{\boldsymbol{k}\times\boldsymbol{n}}{k_\perp}. \tag{26}$$

In this article, we want to keep our discussion as general as possible and therefore do not resort to any explicit model, such as the Rashba model, to describe the SO coupling. Our results are based only on the symmetry considerations and valid for an arbitrary strength of the SO coupling and any band structure.

III. MAGNETIC RESPONSE IN THE SUPERCONDUCTING STATE

A. Crystals with inversion center

Now let us take into account the attractive interaction between the band electrons in the Cooper channel. The total Hamiltonian is given by $H = H_0 + H_{\text{int}}$, where the free electron Hamiltonian H_0 is given by Eq. (4) and, for a BCS-type mechanism of pairing, the interaction part can be written as

$$H_{\text{int}} = \frac{1}{2}\sum_{\mathbf{k},\mathbf{k}',\mathbf{q}} V_{\alpha\beta,\gamma\delta}(\mathbf{k},\mathbf{k}')c^\dagger_{\mathbf{k}+\mathbf{q}/2,\alpha}c^\dagger_{-\mathbf{k}+\mathbf{q}/2,\beta}c_{-\mathbf{k}'+\mathbf{q}/2,\gamma}c_{\mathbf{k}'+\mathbf{q}/2,\delta}. \tag{27}$$

The pairing potential does not depend on the external magnetic field and is assumed to have a factorized form:

$$V_{\alpha\beta,\gamma\delta}(\mathbf{k},\mathbf{k}') = -\frac{1}{2}V\sum_{a=1}^{d}\Psi_{a,\alpha\beta}(\mathbf{k})\Psi^\dagger_{a,\gamma\delta}(\mathbf{k}'), \tag{28}$$

with the coupling constant $V>0$. Here $\Psi_a(\mathbf{k})$ are the 2×2 matrix basis functions of an irreducible representation Γ of dimensionality d of the symmetry group of the system at zero magnetic field.[4] The pairing interaction is nonzero only inside a thin shell of width ϵ_c (the cutoff energy) in the vicinity of the Fermi surface $\epsilon(\mathbf{k})=0$, i.e., $\Psi_a(\mathbf{k}) = \Psi_a(\mathbf{k}_F)f_c[\epsilon(\mathbf{k})]$, where $\mathbf{k}_F$ is a wave vector at the Fermi surface and the cutoff function $f_c(\epsilon)$ is localized about the origin, e.g., $f_c(\epsilon) = \theta(\epsilon_c - |\epsilon|)$. The basis functions are assumed to be orthonormal:

$$\frac{1}{2}\langle \mathrm{tr}[\Psi^\dagger_a(\mathbf{k})\Psi_b(\mathbf{k})]\rangle_\epsilon = \frac{1}{2}\langle \mathrm{tr}[\Psi^\dagger_a(\mathbf{k})\Psi_b(\mathbf{k})]\rangle_0 f_c^2(\epsilon) = \delta_{ab}f_c^2(\epsilon), \tag{29}$$

where the angular brackets denote the averaging over the constant energy surface $\epsilon(\mathbf{k}) = \epsilon$:

$$\langle(\cdots)\rangle_\epsilon = \frac{1}{N_0(\epsilon)}\sum_{\mathbf{k}}(\ldots)\delta[\epsilon - \epsilon(\mathbf{k})], \tag{30}$$

and $N_0(\epsilon) = \Sigma_{\mathbf{k}}\delta[\epsilon - \epsilon(\mathbf{k})]$ is the normal-metal density of states (DoS) per one pseudospin projection.

It follows from anticommutation of the fermionic operators that $\Psi_{a,\beta\alpha}(-\mathbf{k}) = -\Psi_{a,\alpha\beta}(\mathbf{k})$. In the presence of inversion symmetry, the even in $\mathbf{k}$ (pseudospin-singlet) and odd in $\mathbf{k}$ (pseudospin-triplet) pairing states can be considered separately. In the singlet case, the matrix basis functions can be represented in the form

$$\Psi_{a,\alpha\beta}(\mathbf{k}) = (i\sigma_2)_{\alpha\beta}\phi_a(\mathbf{k}), \tag{31}$$

where $\phi_a(\mathbf{k})$ are the even scalar basis functions of the Γ representation. In the triplet case, we have

$$\Psi_{a,\alpha\beta}(\mathbf{k}) = (i\sigma_i\sigma_2)_{\alpha\beta}\phi_{a,i}(\mathbf{k}), \tag{32}$$

where $\boldsymbol{\phi}_a(\mathbf{k})$ are the odd vector basis functions of the Γ representation.[1,4]

The superconducting order parameter can be represented as a linear combination of the basis functions:

$$\Delta_{\alpha\beta}(\mathbf{k},\mathbf{q}) = \sum_a \eta_a(\mathbf{q})\Psi_{a,\alpha\beta}(\mathbf{k}), \tag{33}$$

with the coefficients η_a playing the role of the order parameter components, which determine, for instance, the free energy $\mathcal{F}$ of the superconductor. In the vicinity of the critical temperature $T_c(\boldsymbol{B})$, one can keep only the quadratic terms in the expansion of $\mathcal{F}$:

$$\mathcal{F} = \sum_{ab}\int dr\ \eta^*_a(\boldsymbol{r})S_{ab}\eta_b(\boldsymbol{r}). \tag{34}$$

Here S is a $d\times d$ matrix differential operator of infinite order:

$$S_{ab} = \frac{1}{V}\delta_{ab} - \int d\boldsymbol{R}\overline{S}_{ab}(\boldsymbol{R})e^{-i\boldsymbol{RD}}, \tag{35}$$

where $\boldsymbol{D} = -i\nabla_{\boldsymbol{r}} + (2e/\hbar c)\boldsymbol{A}$, and the translationally-invariant function $\overline{S}_{ab}(\boldsymbol{R})$ is expressed in terms of the Green's functions (12). Its Fourier transform is given by

$$\overline{S}_{ab}(\boldsymbol{q}) = T\sum_n\sum_{\mathbf{k}}\Lambda^{ab}_{\alpha\beta\gamma\delta}(\boldsymbol{k})\overline{G}_{\beta\gamma}\left(\boldsymbol{k}+\frac{\boldsymbol{q}}{2},\omega_n\right)$$

$$\times\overline{G}_{\alpha\delta}\left(-\boldsymbol{k}+\frac{\boldsymbol{q}}{2},-\omega_n\right),$$

$$\Lambda^{ab}_{\alpha\beta\gamma\delta}(\boldsymbol{k}) = \frac{1}{2}\ \exp\left[i\frac{e}{4\hbar c}\boldsymbol{B}\left(\frac{\partial}{\partial \boldsymbol{k}_1}\times\frac{\partial}{\partial \boldsymbol{k}_2}\right)\right] \times \Psi^{\dagger}_{a,\alpha\beta}(\boldsymbol{k}_1)\Psi_{b,\gamma\delta}(\boldsymbol{k}_2)\Big|_{\boldsymbol{k}_1=\boldsymbol{k}_2=\boldsymbol{k}}$$
$$= \frac{1}{2}\Psi^{\dagger}_{a,\alpha\beta}(\boldsymbol{k})\Psi_{b,\gamma\delta}(\boldsymbol{k}) + i\frac{e}{8\hbar c}\boldsymbol{B}(\nabla_{\boldsymbol{k}}\Psi^{\dagger}_{a,\alpha\beta}\times\nabla_{\boldsymbol{k}}\Psi_{b,\gamma\delta}) + O(B^2). \tag{36}$$

The derivation of these formulas is outlined in Appendix A. As obvious from Eq. (35), the operator S is a completely symmetrized function of the components of $\boldsymbol{D}$, which do not commute: $[D_i, D_j] = -i(2e/\hbar c)e_{ijk}B_k$. Also, its Taylor expansion contains only even powers of $\boldsymbol{D}$, because $\overline{S_{ab}}(-\boldsymbol{R}) = \overline{S_{ab}}(\boldsymbol{R})$ due to the inversion symmetry.

