Introduction to unconventional superconductivity in non-centrosymmetric metals

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Abstract. These lecture notes are an extension of my previous notes [1] presented in this lecture series and are concerned with the recently emerging research field of unconventional superconductivity in non-centrosymmetric metals. Inversion symmetry together with time reversal symmetry represent key symmetries for the formation of Cooper pairs in superconductors and allows to distinguish between even-parity spin-singlet and odd-parity spin-triplet pairing. The absence of at least one of two symmetries leads to the spin-splitting of the electronic states, through Zeeman fields (loss of time reversal symmetry) and through antisymmetric spin-orbit coupling (loss of inversion symmetry), which has a strong influence on the Cooper pairing states possible. Anderson's theorems show the basic symmetry requirements for the Cooper pair formation. The meaning of these theorems can be demonstrated in a perturbative analysis of the superconducting instability. The structure of the pairing states are derived for systems without inversion and time reversal symmetry, and are shown to be non-unitary. In the case of non-centrosymmetric materials the pairing interaction displays interesting spin-orbit coupling-induced features which are analyzed within a toy model for the superconductivity in $CePt_3Si$, one of the non-centrosymmetric heavy Fermion superconductors, in order to give a catalogue of possible pairing states in this material. A further important point is the essentially universal behavior of the spin susceptibility in the superconducting phase of a non-centrosymmetric materials. This behavior is spectacularly manifested in the upper critical field of $CeRhSi_3$ and $CeIrSi_3$. Magneto-electric effects represent one of the most extraordinary parts in the phenomenology of non-centrosymmetric superconductors. Two examples of magneto-electric behaviors are discussed: (1) the helical phase in the mixed superconducting state and (2) relation between supercurrent and the spin magnetization. Eventually also the possibility of surface Andreev bound states is discussed and it is shown that such states can carry spin currents.

Keywords: Unconventional superconductivity, high-temperature superconductivity, Sr_2RuO_4

INTRODUCTION

During the last three decades the field of superconductivity has experienced a splendid revival motivated the discovery of a large number of materials displaying properties which are inconsistent with the traditional BCS theory. This theory introduced by Bardeen, Cooper and Schrieffer in 1957 is doubtlessly recognized as the most successful theory in condensed matter physics that explained and predicted an extraordinarily large range of phenomena connected with the mystifying state of superconductivity [2]. With the advent of novel superconductors around 1980 it became soon clear that an extension of the BCS theory would be inevitable, which had been anticipated much earlier, in particular, in connection with superfluid ^3He [3].

The early novel superconductors belong to the class of heavy Fermion materials, such as $CeCu_2Si_2$, UBe_{13} and UPt_3 and numerous organic superconductors discovered mostly in the early eighties [4, 5, 6, 7, 8, 9]. A decisive and lasting impact had the discovery of the high-temperature superconductors which are based on the layered cuprate systems and evolve from doping of Mott insulators. These material class not only displays an unprecedentedly high critical temperature of the order of 100 K, one to two orders of magnitude larger than other novel superconductors, but also exemplifies one of the most intriguing and complex strongly correlated electron systems. Most of these materials have in common that magnetism accompanies superconductivity in some way, as coexisting or competing ordered phases or through strong magnetic fluctuations. During the last decade superconductivity has been found in a number of materials, as a phase at a magnetic quantum critical point which can be reached by chemical doping or even more often simply by applying pressure. Famous examples are the heavy Fermion compounds $CeIn_3$ [10] and $CeMIn_5$ (M=Rh,Co,Ir)[11] as antiferromagnetic systems and UGe_2 [13] and URhGe [14] and UCoGe [16] as ferromagnetic systems. The most recently found new "high-temperature" superconductors among the Fe-oxipnictides (FeAs-compounds) are also closely associated with antiferromagnetism which can be suppressed by doping or pressure in various variants of this material class [15]. The importance of magnetism is less obvious in Sr_2RuO_4 [17, 18] which has been identified as highly intriguing unconventional superconductor and an electronic analogue to the ^{3}He [3].

