

Superconductivity without Inversion Symmetry: MnSi versus CePt₃Si

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Superconductivity in materials without spatial inversion symmetry is studied. We show that in contrast to common belief, spin-triplet pairing is not entirely excluded in such systems. Moreover, paramagnetic limiting is analyzed for both spin-singlet and -triplet pairing. The lack of inversion symmetry reduces the effect of the paramagnetic limiting for spin-singlet pairing. These results are applied to MnSi and CePt₃Si.

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Cooper pairing in the spin-singlet channel relies on the presence of time-reversal symmetry (Anderson's theorem); the paired electron states are related by time reversal and are consequently degenerate [1]. If this degeneracy is lifted, for example, by a magnetic field or magnetic impurities coupling to the electron spins, then superconductivity is weakened or even suppressed. For spin-triplet pairing, Anderson noticed that additionally inversion symmetry is required to obtain the necessary degenerate electron states [2]. Consequently, it became a widespread view that a material lacking an inversion center would be an unlikely candidate for spin-triplet pairing. For example, the absence of superconductivity in the paramagnetic phase of MnSi close to the quantum critical point to itinerant ferromagnetism was interpreted from this point of view [3,4]. Near this quantum critical point the most natural spin fluctuation mediated Cooper pairing would occur in the spin-triplet channel. However, MnSi has the so-called *B20* structure (*P2₁3*), without an inversion center, inhibiting spin-triplet pairing.

Recently, superconductivity has been discovered in the heavy fermion compound CePt₃Si, another system without inversion symmetry (*P4mm*) [5]. The upper critical field H_{c2} exceeds the usual paramagnetic limiting field, which might indicate that here nevertheless spin-triplet pairing is realized. Since there is no experimental information on the pairing symmetry in this material so far, it is worth examining the options for Cooper pairing in this case.

The aim of this Letter is to discuss two points for time-reversal invariant materials without inversion centers. The first is concerned with the possible existence of spin-triplet pairing. The second addresses the problem of paramagnetic limiting (Clogston-Chandrasekar-Pauli limiting). The result of this discussion will be applied to the two materials mentioned above: MnSi and CePt₃Si.

Model.—We use a single-band model with electron band energy ξ_k measured from the Fermi energy where electrons with momentum \mathbf{k} and spin s are created (an-

nihilated) by the operators c_{ks}^\dagger (c_{ks}). The Hamiltonian including the pairing interaction is

$$H = \sum_{k,s} \xi_k c_{ks}^\dagger c_{ks} + \frac{1}{2} \sum_{k,k'} \sum_{s,s'} V_{k,k'} c_{ks}^\dagger c_{-k's'}^\dagger c_{-k's'} c_{k's}. \quad (1)$$

This system possesses time reversal and inversion symmetry ($\xi_k = \xi_{-k}$), and the pairing interaction does not depend on the spin and favors either even-parity (spin-singlet) or odd-parity (spin-triplet) pairing as required. Following the standard weak-coupling approach, we define the interaction to be finite and attractive close to the Fermi energy with the cutoff energy ϵ_c , and to depend on the momenta only through the angular dependence. The absence of inversion symmetry is introduced by an additional term, H_p , to the Hamiltonian which removes parity but conserves time-reversal symmetry, i.e., $IH_p I^{-1} = -H_p$ and $TH_p T^{-1} = H_p$. We can write such a single-particle term as

$$H_p = \alpha \sum_{k,s,s'} \mathbf{g}_k \cdot \boldsymbol{\sigma}_{ss'} c_{ks}^\dagger c_{k's'}, \quad (2)$$

where $\boldsymbol{\sigma}$ denotes the Pauli matrices and $\mathbf{g}_{-k} = -\mathbf{g}_k$ (this satisfies the above condition since $I\boldsymbol{\sigma}I^{-1} = \boldsymbol{\sigma}$ and $T\boldsymbol{\sigma}T^{-1} = -\boldsymbol{\sigma}$). It is convenient to normalize \mathbf{g}_k so that the average over the Fermi surface $\langle \mathbf{g}_k^2 \rangle_k = 1$; in the numerical calculations we will impose this constraint. We will keep \mathbf{g}_k arbitrary and later provide a specific form of \mathbf{g}_k for MnSi and CePt₃Si. The normal state Green's function becomes