The field dependence of the phase transition temperature at arbitrary $\boldsymbol{B}$ can be found from Eq. (34): $T_c(\boldsymbol{B})$ is defined as the temperature at which the minimum eigenvalue of the operator S passes through zero. For an isotropic s-wave order parameter, the corresponding equations were derived and solved in Ref. 27, while for an isotropic p-wave case it was done in Ref. 28. In a general case, i.e., for an arbitrary band structure and pairing symmetry, $T_c(\boldsymbol{B})$ can only be calculated numerically.

Here we focus on the properties of our superconductor in the weak field limit. We have $\mathcal{F} = \int F d\boldsymbol{r}$, where the free energy density can be represented as

$$F = A_{ab}\eta^*_a\eta_a + K_{ab,ij}\eta^*_a D_i D_j \eta_b - \boldsymbol{M}\boldsymbol{B}. \tag{37}$$

This expression has the usual form expected on the phenomenological grounds, with $K_{ab,ij}$ being the generalized effective mass tensor, and $\boldsymbol{M}$ having the meaning of the intrinsic magnetic moment of the Cooper pairs. The linearized GL equations follow from Eq. (37) after the minimization over the order parameter: $\delta\mathcal{F}/\delta\eta^*_a(\boldsymbol{r}) = 0$. Below we outline how to calculate the free energy density using our weak-coupling model.

The first term in F is obtained by putting $\boldsymbol{q} = \boldsymbol{B} = 0$ in Eqs. (35) and (36), which gives

$$A_{ab} = \frac{1}{V}\delta_{ab} - \frac{1}{2}\sum_{\boldsymbol{k}} \mathrm{tr}[\Psi^{\dagger}_a(\boldsymbol{k})\Psi_b(\boldsymbol{k})]\mathcal{S}[\epsilon(\boldsymbol{k})], \tag{38}$$

and

$$\mathcal{S}(\epsilon) = T\sum_n \frac{1}{\omega_n^2 + \epsilon^2} = \frac{1}{2\epsilon}\tanh\frac{\epsilon}{2T}.$$

The necessary momentum cutoff in Eq. (38) is provided by the basis functions $\Psi_a(\boldsymbol{k})$, which are restricted to the vicinity of the Fermi surface. Calculating the momentum integral with the help of the normalization condition (29), we obtain $A_{ab} = [(1/V) - I]\delta_{ab}$, where

$$I(T) = \int d\epsilon N_0(\epsilon) f_c^2(\epsilon) S(\epsilon) \simeq N_F \ln\frac{2e^C\epsilon_c}{\pi T} \tag{39}$$

($C \simeq 0.577$ is Euler's constant). To obtain this result we made the usual assumption that $N_0(\epsilon)$ is a slowly-varying function within the energy shell of width ϵ_c near the Fermi surface, which allows us to replace it by a constant—the DoS at the Fermi level $N_F = N_0(0)$. At the zero-field critical temperature T_c, we have $I(T_c) = 1/V$, which gives the standard BCS result: $T_c \simeq 1.13\epsilon_c \exp(-1/N_F V)$. Expanding A_{ab} in the vicinity of T_c, we recover the familiar expression for the uniform term in the free energy density,

$$A_{ab} = \alpha(T - T_c)\delta_{ab}, \tag{40}$$

where $\alpha = N_F/T_c$.

Next, we calculate the intrinsic magnetic moment $\boldsymbol{M}$. Using the small-$\boldsymbol{B}$ expansions of the normal-state Green's function $\overline{G}$ and the vertex Λ, we obtain in the singlet case,

$$M_i = \frac{ie}{4\hbar c}\eta^*_a\eta_b\langle(\nabla_{\boldsymbol{k}}\phi^*_a \times \nabla_{\boldsymbol{k}}\phi_b)_i\rangle_0 I,$$

where $\langle(\cdots)\rangle_0$ stands for the Fermi-surface averaging (30), and I is defined by Eq. (39). To derive this expression, we again used the fact that the basis functions are nonzero only in a narrow vicinity of the Fermi surface, which allows one to separate the energy integration from the integration over the Fermi surface. A similar calculation in the triplet case gives

$$M_i = \frac{ie}{4\hbar c}\eta^*_a\eta_b\langle(\nabla_{\boldsymbol{k}}\boldsymbol{\phi}^*_a \times \nabla_{\boldsymbol{k}}\boldsymbol{\phi}_b)_i\rangle_0 I + 2i\eta^*_a\eta_b\langle\mu_{ij}(\boldsymbol{k})(\boldsymbol{\phi}^*_a \times \boldsymbol{\phi}_b)_j\rangle_0 I_1,$$

where

$$I_1(T) = \int d\epsilon\ N_0(\epsilon) f_c^2(\epsilon)\mathcal{S}_1(\epsilon) \simeq -\frac{N_F'}{2}\ln\frac{2e^C\epsilon_c}{\pi T},$$

$$\mathcal{S}_1(\epsilon) = T\sum_n \frac{1}{(i\omega_n - \epsilon)^2}\frac{1}{-i\omega_n - \epsilon} = \frac{1}{2}\frac{\partial\mathcal{S}(\epsilon)}{\partial\epsilon}. \tag{41}$$

Here $N_F' = N_0'(0)$ is a measure of the electron-hole asymmetry near the Fermi surface. Putting $T = T_c$, using the BCS result for the critical temperature, and choosing real basis functions (which can always be done if the normal state is nonmagnetic) we finally obtain the density of the intrinsic magnetic moment of the Cooper pairs:

$$\boldsymbol{M} = i\gamma_{ab}\eta^*_a\eta_b, \tag{42}$$

where $\gamma_{ab} = -\gamma_{ba}$ is given by

$$\gamma_{i,ab} = \frac{e}{4\hbar c}\frac{1}{V}e_{ijl}\left\langle\frac{\partial\phi_a(\boldsymbol{k})}{\partial k_j}\frac{\partial\phi_b(\boldsymbol{k})}{\partial k_l}\right\rangle_0 \tag{43}$$

in the singlet case, and

$$\gamma_{i,ab} = \frac{e}{4\hbar c}\frac{1}{V}e_{ijl}\left\langle\frac{\partial\phi_{a,m}(\boldsymbol{k})}{\partial k_j}\frac{\partial\phi_{b,m}(\boldsymbol{k})}{\partial k_l}\right\rangle_0$$

$$-\frac{N_F'}{N_F}\frac{1}{V}e_{jkl}\langle\mu_{ij}(\boldsymbol{k})\phi_{a,k}(\boldsymbol{k})\phi_{b,l}(\boldsymbol{k})\rangle_0 \tag{44}$$

in the triplet case. It follows from these expressions that $\boldsymbol{M}=0$ for any order parameter corresponding to a one-dimensional representation of the point group, both in the singlet and triplet cases.