The feature distinguishing many of the mentioned superconductors from the traditional ones is the strong electron correlation due to Coulomb interaction, which is, for instance, responsible for the magnetic behavior. Such strong Coulomb repulsion apparently counteracts the standard BCS mechanism, based on the formation of Cooper pairs which are bound state of two electrons of opposite momentum and spin close to the Fermi energy, which form a coherent condensate. This coherent state allows to freely insert or remove pairs of electrons, while the spectrum of single electrons has an energy gap. In the original BCS theory, the pair formation is caused by electron-phonon coupling, i.e. through the polarizable ionic lattice of a metal. This interaction is very short ranged such that only pairing states are favorable possessing the highest possible symmetry. In the case of full rotational symmetry, this corresponds to a relative angular momentum $\ell = 0$ and a spin-singlet configuration ($S = 0$). This so-called "s-wave" pairing state represents the *conventional* superconducting phase. However, this phase is most vulnerable to Coulomb repulsion whose repulsive effect is only weakened due to screening and the large difference in time scales of electron motion (fast) and ion motion (slow) in usual metals, leading to the so-called retardation effect. In strongly correlated electron systems the retardation effect is not sufficient to stabilize the s-wave pairing state. Superconductors can evade this problem by Cooper pairing in higher momentum channels (lower symmetry) where the screened (short-ranged) Coulomb interaction is less effective, since electrons do not approach each other closely. Higher angular momenta are often also favored by specific momentum structures of the pairing interactions based on magnetic fluctuations or other alternative longer-ranged pairing interactions. All superconducting phases not based on s-wave Cooper pairing are called *unconventional*. We refer here to the previous lecture notes in this series where this aspect was discussed in much detail [1].

The additional internal structure of the unconventional pairing state results in a wealth of novel properties many of which are subject of actual research. Symmetry aspects play here an important role. While superconductivity in general corresponds to phase that spontaneously breaks $U(1)$-gauge symmetry leading to the basic macroscopic properties such as Meissner-Ochsenfeld screening (London theory), persistent currents and the flux quantization, unconventional superconductors can violate spontaneously further symmetries such as time reversal and crystal symmetry. Especially the former has received considerable attention as several systems are believed to belong to this category, such as $U_{1-x}Th_xBe_{13}$, Sr_2RuO_4 and $PrOs_4Sb_{12}$.

While these symmetries and their violation are connected with the superconducting order parameter (the complex macroscopic wave function of the superconducting condensate) the formation of Cooper pairs relies on basic symmetries irrespective of the global symmetries broken. These key symmetries are *time reversal* and *inversion* symmetry. We may expect strong deviations from usual Cooper pairing, if one or both symmetries are missing in the normal state.

In these lecture notes we would like to add an extension to the previous notes [1], which is concerned with superconductors that lack these key symmetries. In particular, our attention is devoted to the so-called non-centrosymmetric superconductors, materials without an inversion center. This focus is motivated by the recent discovery of a number of new superconductors without inversion symmetry, especially among the heavy Fermion superconductors. Here we will give an introduction to a few basic feature of such superconductors.

KEY SYMMETRIES FOR COOPER PAIRING

Superconductivity affect electrons near the Fermi surface and changes the quasiparticle low-energy spectrum profoundly by opening of an energy gap. Among the Fermi surface instabilities superconductivity requires the least prerequisites in terms of band structure. Other instabilities such as spin and charge density wave phases rely on Fermi surface nesting properties and are, therefore, possible only under restrictive conditions. However, also superconductivity has to satisfy certain basic requirements in order to facilitate the formation of Cooper pairs.

In the superconducting phase Cooper pairs are built from two *degenerate* electron states of opposite momentum in the immediate vicinity of the Fermi surface [23, 24]. The pair amplitude or pair wavefunction as the expectation values of the electron operators $c_{\vec{k}s}$ (annihilating an electron of momentum $\vec{k}$ and spin s) can be decomposed in the following way:

$$\Psi_{\vec{k}ss'} = \langle c_{-\vec{k}s'} c_{\vec{k}s} \rangle = \phi(\vec{k})\chi(s,s') \tag{1}$$

where we separated the orbital ($\phi(\vec{k})$) and the spin part ($\chi(s,s')$). The Pauli principle requires that this wave function is totally antisymmetric under electron exchange, $\vec{k} \to -\vec{k}$ and $s \leftrightarrow s'$. The antisymmetry is either carried by the orbital or the spin part. Thus we distinguish:

pairing type	orbital	spin
even parity / spin singlet	$\phi(\vec{k}) = +\phi(-\vec{k})$	$\chi(ss') = \frac{1}{\sqrt{2}}\{\mid\uparrow\downarrow\rangle - \mid\downarrow\uparrow\rangle\}$
odd parity / spin triplet	$\phi(\vec{k}) = -\phi(-\vec{k})$	$\chi(ss') = \begin{cases} \mid\uparrow\uparrow\rangle \\ \frac{1}{\sqrt{2}}\{\mid\uparrow\downarrow\rangle - \mid\downarrow\uparrow\rangle\} \\ \mid\downarrow\downarrow\rangle \end{cases}$