$$G^0(\mathbf{k}, i\omega_n) = G_+(\mathbf{k}, i\omega_n)\sigma_0 + \hat{\mathbf{g}}_k \cdot \boldsymbol{\sigma} G_-(\mathbf{k}, i\omega_n), \quad (3)$$

where σ_0 is the unit matrix and

$$G_\pm(\mathbf{k}, i\omega_n) = \frac{1}{2}[(i\omega_n - \epsilon_{k,+})^{-1} \pm (i\omega_n - \epsilon_{k,-})^{-1}], \quad (4)$$

$\epsilon_{k,\pm} = \xi_k \pm \alpha|\mathbf{g}_k|$ and $\hat{\mathbf{g}}_k = \mathbf{g}_k/|\mathbf{g}_k|$ ($|\mathbf{g}| = \sqrt{\mathbf{g}^2}$) [6]. The Fermi surface splits into two sheets with different spin structure. These two sheets touch whenever $\mathbf{g}(\mathbf{k}) = 0$.

Superconducting instability.—We now use the BCS decoupling scheme and determine the linearized gap equation in order to calculate the transition temperature T_c :

$$\Delta_{ss'}(\mathbf{k}) = -k_B T \sum_{n,k'} \sum_{s_1, s_2} V_{k,k'} G_{ss_1}^0(\mathbf{k}', i\omega_n) \times \Delta_{s_1, s_2}(\mathbf{k}') G_{s's_2}^0(-\mathbf{k}', -i\omega_n). \quad (5)$$

The gap function is decomposed into a spin-singlet [$\psi(\mathbf{k})$] and a -triplet [$\mathbf{d}(\mathbf{k})$] part, $\Delta(\mathbf{k}) = \{\psi(\mathbf{k})\sigma_0 + \mathbf{d}(\mathbf{k}) \cdot \boldsymbol{\sigma}\}i\sigma_y$. For simplicity we assume that the gap functions have the same magnitude on both Fermi surface sheets. This allows us to write the linearized gap equations as

$$\psi(\mathbf{k}) = -k_B T \sum_{n,k'} V_{k,k'} \{ [G_+ G_+ + G_- G_-] \psi(\mathbf{k}') + [G_+ G_- + G_- G_+] \hat{\mathbf{g}}_{k'} \cdot \mathbf{d}(\mathbf{k}') \} \quad (6)$$

and

$$\mathbf{d}(\mathbf{k}) = -k_B T \sum_{n,k'} V_{k,k'} \{ [G_+ G_+ + G_- G_-] \mathbf{d}(\mathbf{k}') + 2G_- G_- [\hat{\mathbf{g}}_{k'} (\hat{\mathbf{g}}_{k'} \cdot \mathbf{d}(\mathbf{k}')) - \mathbf{d}(\mathbf{k}')] + [G_+ G_- + G_- G_+] \hat{\mathbf{g}}_{k'} \psi(\mathbf{k}') \}, \quad (7)$$

where we have used the short notation for the products: $G_a G_b = G_a(\mathbf{k}, i\omega_n) G_b(-\mathbf{k}, -i\omega_n)$ with $a, b = \pm$. For finite α , the spin-singlet and -triplet channels are coupled, an effect of the missing parity [7]. However, this coupling depends on the degree of particle-hole asymmetry or the difference of the density of states on the two Fermi surface sheets, which yields a coupling of the order $\alpha/\epsilon_F \ll 1$. Thus, we ignore these coupling terms here and consider the “singlet” and “triplet” channels of pairing separately.