Finally, let us evaluate the gradient terms in Eq. (37). The magnetic field dependence of the coefficients $K_{ab,ij}$ can be neglected, which follows from the fact that the lowest eigenvalue of the operator $K_{ab,ij}D_iD_j$ is already linear in $|\boldsymbol{B}|$, see Appendix B. The physical meaning of this is simple: the suppression of the critical temperature due to the gradient energy is always linear in a weak field, regardless of the dimensionality of the order parameter and the shape of the Fermi surface. Taking the second order derivative in Eq. (36) at $\boldsymbol{B}=0$ and calculating the Matsubara sums, we obtain

$$K_{ab,ij}=-\frac{1}{4}\hbar^2\langle\mathrm{tr}[\Psi_a^\dagger(\boldsymbol{k})\Psi_b(\boldsymbol{k})]v_i(\boldsymbol{k})v_j(\boldsymbol{k})\rangle_0 I_2$$

$$-\frac{1}{8}\hbar^2\langle\mathrm{tr}[\Psi_a^\dagger(\boldsymbol{k})\Psi_b(\boldsymbol{k})]m_{ij}^{-1}(\boldsymbol{k})\rangle_0 I_1.$$

Here $m_{ij}^{-1}(\boldsymbol{k})=(1/\hbar^2)\partial^2\epsilon(\boldsymbol{k})/\partial k_j\partial k_j$ is the inverse tensor of effective masses, I_1 is defined by Eq. (41), and

$$I_2(T)=\int d\epsilon N_0(\epsilon)f_c^2(\epsilon)\mathcal{S}_2(\epsilon)\simeq-\frac{7\zeta(3)}{8\pi^2T^2}N_F, \tag{45}$$

where

$$\mathcal{S}_2(\epsilon)=T\sum_n\left[\frac{1}{(i\omega_n-\epsilon)^3}\frac{1}{-i\omega_n-\epsilon}-\frac{1}{2}\frac{1}{(i\omega_n-\epsilon)^2}\frac{1}{(-i\omega_n-\epsilon)^2}\right]$$

$$=-\frac{1}{16T^2\epsilon}\sinh\left(\frac{\epsilon}{2T}\right)\cosh^{-3}\left(\frac{\epsilon}{2T}\right)$$

has a peak near $\epsilon=0$, and $\zeta(s)$ is Riemann's zeta-function.

Putting all the pieces together, replacing T with T_c, and using real basis functions, we finally have

$$K_{ab,ij}=\frac{7\zeta(3)\hbar^2}{16\pi^2T_c^2}N_F\langle\phi_a(\boldsymbol{k})\phi_b(\boldsymbol{k})v_i(\boldsymbol{k})v_j(\boldsymbol{k})\rangle_0$$

$$+\frac{\hbar^2}{8V}\frac{N_F'}{N_F}\langle\phi_a(\boldsymbol{k})\phi_b(\boldsymbol{k})m_{ij}^{-1}(\boldsymbol{k})\rangle_0 \tag{46}$$

in the singlet case, and

$$K_{ab,ij}=\frac{7\zeta(3)\hbar^2}{16\pi^2T_c^2}N_F\langle\phi_{a,l}(\boldsymbol{k})\phi_{b,l}(\boldsymbol{k})v_i(\boldsymbol{k})v_j(\boldsymbol{k})\rangle_0$$

$$+\frac{\hbar^2}{8V}\frac{N_F'}{N_F}\langle\phi_{a,l}(\boldsymbol{k})\phi_{b,l}(\boldsymbol{k})m_{ij}^{-1}(\boldsymbol{k})\rangle_0 \tag{47}$$

in the triplet case. Assuming a spherical Fermi surface, a completely isotropic pairing corresponding to the unity representation of G, and neglecting the electron-hole asymmetry, Eq. (46) yields $K_{ij}=\delta_{ij}[7\zeta(3)\hbar^2/48\pi^2T_c^2]N_Fv_F^2$.[22] For an anisotropic Fermi surface, but still a conventional pairing, the results of Ref. 29 are recovered.

Now we would like to make a few comments about our results. The internal magnetism of superconductors has been discussed before mostly for a charged isotropic Fermi liquid without SO coupling, see, e.g., Ref. 30. In this case, the density of the pair magnetic moment can be divided into the orbital and spin parts, both being small due to the smallness of both the quasiclassical parameter $(k_F\xi_0)^2\ll1$ (ξ_0 is the coherence length), and the electron-hole asymmetry N_F'.[4] Here we do not make any assumptions about the strength of the SO coupling, therefore the orbital and the spin magnetic moments cannot be separated, in general. For a general band dispersion, one can neglect neither of these contributions *a priori*, before calculating the Fermi-surface averages in Eqs. (43) and (44). In particular, the energy dependence of the single-electron DoS in the metals with *d*- and *f*-electrons is usually quite significant, which can lead to an appreciable electron-hole asymmetry near the Fermi level.

In terms of the response of the superconductor on a weak external field, the gradient terms produce a linear in $\boldsymbol{B}$ suppression of T_c, see Appendix B. The value of the slope dH_{c2}/dT can be calculated either analytically (in very few cases), or using a variational approach. On the other hand, the pair magnetism can compete with the gradient energy, leading even to the possibility of increasing T_c as a function of $\boldsymbol{B}$, if the internal magnetic moment is large enough. Such mechanism was recently proposed in Ref. 31 to explain the phase diagram of the ferromagnetic superconductor $ZrZn_2$.

B. Crystals without inversion center

In this case, the calculations are somewhat simpler because the bands are nondegenerate. We assume that the Cooper pairing occurs only between the electrons in the states with opposite momenta, which are transformed into each other by time reversal. Then the most general BCS-type Hamiltonian can be written in the form

$$H_{\mathrm{int}}=H_{\mathrm{int}}^{(1)}+H_{\mathrm{int}}^{(2)}+H_{\mathrm{int}}^{(3)}, \tag{48}$$

where

$$H_{\mathrm{int}}^{(1)}=\frac{1}{2}\sum_n\sum_{\boldsymbol{k},\boldsymbol{k}'}V_n^{(1)}(\boldsymbol{k},\boldsymbol{k}')c_{\boldsymbol{k}n}^\dagger c_{-\boldsymbol{k}n}^\dagger c_{-\boldsymbol{k}'n}c_{\boldsymbol{k}'n},$$

$$H_{\mathrm{int}}^{(2)}=\frac{1}{2}\sum_{n\neq m}\sum_{\boldsymbol{k},\boldsymbol{k}'}V_{nm}^{(2)}(\boldsymbol{k},\boldsymbol{k}')c_{\boldsymbol{k}n}^\dagger c_{-\boldsymbol{k}n}^\dagger c_{-\boldsymbol{k}'m}c_{\boldsymbol{k}'m},$$

$$H_{\mathrm{int}}^{(3)}=\frac{1}{2}\sum_{n\neq m}\sum_{\boldsymbol{k},\boldsymbol{k}'}V_{nm}^{(3)}(\boldsymbol{k},\boldsymbol{k}')c_{\boldsymbol{k}n}^\dagger c_{-\boldsymbol{k}m}^\dagger c_{-\boldsymbol{k}'m}c_{\boldsymbol{k}'n}.$$

Here n and m label the nondegenerate single-electron bands, e.g., the Rashba bands (24). The Hamiltonian $H_{\mathrm{int}}^{(1)}$ describes the intraband pairing, $H_{\mathrm{int}}^{(2)}$ describes the pair scattering between the bands, which can result in the superconducting gaps induced on more than one sheet of the Fermi surface, and $H_{\mathrm{int}}^{(3)}$ corresponds to the pairing of electrons from different bands.