Parity in case of full spherical symmetry is related to the internal angular momentum of the wave function: even parity $\ell = 0, 2, 4, 6, \ldots$ and odd parity $\ell = 1, 3, 5, \ldots$. Apart from the even-parity spin-singlet state with $\ell = 0$ which constitutes *conventional* pairing all states are considered as unconventional.

Anderson gives the following conditions to guarantee the presence of two electron (quasiparticle) states necessary to form a Cooper pair. For even-parity spin-singlet pairing it is required that the system is at least *time reversal invariant*, since the two particles,

$$|\vec{k}\uparrow\rangle \qquad \text{and} \qquad \mathscr{K}|\vec{k}\uparrow\rangle \rightarrow |-\vec{k}\downarrow\rangle\,, \tag{2}$$

are degenerate and allow for the combination of a spin-singlet state with vanishing total momentum. On the other hand, odd-parity spin-triplet pairing needs lit inversion symmetry,

$$|\vec{k}\uparrow\rangle \qquad \text{and} \qquad \mathscr{I}|\vec{k}\uparrow\rangle \rightarrow |-\vec{k}\uparrow\rangle\,, \tag{3}$$

which lead to two degenerate state with parallel spins. Including time reversal and/or spin rotation symmetry all three spin-triplet configuration can be constructed in this way. These two conditions are known as Anderson's theorem [23, 24]. It is obvious that time reversal and inversion symmetry take the role of *key symmetries* for superconductivity. We will see below how the lack of these symmetries influences the property of the superconducting state.

The symmetry of the pair wave function is also reflected in the gap function which will be the order parameter which we will use in the following to characterize the superconducting phase. In general, this is a 2x2-matrix in spin space, $\Delta_{ss'}$, which is represented by a scalar function $\psi(\vec{k})$ in case of an even-parity spin-singlet state,

$$\hat{\Delta}(\vec{k}) = i\psi(\vec{k})\hat{\sigma}^y = \begin{pmatrix} 0 & -\psi \\ \psi & 0 \end{pmatrix} \tag{4}$$

with $\psi(-\vec{k}) = +\psi(\vec{k})$, and by a vector function $\vec{d}(\vec{k})$ for an odd-parity spin-triplet state,

$$\hat{\Delta}(\vec{k}) = i\vec{d}(\vec{k})\cdot\hat{\vec{\sigma}}\hat{\sigma}^y = \begin{pmatrix} -d_x + id_y & d_z \\ d_z & d_x + id_y \end{pmatrix} \tag{5}$$

where $\vec{d}(-\vec{k}) = -\vec{d}(\vec{k})$. In most cases these matrices have the property $\hat{\Delta}\hat{\Delta}^\dagger \propto \hat{\sigma}^0$ (unit matrix), and are called unitary. In the absence of time reversal and/or inversion symmetry this property is lost and we call such states *non-unitary*.

ELECTRONIC PROPERTIES IN THE NORMAL STATE

First we consider the influence of time reversal and inversion symmetry for electronic spectrum. We introduce the general single-particle Hamiltonian assuming a single electronic orbital,

$$\mathscr{H} = \sum_{\vec{k},s} \varepsilon_{\vec{k}} c^{\dagger}_{\vec{k}s} c_{\vec{k}s} + \sum_{\vec{k},s,s'} \vec{g}_{\vec{k}} \cdot \{ c^{\dagger}_{\vec{k}s} \vec{\sigma}_{ss'} c_{\vec{k}s'} \} . \tag{6}$$