For spin-singlet pairing we find that the transition temperature (T_c) is given by

$$\ln\left(\frac{T_c}{T_{cs}}\right) = O\left(\frac{\alpha^2}{\epsilon_F^2}\right). \quad (8)$$

The transition temperature remains essentially unchanged from $k_B T_{cs} = \epsilon_c \exp(-1/\lambda_s)$ (here T_{cs} is T_c for $\alpha = 0$) with $\lambda_s \psi(\mathbf{k}) = N(0) \langle V_{k,k'} \psi(\mathbf{k}') \rangle_{k'}$. For triplet pairing the equation for T_c reads

$$\ln\left(\frac{T_c}{T_{ct}}\right) = 2 \langle \{ |\mathbf{d}(\mathbf{k})|^2 - |\hat{\mathbf{g}}_{\mathbf{k}} \cdot \mathbf{d}(\mathbf{k})|^2 \} f(\rho_{\mathbf{k}}) \rangle_{\mathbf{k}} + O\left(\frac{\alpha^2}{\epsilon_F^2}\right), \quad (9)$$

where $k_B T_{ct} = \epsilon_c \exp(-1/\lambda_t)$ with $\lambda_t \mathbf{d}(\mathbf{k}) = N(0) \langle V_{k,k'} \mathbf{d}(\mathbf{k}') \rangle_{k'}$ and $\rho_{\mathbf{k}} = \alpha |\mathbf{g}_{\mathbf{k}}| / \pi k_B T_c$. We use the normalized gap function with $\langle |\mathbf{d}(\mathbf{k})|^2 \rangle_{\mathbf{k}} = 1$ in all numerical calculations. The function $f(\rho)$ is defined as

$$f(\rho) = \text{Re} \sum_{n=1}^{\infty} \left(\frac{1}{2n-1+i\rho} - \frac{1}{2n-1} \right). \quad (10)$$

The correction term in Eq. (9) suppresses T_c in general. For a spherical Fermi surface and $\alpha = 0$ all gap functions with a given relative angular momentum ℓ have the same T_c . Equation (10) determines how this degeneracy is lifted by the broken inversion symmetry. The highest T_c is obtained for a state with $\mathbf{d}(\mathbf{k}) \parallel \mathbf{g}_{\mathbf{k}}$, for which the right-hand side of Eq. (9) vanishes and $T_c = T_{ct}$. Hence we conclude that spin-triplet pairing is not indiscriminately suppressed in the absence of an inversion center. In principle, there may be spin-triplet pairing states which are completely unaffected by the lack of inversion symmetry, taking advantage of the spinor structure induced by $\mathbf{g}_{\mathbf{k}}$.

Structure of \mathbf{g} .—The vector $\alpha \mathbf{g}_{\mathbf{k}}$ characterizes and quantifies the absence of an inversion center in a crystal lattice. In many cases the loss of an inversion center can be viewed as moving certain ions in the crystal lattice out of their high-symmetry position. This gives rise to internal electric fields that yield, through relativistic corrections, spin-orbit coupling [8]. Furthermore, shifted ions can open new hopping paths which involve atomic spin-orbit coupling on intermediate ions.

We consider the form of $\mathbf{g}_{\mathbf{k}}$ for our two examples: MnSi and CePt₃Si. We start with the space group that corresponds to the basic “point group” symmetry G . Because of the lack of inversion symmetry this group is reduced to a subgroup G' . The correction term $\mathbf{g}_{\mathbf{k}} \cdot \boldsymbol{\sigma}$ is invariant under all transformations of G' , but not of G . MnSi has the cubic space group $P2_13$. The point group is only the tetrahedral group $T \in O_h$. The symmetry breaking term satisfying the above conditions corresponds to the irreducible representation A_{2u} of O_h which maps to A_1 of T . The expansion in \mathbf{k} leads to (we assume a spherical Fermi surface for simplicity)

$$\mathbf{g}_{\mathbf{k}} \cdot \boldsymbol{\sigma} = k_y k_z (k_y \sigma_z - k_z \sigma_y) + \text{cyclic perm. of } x, y, z \quad (11)$$