A considerable simplification occurs if the superconducting gaps are much smaller than the interband energies. For example, the band structure calculations of Ref. 23 show that the SO band splitting in $CePt_3Si$ exceeds the superconducting gap by orders of magnitude. In this situation, the formation of interband pairs described by $H_{\rm int}^{(3)}$ is strongly suppressed for the same reasons as for the paramagnetically limited singlet superconductors:[32] the interband splitting cuts off the logarithmic singularity in the Cooper channel, thus reducing the critical temperature. Although the bands may touch at some isolated points at the Fermi surface, as is the case for the Rashba bands (24) at $\boldsymbol{k}\|\hat{z}$, the interband pairing in the vicinity of those points is still suppressed due to the phase space limitations. We also neglect the possibility of the Cooper pairs having a nonzero momentum (Larkin-Ovchinnikov-Fulde-Ferrell phase),[33] which is expected to be suppressed as well by the large depairing effect of the SO band splitting.

In this paper, we further neglect the interband pair scattering process described by $H_{\rm int}^{(2)}$, leaving the investigation of its effects for future work. Thus, we focus on a single nondegenerate band for which the pairing between time-reversed states $|\boldsymbol{k}\rangle$ and $K|\boldsymbol{k}\rangle\sim|-\boldsymbol{k}\rangle$ near the Fermi surface can be written as

$$H_{\rm int}=\frac{1}{2}\sum_{\boldsymbol{k},\boldsymbol{k}'}\tilde{V}(\boldsymbol{k},\boldsymbol{k}')c_{\boldsymbol{k}}^{\dagger}c_{K\boldsymbol{k}}^{\dagger}c_{K\boldsymbol{k}'}c_{\boldsymbol{k}'}, \tag{49}$$

where $c_{K\boldsymbol{k}}^{\dagger}$ denotes the creation operator of an electron in the state $K|\boldsymbol{k}\rangle$, and the pairing potential is assumed to have a factorized form

$$\tilde{V}(\boldsymbol{k},\boldsymbol{k}')=-V\sum_{a=1}^{d}\phi_a(\boldsymbol{k})\phi_a^*(\boldsymbol{k}') \tag{50}$$

with $V>0$. Here $\phi_a(\boldsymbol{k})$ are the scalar basis functions of an irreducible representation Γ of the point group of the crystal in the absence of magnetic field, which are nonzero only inside the energy shell of width ϵ_c near the Fermi surface $\phi_a(\boldsymbol{k})=\phi_a(\boldsymbol{k}_F)f_c[\epsilon(\boldsymbol{k})]$, and orthonormal

$$\langle\phi_a^*(\boldsymbol{k})\phi_b(\boldsymbol{k})\rangle_{\epsilon}=\langle\phi_a^*(\boldsymbol{k})\phi_b(\boldsymbol{k})\rangle_0 f_c^2(\epsilon)=\delta_{ab}f_c^2(\epsilon). \tag{51}$$

The parity of the basis functions can be determined using the following arguments.[34] Although the time-reversed state $K|\boldsymbol{k}\rangle$ belongs to the wave vector $-\boldsymbol{k}$, it is not the same as $|-\boldsymbol{k}\rangle$. In fact, $K|\boldsymbol{k}\rangle=t(\boldsymbol{k})|-\boldsymbol{k}\rangle$, where $t(\boldsymbol{k})$ is a nontrivial phase factor, which satisfies $t(-\boldsymbol{k})=-t(\boldsymbol{k})$. This allows us to write $c_{K\boldsymbol{k}}^{\dagger}=t(\boldsymbol{k})c_{-\boldsymbol{k}}^{\dagger}$ and $c_{K\boldsymbol{k}}=t^*(\boldsymbol{k})c_{-\boldsymbol{k}}$. Inserting these relations in Eq. (49), we have

$$H_{\rm int}=\frac{1}{2}\sum_{\boldsymbol{k},\boldsymbol{k}'}V(\boldsymbol{k},\boldsymbol{k}')c_{\boldsymbol{k}}^{\dagger}c_{-\boldsymbol{k}}^{\dagger}c_{-\boldsymbol{k}'}c_{\boldsymbol{k}'}, \tag{52}$$

where $V(\boldsymbol{k},\boldsymbol{k}')=t(\boldsymbol{k})t^*(\boldsymbol{k}')\tilde{V}(\boldsymbol{k},\boldsymbol{k}')$. From the anticommutation of fermionic operators it follows that $\tilde{V}(\boldsymbol{k},\boldsymbol{k}')$ has to be an even function of both arguments, i.e., one should choose even basis functions $\phi_a(\boldsymbol{k})$ in the expansion (50). Treating the interaction (52) in the mean-field approximation, one obtains the order parameter $\Delta(\boldsymbol{k})=t(\boldsymbol{k})\Sigma_a\eta_a\phi_a(\boldsymbol{k})$, which is odd in $\boldsymbol{k}$. In Ref. 23, the nodal structure of $\Delta(\boldsymbol{k})$ was analyzed in terms of the odd basis functions. This has been corrected in Ref. 34, where the the importance of the phase factor $t(\boldsymbol{k})$ was recognized.

Allowing for the possibility of a non-uniform superconducting order parameter, the Hamiltonian (52) becomes

$$H_{\rm int}=\frac{1}{2}\sum_{\boldsymbol{k},\boldsymbol{k}',\boldsymbol{q}}V(\boldsymbol{k},\boldsymbol{k}')c_{\boldsymbol{k}+\boldsymbol{q}/2}^{\dagger}c_{-\boldsymbol{k}+\boldsymbol{q}/2}^{\dagger}c_{-\boldsymbol{k}'+\boldsymbol{q}/2}c_{\boldsymbol{k}'+\boldsymbol{q}/2}. \tag{53}$$

The order parameter can be represented as

$$\Delta(\boldsymbol{k},\boldsymbol{q})=\sum_a\eta_a(\boldsymbol{q})\Psi_a(\boldsymbol{k}), \tag{54}$$

where $\Psi_a(\boldsymbol{k})=t(\boldsymbol{k})\phi_a(\boldsymbol{k})=-\Psi_a(-\boldsymbol{k})$ satisfy the orthonormality condition $\langle\Psi_a^*(\boldsymbol{k})\Psi_b(\boldsymbol{k})\rangle_{\epsilon}=\delta_{ab}f_c^2(\epsilon)$, see Eq. (51).

The contribution to the free energy quadratic in the order parameter has the form (34) with the kernel now given by

$$S_{ab}=\frac{1}{2V}\delta_{ab}-\frac{1}{2}\int d\boldsymbol{R}\overline{S}_{ab}(\boldsymbol{R})e^{-i\boldsymbol{R}\boldsymbol{D}}, \tag{55}$$

where $S_{ab}(\boldsymbol{R})$ is the Fourier transform of

$$\overline{S}_{ab}(\boldsymbol{q})=T\sum_n\sum_{\boldsymbol{k}}\Lambda_{ab}(\boldsymbol{k})\overline{G}\left(\boldsymbol{k}+\frac{\boldsymbol{q}}{2},\omega_n\right)\overline{G}\left(-\boldsymbol{k}+\frac{\boldsymbol{q}}{2},-\omega_n\right),$$

$$\Lambda_{ab}(\boldsymbol{k})=\exp\left[i\frac{e}{4\hbar c}\boldsymbol{B}\left(\frac{\partial}{\partial\boldsymbol{k}_1}\times\frac{\partial}{\partial\boldsymbol{k}_2}\right)\right]\Psi_a^*(\boldsymbol{k}_1)\Psi_b(\boldsymbol{k}_2)\Big|_{\boldsymbol{k}_1=\boldsymbol{k}_2=\boldsymbol{k}}$$

$$=\Psi_a^*(\boldsymbol{k})\Psi_b(\boldsymbol{k})+i\frac{e}{4\hbar c}\boldsymbol{B}(\nabla_{\boldsymbol{k}}\Psi_a^*\times\nabla_{\boldsymbol{k}}\Psi_b)+O(B^2). \tag{56}$$

The derivation is similar to the centrosymmetric case, see Appendix A.