The first term is the usual band energy $\varepsilon_{\vec{k}}$. The second term involves the spin density and corresponds to a Zeeman term, if $\vec{g}_{\vec{k}} = -g\mu_B H/2 = -\mu_B H$, but in general represent a spin-orbit coupling contribution characterized by the vector $\vec{g}_{\vec{k}}$. The Hamiltonian transforms under time reversal $\mathscr{K} = -i\hat{\sigma}_y K_0$ (K_0: complex conjugation) and inversion $\mathscr{I}$ as

$$\begin{aligned} &\text{time reversal:} \quad \mathscr{K}\mathscr{H}\mathscr{K}^{\dagger} = \sum_{\vec{k},s} \varepsilon_{-\vec{k}} c^{\dagger}_{\vec{k}s} c_{\vec{k}s} - \sum_{\vec{k},s,s'} \vec{g}_{-\vec{k}} \cdot \{ c^{\dagger}_{\vec{k}s} \vec{\sigma}_{ss'} c_{\vec{k}s'} \} \\ &\text{inversion:} \quad \mathscr{I}\mathscr{H}\mathscr{I}^{\dagger} = \sum_{\vec{k},s} \varepsilon_{-\vec{k}} c^{\dagger}_{\vec{k}s} c_{\vec{k}s} + \sum_{\vec{k},s,s'} \vec{g}_{-\vec{k}} \cdot \{ c^{\dagger}_{\vec{k}s} \vec{\sigma}_{ss'} c_{\vec{k}s'} \} \end{aligned} \tag{7}$$

In order to conserve time reversal symmetry we have to require that,

$$\varepsilon_{\vec{k}} = \varepsilon_{-\vec{k}} \qquad \text{and} \qquad \vec{g}_{\vec{k}} = -\vec{g}_{-\vec{k}} , \tag{8}$$

while invariance under inversion symmetry needs,

$$\varepsilon_{\vec{k}} = \varepsilon_{-\vec{k}} \qquad \text{and} \qquad \vec{g}_{\vec{k}} = +\vec{g}_{-\vec{k}} . \tag{9}$$

Note if both symmetries are intact then it is required that $\vec{g}_{\vec{k}} = 0$.

Electron spectra in the absence of key symmetries

Lack of time reversal symmetry

We now consider a standard situation of violated time reversal symmetry, a uniform external magnetic field or a ferromagnetic state. In both cases we may replace $\vec{g}_{\vec{k}}$ by a $\vec{k}$-independent vector which we choose to point along the z-axis,

$$\vec{g}_{\vec{k}} = -\mu_B H s\hat{z} \quad \text{or} \quad \vec{g}_{\vec{k}} = -\mu_B M s\hat{z} , \tag{10}$$

with $M\hat{z}$ being the magnetization of the ferromagnet. The Hamiltonian is then given by

$$\mathscr{H} = \sum_{\vec{k},s} \{ \varepsilon_{\vec{k}} + hs \} c^{\dagger}_{\vec{k}s} c_{\vec{k}s} \quad \Rightarrow \quad \tilde{\varepsilon}_{\vec{k}s} = \varepsilon_{\vec{k}} + sh . \tag{11}$$

The lack of inversion symmetry yields a spin splitting of the Fermi surface into a majority and a minority spin band. Consequently also the Fermi surface is split and spin degeneracy is lost (see Fig.1). Note that here $\vec{g}_{\vec{k}} = +\vec{g}_{-\vec{k}}$ is an even function of $\vec{k}$ such that inversion symmetry is conserved ($\varepsilon_{\vec{k}} = \varepsilon_{-\vec{k}}$ is always assumed to be valid).