which transforms like xyz , a basis function of A_{2u} of O_h . The \mathbf{g} vector has 14 nodes on the Fermi surface, six along the [100] and eight along the [111] direction. The \mathbf{d} vector which remains unaffected by the lack of inversion symmetry is parallel to $\mathbf{g}_{\mathbf{k}}$:

$$\mathbf{d}(\mathbf{k}) = \hat{\mathbf{x}} k_x (k_y^2 - k_z^2) + \hat{\mathbf{y}} k_y (k_z^2 - k_x^2) + \hat{\mathbf{z}} k_z (k_x^2 - k_y^2) \quad (12)$$

which also belongs to A_{2u} , has the same number of nodes as \mathbf{g} and represents an f -wave spin-triplet pairing state.

CePt₃Si is a tetragonal system with space group $P4mm$. Here the removal of the inversion center leads to the point group $C_{4v} \in D_{4h}$ which corresponds to the loss of the basal plane as a mirror plane ($z \rightarrow -z$). One finds that $\mathbf{g}_{\mathbf{k}} \cdot \boldsymbol{\sigma} = k_x \sigma_y - k_y \sigma_x$, which is a basis function of A_{2u} of D_{4h} . This term has the form of the well-known Rashba

spin-orbit coupling [8]. The \mathbf{g} vector has only two nodes lying along the [001] direction. In Fig. 1 we show the reduction of various spin-triplet pairing states with this \mathbf{g} vector. The favored pairing state is of the p -wave type: $\mathbf{d}(\mathbf{k}) = \hat{x}k_y - \hat{y}k_x$ in A_{2u} of D_{4h} , while other pairing states are severely suppressed for $\alpha > k_B T_c$.

With the reduced symmetry of a crystal, it is usually not possible to find $\mathbf{d}(\mathbf{k}) \parallel \mathbf{g}_k$ which satisfies the linearized gap equation for a given pairing interaction $V_{k,k'}$. Nevertheless, we could determine a nearly optimal spin-triplet state compromising between the pairing interaction and the effect of H_p . Very recently, Samokhin *et al.* carried out relativistic band structure calculations which indicate that $\alpha \gg k_B T_c$ in CePt₃Si [9]. They also give a symmetry classification of the possible pairing states [9].

The stability of the pairing state is not only decided by T_c , but also by the condensation energy, which is determined by the shape of the quasiparticle gap in the weak-coupling limit. The Balian-Werthamer state (with a nodeless gap), $\mathbf{d}(\mathbf{k}) = \hat{x}k_x + \hat{y}k_y + \hat{z}k_z$, is the most stable weak-coupling state in a spherically symmetric (or cubic) system. However, in the presence of broken inversion symmetry, Eq. (9) shows this state would generally have a lowered T_c . Thus, for small enough α ($\alpha < k_B T_{ct}$) there could be a second superconducting phase transition below the onset of superconductivity leading to a nodeless gap.

Paramagnetic limiting.—Lifting the degeneracy of the spins is detrimental to spin-singlet superconductivity, an effect known as paramagnetic limiting. Spin-triplet pairing is less vulnerable in this respect. In the absence of inversion symmetry, however, this effect of pair breaking is modified. It is well known that impurity spin-orbit scattering reduces the effect of paramagnetic limiting