An important difference from the previous case is that, although the functions $\Psi_a(\boldsymbol{k})$ still have a definite parity, the Green's functions (22) do not: $\overline{G}(-\boldsymbol{k},\omega_n)\neq\overline{G}(\boldsymbol{k},\omega_n)$ in general, therefore $\overline{S}_{ab}(-\boldsymbol{R})\neq\overline{S}_{ab}(\boldsymbol{R})$. This means that the expansion of the free energy density now contains gradient terms of an odd degree in $\boldsymbol{D}$:

$$F=f_{ab}^{(0)}\eta_a^*\eta_b+f_{ab,i}^{(1)}\eta_a^*D_i\eta_b+f_{ab,ij}^{(2)}\eta_a^*D_iD_j\eta_b+\cdots, \tag{57}$$

where

$$f_{ab}^{(0)}=\frac{1}{2V}\delta_{ab}-\overline{S}_{ab}(\boldsymbol{q}=0),$$

$$f_{ab,i}^{(1)}=-\left.\frac{\partial\overline{S}_{ab}(\boldsymbol{q})}{\partial q_i}\right|_{\boldsymbol{q}=0},\quad f_{ab,ij}^{(2)}=-\frac{1}{2}\left.\frac{\partial^2\overline{S}_{ab}(\boldsymbol{q})}{\partial q_i\partial q_j}\right|_{\boldsymbol{q}=0},$$

etc.

Using Eq. (22), it is easy to see that $f_{ab,i}^{(1)}=0$ at $\boldsymbol{B}=0$.

Keeping only the lowest order terms in the free energy density expansion in a weak field, we have

$$F = A_{ab}\eta_a^*\eta_b + K_{ab,ij}\eta_a^* D_i D_j \eta_b - \boldsymbol{MB} + \tilde{K}_{ab,ij} B_i \eta_a^* D_j \eta_b, \tag{58}$$

where $\tilde{K}_{ab,ij} = \partial f^{(1)}_{ab,j}/\partial B_i|_{T=T_c,B=0}$. The uniform contribution to F can be calculated in the same fashion as in the previous section, and we obtain

$$A_{ab} = \alpha(T - T_c)\delta_{ab}, \tag{59}$$

where the critical temperature T_c is given by the same BCS expression as in the centrosymmetric case, but now $\alpha = N_F/2T_c$.

The pair magnetic moment $\boldsymbol{M}$ and the generalized effective mass tensor $K_{ab,ij}$ can be calculated similarly to the centrosymmetric case. Using real basis functions $\phi_a(\boldsymbol{k})$, we obtain

$$\boldsymbol{M} = i\frac{e}{8\hbar c}\frac{1}{V}e_{ijl}\left\langle \frac{\partial \Psi_a^*(\boldsymbol{k})}{\partial k_j}\frac{\partial \Psi_b(\boldsymbol{k})}{\partial k_l}\right\rangle_0 \eta_a^*\eta_b, \tag{60}$$

and

$$K_{ab,ij} = \frac{7\zeta(3)\hbar^2}{32\pi^2 T_c^2} N_F \langle \phi_a(\boldsymbol{k})\phi_b(\boldsymbol{k}) v_i(\boldsymbol{k}) v_j(\boldsymbol{k})\rangle_0 + \frac{\hbar^2}{16V}\frac{N_F'}{N_F}\langle \phi_a(\boldsymbol{k})\phi_b(\boldsymbol{k}) m_{ij}^{-1}(\boldsymbol{k})\rangle_0. \tag{61}$$

To calculate the coefficient $\tilde{K}_{ab,ij}$, we expand $\overline{S_{ab}}(\boldsymbol{q})$ to the first order in both $\boldsymbol{B}$ and $\boldsymbol{q}$ and evaluate the Matsubara sums, which gives

$$\tilde{K}_{ab,ij} = \hbar\langle \phi_a^*(\boldsymbol{k})\phi_b(\boldsymbol{k})\lambda_i(\boldsymbol{k}) v_j(\boldsymbol{k})\rangle_0 I_2 + \frac{1}{2}\left\langle \phi_a^*(\boldsymbol{k})\phi_b(\boldsymbol{k})\frac{\partial \lambda_i(\boldsymbol{k})}{\partial k_j}\right\rangle_0 I_1,$$

where $\boldsymbol{\lambda}(\boldsymbol{k})$ is the momentum-dependent pseudovector that determines the linear response of the band electrons on a weak magnetic field, see Eq. (17), and $I_{1,2}$ are defined by Eqs. (41) and (45), respectively. Using real basis functions, we finally have

$$\tilde{K}_{ab,ij} = -\frac{7\zeta(3)\hbar}{8\pi^2 T_c^2} N_F \langle \phi_a(\boldsymbol{k})\phi_b(\boldsymbol{k})\lambda_i(\boldsymbol{k}) v_j(\boldsymbol{k})\rangle_0 - \frac{1}{4V}\frac{N_F'}{N_F}\left\langle \phi_a(\boldsymbol{k})\phi_b(\boldsymbol{k})\frac{\partial \lambda_i(\boldsymbol{k})}{\partial k_j}\right\rangle_0. \tag{62}$$

Note that the phase factors $t(\boldsymbol{k})$ have dropped out of both $K_{ab,ij}$ and $\tilde{K}_{ab,ij}$. To evaluate the Fermi-surface averages in Eqs. (60)–(62) explicitly, one has to know the band structure [including $\boldsymbol{\lambda}(\boldsymbol{k})$ and $t(\boldsymbol{k})$] and the momentum dependence of the order parameter.

IV. APPLICATIONS TO $CePt_3Si$

$CePt_3Si$ is a heavy-fermion material without inversion center, which was recently found to become superconducting at $T \simeq 0.75$ K.[16] It has a tetragonal lattice symmetry described by the point group $G = \boldsymbol{C}_{4v}$, which is generated by the rotations $\boldsymbol{C}_{4z}$ about the z axis by an angle $\pi/2$ and the reflections σ_x in the vertical plane (100). The Fermi surface is invariant under all the operations from $\boldsymbol{C}_{4v}$ and also the inversion, the latter being the consequence of the time-reversal symmetry. The band structure calculations of Ref. 23 show that the SO coupling in this material is strong and therefore the degeneracy of the bands is lifted everywhere, except along the z axis.

TABLE I. The character table and the examples of the basis functions of the irreducible representations of $\boldsymbol{C}_{4v}$.