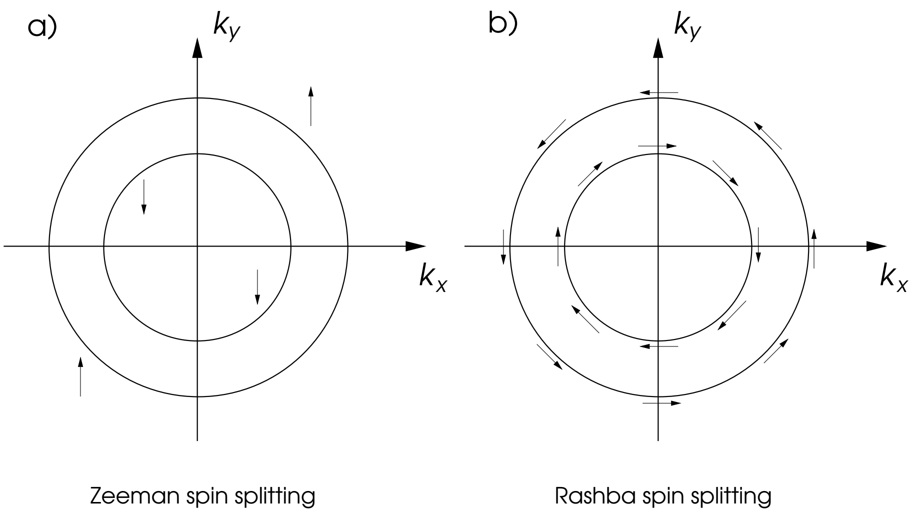

FIGURE 1. Spin-splitting of the Fermi surfaces: a) spin splitting in a majority and minority spin Fermi surface due to a Zeeman field; b) spin splitting with a $\vec{k}$-dependent antisymmetric spin-orbit coupling, here due to Rashba-like spin-orbit coupling $((\vec{k}\times\hat{z})\cdot\vec{S})$.

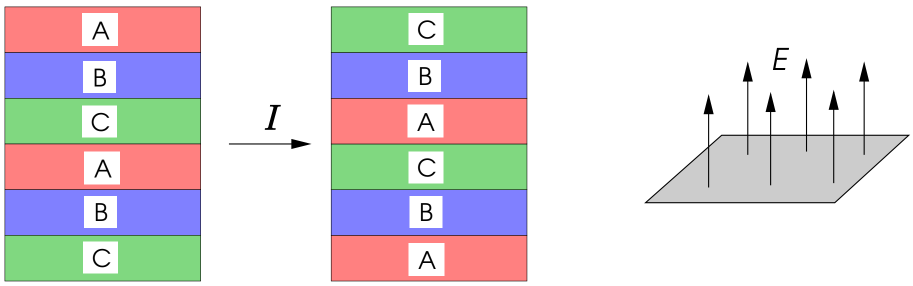

FIGURE 2. Non-centrosymmetricity: Left panel: The ABC-stacking yields a non-centrosymmetric structure. Under inversion operation it is turned in to a CBA-stacking, such that the $z \rightarrow -z$-symmetry is lacking. The equivalent situation is depicted in the right panel where an electric field is applied perpendicular to a thin film. Under inversion $\vec{E} \rightarrow -\vec{E}$.

Lack of inversion symmetry

Inversion symmetry is absent in materials whose crystals lattices has no inversion center (”non-centrosymmetric” materials). It can also be broken by electric fields. However, since generally metals screen external electric fields, an external electric field could only have such an effect, if is applied perpendicular to a very thin metallic film. There are many different space groups of materials without inversion center. We consider here one of the most simple cases, a tetragonal crystal with a non-centrosymmetric stacking along the z-axis (Fig. 2). There is not mirror plane parallel to the basal plane, so that the operation $z \rightarrow -z$ is missing as becomes clear in Fig.2. Thus, the point group is not D_{4h} but C_{4v} only which does not contain the symmetry element of inversion. This situation is analogue to a thin film with a transverse electric field. This field does not exert any work on the electron. However, through relativistic effects it introduces the spin-orbit coupling,

$$-\frac{e}{2mc^2}(\vec{\nabla}U(\vec{r})\times\vec{v})\cdot\vec{S}=\frac{e}{2mc^2}\{\vec{E}\times\vec{v}\}\cdot\vec{S}\,. \tag{12}$$

Here $U(\vec{r})$ is an internal potential which whose gradient we replace here with uniform electric field as in right panel of Fig.2. This term leads directly to the second term in the Hamiltonian (6) which we can formulate with

$$\vec{g}_{\vec{k}}=\alpha(\hat{z}\times\vec{k}) \tag{13}$$

in a small-$\vec{k}$ expansion. This corresponds to a Rashba-type spin-orbit coupling, an antisymmetric spin-orbit coupling, since, as expected, $\vec{g}_{\vec{k}}=-\vec{g}_{-\vec{k}}$. The electronic spectrum has now the form

$$\tilde{\varepsilon}_{\vec{k}\pm}=\varepsilon_{\vec{k}}\pm|\vec{g}_{\vec{k}}| \tag{14}$$

with eigenstates described by the quasiparticle operators

$$a_{\vec{k}\lambda}=\sum_{s=\uparrow,\downarrow}u_{\lambda s}(\vec{k})c_{\vec{k}s}\quad\text{with}\quad\begin{pmatrix}u_{\lambda\uparrow}\\ u_{\lambda\downarrow}\end{pmatrix}=\frac{1}{\sqrt{2|\vec{g}_{\vec{k}}|(|\vec{g}_{\vec{k}}|+\lambda g^z_{\vec{k}})}}\begin{pmatrix}|\vec{g}_{\vec{k}}|+\lambda g^z_{\vec{k}}\\ \lambda(g^x_{\vec{k}}+ig^y_{\vec{k}})\end{pmatrix}. \tag{15}$$