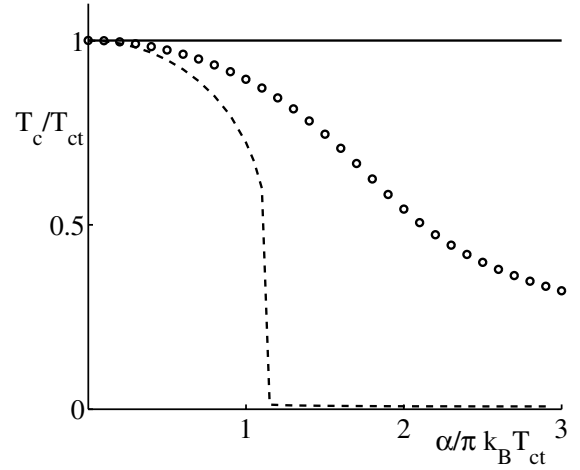


FIG. 1. Transition temperature as a function of α for $\mathbf{g}_k = (-k_y, k_x, 0)$. The curves from top to bottom correspond to $\mathbf{d} = \hat{y}k_x - \hat{x}k_y$, $\mathbf{d} = \hat{y}k_x + \hat{x}k_y$, and $\mathbf{d} = \hat{x}k_x + \hat{y}k_y + \hat{z}k_z$, respectively.

[10]. We show that an analogous effect occurs in systems with broken inversion symmetry. For simplicity, we ignore the effect of orbital pair breaking and include the magnetic field only through its coupling to the spin. Our aim is to demonstrate the effect of finite α on the paramagnetic limiting and an extended discussion for the upper critical field H_{c2} will be given elsewhere. We replace $\alpha \mathbf{g}_k \rightarrow \alpha \tilde{\mathbf{g}}_k = \alpha \mathbf{g}_k - \mathbf{h}$ with $\mathbf{h} = \mu_B \mathbf{H}$ (note $\tilde{\mathbf{g}}_{-k} \neq -\tilde{\mathbf{g}}_k$). The linear gap equations yield the transition temperatures for a continuous onset of superconductivity [11]. We first consider a dominant spin-singlet pairing [$\psi(\mathbf{k})$] and ignore the induced spin-triplet pairing. Then the equation determining T_c is

$$\ln\left(\frac{T_c}{T_{cs}}\right) = \left\langle |\psi(\mathbf{k})|^2 \left[f(\rho_k^-) + f(\rho_k^+) + \frac{\alpha^2 \mathbf{g}_k^2 - \mathbf{h}^2}{[(\alpha \mathbf{g}_k + \mathbf{h})^2 (\alpha \mathbf{g}_k - \mathbf{h})^2]^{1/2}} [f(\rho_k^-) - f(\rho_k^+)] \right] \right\rangle_k \quad (13)$$

with $\rho_k^\pm = |\alpha \mathbf{g}_k + \mathbf{h}|/2\pi k_B T_c \pm |\alpha \mathbf{g}_k - \mathbf{h}|/2\pi k_B T_c$. If it is possible to choose $\mathbf{h} \perp \mathbf{g}_k$ for all \mathbf{k} (as it is for CePt₃Si), then in the small $T_c(h)/T_{cs}$ limit, the paramagnetic limiting field obeys $h^2 \ln h' = -\alpha^2 \ln(T_c/T_{cs})$, with $h' = |\mathbf{h}|/\pi k_B T_{cs}$. In particular, the paramagnetic limiting field diverges as $T \rightarrow 0$ (Fig. 2).

For the spin-triplet channel we obtain analogously

$$\ln\left(\frac{T_c}{T_{ct}}\right) = \left\langle |\mathbf{d}(\mathbf{k})|^2 \left[f(\rho_k^+) + f(\rho_k^-) + \frac{\alpha^2 \mathbf{g}_k^2 - \mathbf{h}^2}{[(\alpha \mathbf{g}_k + \mathbf{h})^2 (\alpha \mathbf{g}_k - \mathbf{h})^2]^{1/2}} [f(\rho_k^+) - f(\rho_k^-)] \right] \right\rangle_k + 2 \left\langle [f(\rho_k^+) - f(\rho_k^-)] \frac{|\mathbf{h} \cdot \mathbf{d}(\mathbf{k})|^2 - \alpha^2 |\mathbf{g}_k \cdot \mathbf{d}(\mathbf{k})|^2}{[(\alpha \mathbf{g}_k + \mathbf{h})^2 (\alpha \mathbf{g}_k - \mathbf{h})^2]^{1/2}} \right\rangle_k. \quad (14)$$