Γ	E	C_{4z}	σ_x	Even $\phi_\Gamma(\boldsymbol{k})$	Odd $\phi_\Gamma(\boldsymbol{k})$
A_1	1	1	1	$k_x^2+k_y^2+ck_z^2$	k_z
A_2	1	1	−1	$(k_x^2-k_y^2)k_xk_y$	$(k_x^2-k_y^2)k_xk_yk_z$
B_1	1	−1	1	$k_x^2-k_y^2$	$(k_x^2-k_y^2)k_z$
B_2	1	−1	−1	k_xk_y	$k_xk_yk_z$
E	2	0	0	k_xk_z, k_yk_z	k_x, k_y

The point group $\boldsymbol{C}_{4v}$ has five irreducible representations: four one-dimensional (A_1, A_2, B_1, and B_2), and one two-dimensional (E), see Table I. Although the order parameter is odd in k,[23] its nodal structure is determined by the even basis functions.[34] Here we consider only the case of a one-component order parameter, for which

$$\Delta(\boldsymbol{k},\boldsymbol{r}) = \eta(\boldsymbol{r})\Psi(\boldsymbol{k}) = \eta(\boldsymbol{r})t(\boldsymbol{k})\phi(\boldsymbol{k}), \tag{63}$$

where $\phi(\boldsymbol{k}) = \phi(-\boldsymbol{k})$. The pair magnetic moment vanishes, and the GL free energy (58) takes the form

$$F = \alpha(T - T_c)|\eta|^2 + K_{ij}\eta^* D_i D_j \eta + \tilde{K}_{ij} B_i \eta^* D_j \eta.$$

Dropping the terms proportional to N_F and using the symmetry of the Fermi surface, we have

$$K_{xx} = K_{yy} = K_1 = \frac{7\zeta(3)\hbar^2}{32\pi^2 T_c^2} N_F \langle \phi^2(\boldsymbol{k}) v_x^2(\boldsymbol{k})\rangle_0,$$

$$K_{zz} = K_2 = \frac{7\zeta(3)\hbar^2}{32\pi^2 T_c^2} N_F \langle \phi^2(\boldsymbol{k}) v_z^2(\boldsymbol{k})\rangle_0. \tag{64}$$

In order to calculate $\tilde{K}_{ij}$, we need an expression for $\boldsymbol{\lambda}(\boldsymbol{k})$, which satisfies the following symmetry requirements $\boldsymbol{\lambda}(-\boldsymbol{k}) = -\boldsymbol{\lambda}(\boldsymbol{k})$, $(C_{4z}\boldsymbol{\lambda})(C_{4z}^{-1}\boldsymbol{k}) = \boldsymbol{\lambda}(\boldsymbol{k})$, and $(\sigma_x\boldsymbol{\lambda})(\sigma_x^{-1}\boldsymbol{k}) = \boldsymbol{\lambda}(\boldsymbol{k})$ (since $\boldsymbol{\lambda}$ is a pseudovector, we have $\sigma_x\boldsymbol{\lambda} \equiv IC_{2x}\boldsymbol{\lambda} = C_{2x}\boldsymbol{\lambda}$, where C_{2x} is a rotation by an angle π about the x axis). To solve these constraints, we represent λ as an expansion over the odd basis functions of the irreducible representations of $\boldsymbol{C}_{4v}$, see Table I,

$$\boldsymbol{\lambda}(\boldsymbol{k}) = \sum_\Gamma \sum_{a=1}^{d_\Gamma} \boldsymbol{\lambda}_{\Gamma,a}\tilde{\phi}_{\Gamma,a}(\boldsymbol{k}), \tag{65}$$

where $\tilde{\phi}(-\boldsymbol{k}) = -\tilde{\phi}(\boldsymbol{k})$. It is straightforward to check that only the representations A_2 and E contribute to the expansion (65), so that the most general expression for $\boldsymbol{\lambda}(\boldsymbol{k})$, which satisfies all the symmetry requirements, is given by

$$\boldsymbol{\lambda}(\boldsymbol{k}) = \lambda_E[\tilde{\phi}_{E,2}(\boldsymbol{k})\hat{x} - \tilde{\phi}_{E,1}(\boldsymbol{k})\hat{y}] + \lambda_{A_2}\tilde{\phi}_{A_2}(\boldsymbol{k})\hat{z}, \quad (66)$$

where λ_E and λ_{A_2} are constants. Substituting it into Eq. (62), using the fact that the Fermi velocity $\boldsymbol{v}(\boldsymbol{k})$ transforms according to a vector representation $E+A_1$, and dropping the terms proportional to N_F', we finally have

$$\tilde{K}_{xy} = -\tilde{K}_{yx} = \tilde{K} = -\frac{7\zeta(3)\hbar}{8\pi^2 T_c^2} N_F \langle \phi^2(\boldsymbol{k})\tilde{\phi}_{E,1}(\boldsymbol{k})v_x(\boldsymbol{k})\rangle_0. \quad (67)$$

All other $\tilde{K}_{ij}$ vanish by symmetry.

Finally, the GL free energy density can be written as

$$F = \alpha(T-T_c)|\eta|^2 + \eta^*[K_1(D_x^2+D_y^2)+K_2D_z^2]\eta + \tilde{K}\eta^*(B_xD_y - B_yD_x)\eta. \quad (68)$$

While the second-order gradient terms here are typical for a one-component order parameter in a uniaxial crystal, the last, linear in both $\boldsymbol{D}$ and $\boldsymbol{B}$, term is unusual and occurs only because of the absence of inversion symmetry.

As an application of the above results, let us calculate the upper critical fields for $\boldsymbol{B}$ parallel and perpendicular to the z axis. To this end, we solve the linearized GL equation obtained from Eq. (68). If $\boldsymbol{B}=B(0,0,1)$, then

$$H_{c2,z}(T) = \frac{\hbar c}{2e}\frac{\alpha}{K_1}(T_c - T). \quad (69)$$

If $B=B(\cos\varphi, \sin\varphi, 0)$, we choose the gauge $\boldsymbol{A}=Bz(\sin\varphi, -\cos\varphi, 0)$. The lowest eigenvalue of the GL operator corresponds to the order parameter with no modulation along the field direction:

$$\eta(\boldsymbol{r}) = \exp\left[i\frac{2e}{\hbar c}(\boldsymbol{B}\times\boldsymbol{r})_z z_0\right] f(z),$$

where z_0 is an arbitrary parameter. The function $f(z)$ satisfies an equation which can be reduced to the standard harmonic oscillator equation by a shift in the coordinate: $z=Z+z_0+(\hbar c\tilde{K}/4eK_1)$. Thus we find

$$f(z) \propto \exp\left(-\frac{eB}{\hbar c}\sqrt{\frac{K_1}{K_2}}Z^2\right), \quad (70)$$

and the field-dependent critical temperature

$$T_c(\boldsymbol{B}) = T_c(\boldsymbol{B}=0) - \frac{2e}{\hbar c}\frac{\sqrt{K_1K_2}}{\alpha}B + \frac{\tilde{K}^2}{4\alpha K_1}B^2, \quad (71)$$

which is completely isotropic in the xy-plane. We see that, surprisingly, the $\tilde{K}$-term does not affect the linear in $\boldsymbol{B}$ suppression of T_c, giving rise only to a small, quadratic in field, correction. Neglecting the latter effect, we find

$$H_{c2,xy}(T) = \frac{\hbar c}{2e}\frac{\alpha}{\sqrt{K_1K_2}}(T_c - T). \quad (72)$$

The last term in Eq. (71) could become dominant in a film of $CePt_3Si$. If the thickness of the film is less than the correlation length $\xi_z = K_2/\alpha(T_c - T)$, then the order parameter (70) becomes z-independent and the linear in $\boldsymbol{B}$ term in Eq. (71) is absent. Thus, in this case the superconductivity can be promoted by a parallel magnetic field, at least in the weak field limit. This agrees with the results of Ref. 35, where the gradient term linear in $\boldsymbol{B}$ and $\boldsymbol{D}$ was introduced on the phenomenological grounds for a surface superconductor. The order parameter which occurs at T_c at nonzero $\boldsymbol{B}$ is modulated in the xy plane: $\eta(\boldsymbol{r}) = \eta_0 e^{i\boldsymbol{Q}\boldsymbol{r}}$, with $\boldsymbol{Q}\propto(\hat{z}\times\boldsymbol{B})$,[35] see also Ref. 24. It should be noted though that the field-induced increase in T_c may indicate the onset of a magnetic instability of the superconducting state, the investigation of which is beyond the scope of the present work.

V. CONCLUSIONS

We studied the magnetic properties of a clean superconductor with spin-orbit coupling. We focused on the weak-field limit near the critical temperature, where the Ginzburg-Landau theory is applicable. Starting from the effective single-band Hamiltonian in the magnetic field, we obtained the expressions for the GL effective masses and the internal magnetic moments of the Cooper pairs in terms of the Fermi-surface averages, for an arbitrary pairing symmetry and crystal structure, both in the centrosymmetric and noncentrosymmetric cases.

For a superconductor without inversion symmetry, unusual terms, linear in both the magnetic field and the order parameter gradients, were found in the free energy expansion. The order parameter itself corresponds to the pairing of electrons in the time-reversed states within the same nondegenerate band. As a simple application of our general formalism, we derived the GL functional for $CePt_3Si$. It was found that although the unusual gradient term does not affect the upper critical field in a bulk sample, it could result in a field-induced enhancement of T_c in a thin film.

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APPENDIX A: DERIVATION OF EQ. (34)

To derive the free energy for a nonuniform distribution of the order parameter, we start with a representation of the partition function for the BCS Hamiltonian (27) in terms of a functional integral over the Grassmann fields $c_{\boldsymbol{k}\alpha}(\tau)$ and $\overline{c_{\boldsymbol{k}\alpha}}(\tau)$:

$$Z = \int \mathcal{D}c\mathcal{D}\overline{c}e^{-S}, \quad (A1)$$

where $S=\int_0^\beta d\tau[\Sigma_{\boldsymbol{k}}\overline{c_{\boldsymbol{k}\alpha}}\partial_\tau c_{\boldsymbol{k}\alpha} + H(\tau)]$. The interaction term in the action can be written as

$$S_{\rm int} = -\frac{V}{4}\sum_a \int_0^\beta d\tau \sum_{\boldsymbol{q}} B_a^\dagger(\boldsymbol{q},\tau) B_a(\boldsymbol{q},\tau),$$

where

$$B_a(\boldsymbol{q},\tau) = \sum_{\boldsymbol{k}} \Psi^\dagger_{a,\alpha\beta}(\boldsymbol{k}) c_{-\boldsymbol{k}+\boldsymbol{q}/2,\alpha}(\tau) c_{\boldsymbol{k}+\boldsymbol{q}/2,\beta}(\tau).$$

The interaction term is then decoupled by means of the Habbard-Stratonovich transformation, introducing a complex bosonic field $\eta_a(\boldsymbol{q},\tau)$:

$$e^{-S_{\rm int}} \to \int \mathcal{D}\eta_a^* \mathcal{D}\eta_a \exp\left\{ -\sum_a \int_0^\beta d\tau \times \sum_{\boldsymbol{q}} \left[\frac{1}{V}|\eta_a|^2 + \frac{1}{2}(B_a^\dagger \eta_a + \eta_a^* B_a) \right] \right\}.$$

The last two terms in the exponent can be written as

$$\frac{1}{2}\int_0^\beta d\tau \sum_{\boldsymbol{k},\boldsymbol{q}} \Delta_{\alpha\beta}(\boldsymbol{k},\boldsymbol{q};\tau) \overline{c}_{\boldsymbol{k}+\boldsymbol{q}/2,\alpha}(\tau) \overline{c}_{-\boldsymbol{k}+\boldsymbol{q}/2,\beta}(\tau) + \text{H.c.},$$

where

$$\Delta_{\alpha\beta}(\boldsymbol{k},\boldsymbol{q};\tau) = \sum_a \eta_a(\boldsymbol{q},\tau)\Psi_{a,\alpha\beta}(\boldsymbol{k}) \tag{A2}$$

is the order parameter matrix in the pseudospin space [cf. Eq. (33)].

The next step is to integrate out the fermionic degrees of freedom, which can be achieved by using the four-component Nambu spinor fields $C_{\boldsymbol{k}}(\tau) = [c_{\boldsymbol{k}\alpha}(\tau), \overline{c}_{-\boldsymbol{k}\alpha}(\tau)]^T$ and calculating a Gaussian fermionic integral. As a result we arrive at the following representation of the partition function:

$$Z = \int \mathcal{D}\eta_a^* \mathcal{D}\eta_a e^{-S_{eff}[\eta^*,\eta]}, \tag{A3}$$

where

$$S_{\rm eff} = \frac{1}{V}\sum_a \int_0^\beta d\tau \sum_{\boldsymbol{q}} |\eta_a|^2 - \frac{1}{2}\mathrm{Tr}\,\ln(1 - G_0\Sigma) \tag{A4}$$

is the effective action for the superconducting order parameter. Here $\mathcal{G}_0$ is the Gor'kov-Nambu Green's function at $\eta = \eta^* = 0$ (i.e., in the normal state):

$$G_0 = \begin{pmatrix} G & 0 \\ 0 & -G^T \end{pmatrix}, \tag{A5}$$

where $G = (-\partial_\tau - \mathcal{E})^{-1}$ is a 2×2 matrix in the pseudospin space, which satisfies Eq. (7), and Σ is the 4×4 matrix self-energy function describing the superconducting pairing:

$$\Sigma = \begin{pmatrix} 0 & \Delta \\ \Delta^\dagger & 0 \end{pmatrix}, \tag{A6}$$

with the order parameter matrix defined by Eq. (A2). The trace in the action (A4) should be understood as the matrix trace in the four-dimensional Nambu $\times$ pseudospin space, accompanied by the operator trace in the $\boldsymbol{k}\tau$-space.

Using the partition function (A3), we can calculate the free energy of the system: $\mathcal{F} = -(1/\beta)\ln Z$. The BCS mean-field approximation corresponds to a stationary saddle point of the effective action (A4). For $\eta_a(\boldsymbol{q},\tau) = \eta_a(\boldsymbol{q})$, the saddle-point action becomes $S_{\rm eff}^{\rm sp} = \beta\mathcal{F}$, with the free energy (or, more precisely, the difference between the free energies of the superconducting and the normal states at the same temperature) given by

$$\mathcal{F} = \frac{1}{V}\sum_a \sum_{\boldsymbol{q}} |\eta_a(\boldsymbol{q})|^2 - \frac{1}{2\beta}\mathrm{Tr}\,\ln(1 - G_0\Sigma). \tag{A7}$$

The order parameter components satisfy the saddle-point equations $\delta\mathcal{F}/\delta\eta_a^* = 0$ (the GL equations). In the vicinity of the critical temperature at arbitrary magnetic field, the order parameter is small, so we can keep only the quadratic in η_a terms in the expansion of the trace in the free energy (A7). In terms of the Fourier-transformed basis functions

$$\Psi_{a,\alpha\beta}(\boldsymbol{\rho}) = \sum_{\boldsymbol{k}} e^{i\boldsymbol{k}\boldsymbol{\rho}} \Psi_{a,\alpha\beta}(\boldsymbol{k}) \tag{A8}$$

and the Green's functions (8), we have

$$\mathcal{F} = \sum_{ab} \int d\boldsymbol{r}_1 d\boldsymbol{r}_2 \eta_a^*(\boldsymbol{r}_1) S_{ab}(\boldsymbol{r}_1,\boldsymbol{r}_2) \eta_b(\boldsymbol{r}_2), \tag{A9}$$

with the kernel

$$S_{ab}(\boldsymbol{r}_1,\boldsymbol{r}_2) = \frac{1}{V}\delta_{ij}\delta(\boldsymbol{r}_1 - \boldsymbol{r}_2) - \frac{1}{2}T\sum_n \int d\boldsymbol{\rho}_1 d\boldsymbol{\rho}_2 \times \Psi^\dagger_{a,\alpha\beta}(\boldsymbol{\rho}_1) G_{\beta\gamma}\left(\boldsymbol{r}_1 + \frac{\boldsymbol{\rho}_1}{2}, r_2 + \frac{\boldsymbol{\rho}_2}{2}; \omega_n\right) \times \Psi_{b,\gamma\delta}(\boldsymbol{\rho}_2) G_{\alpha\delta}\left(\boldsymbol{r}_1 - \frac{\boldsymbol{\rho}_1}{2}, r_2 - \frac{\boldsymbol{\rho}_2}{2}; -\omega_n\right). \tag{A10}$$