For $\alpha = 0$ there is no paramagnetic limiting, provided $\mathbf{d}(\mathbf{k}) \cdot \mathbf{h} = 0$ can be found for all \mathbf{k} . According to Eq. (14) paramagnetic limiting is absent, if for all \mathbf{k} , $\mathbf{h} \perp \mathbf{d}(\mathbf{k})$, and $\mathbf{d}(\mathbf{k}) \parallel \mathbf{g}_k$. For both the spin-singlet and spin-triplet cases, finite \mathbf{q} Fulde-Ferrell-Larkin-Ovchinnikov phases are often found when $\mathbf{h} \cdot \mathbf{g}_k \neq 0$ [13,14]. The role of orbital effects on these phases is currently under investigation [14].

Discussion of the two examples.—We start with MnSi, which does not show superconductivity in the vicinity of the quantum critical point of a ferromagnetic state. Given our result that spin-triplet pairing is not suppressed completely by broken inversion symmetry, it is useful to reexamine the reason why spin-triplet superconductivity is not observed. As one would expect, the lack of inversion

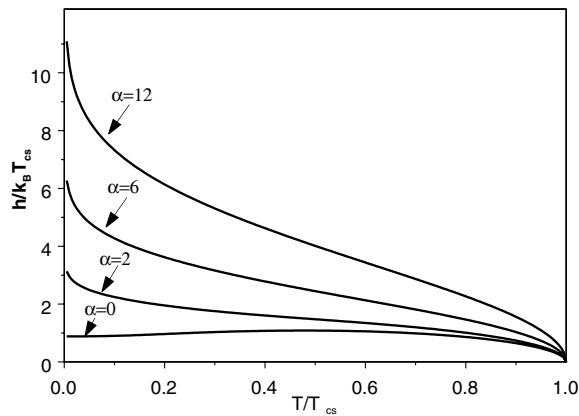


FIG. 2. Paramagnetic limiting field for CePt₃Si for different α (in units $k_B T_{cs}$). The field is applied along the fourfold symmetry axis.

symmetry in this compound with (cubic) $B20$ structure is crucial. According to our analysis the pairing would have to occur in the f -wave channel in order to survive the spin-orbit coupling effect. The fact that the strongly anisotropic f -wave state is more difficult to stabilize by a simple spin fluctuation mechanism than the p -wave pairing state might explain the absence of superconductivity in MnSi.

Turning to CePt₃Si we may adopt two different points of view. First, there is a protected p -wave spin-triplet pairing state ($d(\mathbf{k}) = \hat{x}k_y - \hat{y}k_x$). This may indeed explain the apparent absence of paramagnetic limiting observed in polycrystalline samples[5]. On the other hand, it is important to notice that superconductivity appears here on the background of antiferromagnetic order ($T_N \approx 2$ K), and it seems more natural to assume a spin-singlet type of pairing. In this case, we could argue that paramagnetic limiting for a singlet state is rendered less effective by the presence of spin-orbit coupling. To examine this possibility in more detail we have determined the paramagnetic limiting field as a function of α using Eq. (13) for the field along the fourfold symmetry axis. This is shown in Fig. 2; note that this figure illustrates the divergent paramagnetic limiting field at low temperatures described earlier. It would be very helpful to study this system for single crystals, since for both the spin-singlet and spin-triplet cases a large anisotropy in the paramagnetic limiting field is predicted. The field along the fourfold axis should give no paramagnetic limiting in both cases. Moreover,

the Knight shift should show related effects of the spin-orbit coupling.

In conclusion, the analysis of the symmetry properties for the two materials MnSi and CePt₃Si shows that in the former system the effect of the lack of inversion symmetry leads to more severe restrictions for spin-triplet pairing than in the latter. Furthermore, paramagnetic limiting for spin-singlet superconductors is suppressed by broken inversion symmetry. In many respects, CePt₃Si may become an ideal test system to study the effect of missing inversion symmetry on the superconducting phase [6,7,12].

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