Substitution of the factorized Green's function (10) in (A10) gives the phase factor

$$\exp\left[i\varphi\left(\boldsymbol{r}_1 + \frac{\boldsymbol{\rho}_1}{2}, \boldsymbol{r}_2 + \frac{\boldsymbol{\rho}_2}{2}\right) + i\varphi\left(\boldsymbol{r}_1 - \frac{\boldsymbol{\rho}_1}{2}, \boldsymbol{r}_2 - \frac{\boldsymbol{\rho}_2}{2}\right)\right] = \exp\left[2i\varphi(\boldsymbol{r}_1,\boldsymbol{r}_2) + i\frac{e}{4\hbar c}\boldsymbol{B}(\boldsymbol{\rho}_1 \times \boldsymbol{\rho}_2)\right]$$

[to prove this, one can use the Taylor expansions of the φ's with respect to $\boldsymbol{\rho}_{1,2}$, and also the identities (11)]. The next step is to use

$$\exp\left\{ i\frac{2e}{\hbar c}\int_{r_1}^{r_2} \boldsymbol{A}(\boldsymbol{r}) d\boldsymbol{r} \right\} \eta(\boldsymbol{r}_2) = e^{-i(\boldsymbol{r}_1 - \boldsymbol{r}_2)\boldsymbol{D}_1} \eta(\boldsymbol{r}_1),$$

where $\boldsymbol{D} = -i\nabla_r + (2e/\hbar c)\boldsymbol{A}$, to cast the free energy (A9) in the form (34), with the function $\overline{S}(\boldsymbol{R})$ given by

$$\overline{S}_{ab}(\boldsymbol{R}) = \frac{1}{2}T\sum_n \int d\boldsymbol{\rho}_1 d\boldsymbol{\rho}_2 \Psi^\dagger_{a,\alpha\beta}(\boldsymbol{\rho}_1)\Psi_{b,\gamma\delta}(\boldsymbol{\rho}_2) \times \exp\left[i\frac{e}{4\hbar c}B(\boldsymbol{\rho}_1 \times \boldsymbol{\rho}_2)\right] \times \overline{G}_{\beta\gamma}\left(\boldsymbol{R} + \frac{\boldsymbol{\rho}_1 - \boldsymbol{\rho}_2}{2}, \omega_n\right)\overline{G}_{\alpha\delta}\left(\boldsymbol{R} - \frac{\boldsymbol{\rho}_1 - \boldsymbol{\rho}_2}{2}, -\omega_n\right). \quad \text{(A11)}$$

Finally, taking the Fourier transform of this expression, we arrive at Eq. (36).

The analysis in the noncentrosymmetric case can be done in a similar fashion, the only difference being that there is no pseudospin degrees of freedom, and G, Ψ, and Δ become just scalar functions. The partition function still has the form (A3), but the effective action now reads

$$S_{\text{eff}} = \frac{1}{2V}\sum_a \int_0^\beta d\tau \sum_{\boldsymbol{q}} |\eta_a|^2 - \frac{1}{2}\text{Tr}\,\ln(1 - \mathcal{G}_0\Sigma), \quad \text{(A12)}$$

where G_0 and Σ are 2×2 matrix operators in the Nambu space and the $\boldsymbol{k}\tau$-space. Repeating all the steps leading to Eq. (A11), we arrive at Eqs. (55) and (56).

APPENDIX B: GRADIENT ENERGY NEAR T_c

In this Appendix we estimate the lowest eigenvalue of the matrix differential operator $\hat{\mathcal{K}}_{ab} = K_{ab,ij}D_iD_j$, where $K_{ab,ij}$ are constant coefficients, $a,b = 1\ldots d$, and $i,j = x,y,z$. We choose $\boldsymbol{B}$ along the z axis, i.e., $\boldsymbol{B} = B\hat{z}$ (one can always achieve that by rotating the coordinate system, which is equivalent to a redefinition of $K_{ab,ij}$). It is convenient to introduce new operators

$$a_\pm = \frac{1}{2}\sqrt{\frac{\hbar c}{eB}}(D_x \pm iD_y),$$

$$a_3 = \sqrt{\frac{\hbar c}{eB}}D_z. \quad \text{(B1)}$$

It is easy to check that the operators $a_\pm$ satisfy the relations $a_+ = a_-^\dagger$ and $[a_-, a_+] = 1$, and therefore have the meaning of the lowering and the raising operators, respectively, while the operator $a_3 = a_3^\dagger$ commutes with both of them: $[a_3, a_\pm] = 0$. Representing $\hat{\mathcal{K}}_{ab}$ in terms of the operators (B1), we have

$$\hat{\mathcal{K}}_{ab} = \frac{eB}{\hbar c}\sum_{n,m=\pm,3} \tilde{K}_{ab,nm}a_n^\dagger a_m, \quad \text{(B2)}$$

where the coefficients $\tilde{K}_{ab,nm}$ are linear combinations of $K_{ab,ij}$ and therefore do not depend on B. It immediately follows from the last expression that all eigenvalues of $\hat{\mathcal{K}}$ are linear in B.

To calculate the eigenvalues explicitly, it is convenient to choose the basis of states $|N,p\rangle$ such that

$$a_+|N,p\rangle = \sqrt{N+1}|N+1,p\rangle,$$

$$a_-|N,p\rangle = \sqrt{N}|N-1,p\rangle,$$

$$a_3|N,p\rangle = p|N,p\rangle,$$

where $N = 0,1,\ldots$ has the meaning of the Landau level index and p is a real number which is proportional to the wave vector along the z-axis: $p = k_z\sqrt{\hbar c/eB}$. Expanding the eigenfunctions of $\hat{K}$ in this basis: $\eta_a(\boldsymbol{r}) = \Sigma_{N,p}C_{a,N,p}\langle r|N,p\rangle$, we arrive at a system of linear equations for the coefficients $C_{a,N,p}$, which is infinite in general. The upper critical field then corresponds to the minimum eigenvalue of this system with respect to p (while it is usually assumed that the minimum is achieved for $p = 0$, some exceptions are discussed, e.g., in Ref. 5).

In some simple cases, the diagonalization procedure outlined above can be carried out analytically. For example, for a one-component order parameter in an isotropic s-wave superconductor we have

$$\hat{\mathcal{K}} = K(D_x^2 + D_y^2 + D_z^2) = \frac{eB}{\hbar c}K(4a_+a_- + a_3^2 + 2). \quad \text{(B3)}$$

Since $a_+a_-|N,p\rangle = N|N,p\rangle$, we have

$$\hat{\mathcal{K}}|N,p\rangle = \frac{eB}{\hbar c}K(4N + p^2 + 2)|N,p\rangle. \quad \text{(B4)}$$

The lowest eigenvalue corresponds to $N = p = 0$, which gives the standard expression for the critical temperature suppressed by the field,

$$T_c(\boldsymbol{B}) = T_c(\boldsymbol{B} = 0) - \frac{2e}{\hbar c}\frac{K}{\alpha}B. \quad \text{(B5)}$$

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