The eigenstates are given in the *helicity basis* denoted by the index λ, in contrast to the spin basis denoted by s. Again we encounter a spin splitting of the band structure. However, the spin quantization axis is $\vec{k}$-dependent. Note that the lines $\vec{k}\parallel\hat{z}$ are singular in the sense that the spin splitting vanishes ($\vec{g}_{\vec{k}}$).

This basic properties are realized in the non-centrosymmetric superconductors, such as $CePt_3Si$, $CeRhSi_3$ and $CeIrSi_3$. Based on symmetry the antisymmetric spin-orbit coupling for the point group C_{4v} can be extended to the $\vec{g}$-vector expansion [21, 22]

$$\vec{g}_{\vec{k}}=\alpha(\hat{x}k_y-\hat{y}k_x)+\alpha'\hat{z}k_xk_yk_z(k_x^2-k_y^2)\,. \tag{16}$$

However, we will ignore the higher order term pointing along the z-axis in later discussions, as it is supposed to be small. Other non-centrosymmetric materials have different crystal structures characterized by their specific $\vec{g}_{\vec{k}}$-vectors. For example, Li_2Pd_3B and Li_2Pd_3B have cubic crystal structure and the point group O which has no inversion center. In this case the $\vec{g}_{\vec{k}}$-vector is given by

$$\vec{g}_{\vec{k}}=\alpha_1\vec{k}+\alpha_2\left\{k_x(k_y^2+k_z^2)\hat{x}+k_y(k_z^2+k_x^2)\hat{y}+k_z(k_x^2+k_y^2)\hat{z}\right\}\,. \tag{17}$$

Here the spin structure on the split bands is more complex.

SUPERCONDUCTING INSTABILITY AND ANDERSON'S THEOREM

We will now consider how the lack of key symmetries influences the superconductivity. For this purpose we start with a generic pairing interaction,

$$H_{pair}=\frac{1}{2\Omega}\sum_{\vec{k},\vec{k}'}\sum_{s_1,s_2,s_1',s_2'}V_{s_1,s_2,s_2',s_1'}(\vec{k},\vec{k}')c^\dagger_{\vec{k}s_1}c^\dagger_{-\vec{k}s_2}c_{-\vec{k}'s_2'}c_{\vec{k}'s_1'} \tag{18}$$

where we write the matrix element $V_{s_1,s_2,s_2',s_1'}(\vec{k},\vec{k}')$ in a spectral form

$$\begin{aligned} V_{s_1,s_2,s_2',s_1'}(\vec{k},\vec{k}') &= \sum_a v_a (i\psi_a^*(\vec{k})\hat{\sigma}^y)_{s_1 s_2}(i\psi_a(\vec{k})\hat{\sigma}^y)^\dagger_{s_2' s_1'} \\ &\qquad + \sum_b v_b (i\vec{d}_b(\vec{k})\cdot\hat{\vec{\sigma}}\hat{\sigma}^y)_{s_1 s_2}(i\vec{d}_b(\vec{k}')\cdot\hat{\vec{\sigma}}\hat{\sigma}^y)^\dagger_{s_2' s_1'} . \end{aligned} \tag{19}$$

The different pairing channels are represented by the gap functions $\psi_a(\vec{k})$ and $\vec{d}_b(\vec{k})$ with the corresponding matrix elements v_a and v_b, respectively. Note, that the following orthonormalization applies here:

$$\langle \psi_a^*(\vec{k})\psi_{a'}(\vec{k})\rangle_{\vec{k}} = \delta_{aa'} \quad \text{and} \quad \langle \vec{d}_b^*(\vec{k})\cdot\vec{d}_{b'}(\vec{k})\rangle_{\vec{k}} = \delta_{bb'} , \tag{20}$$

where $\langle\ldots\rangle_{\vec{k}}$ denotes an angular average over the Fermi surface. This pairing interaction conserves both key symmetries. First we consider the question how the superconducting states is affected when we turn on symmetry-reducing terms in the Hamiltonian. For this purpose we use the Hamiltonian in Eq.(6) in combination with H_{pair} and view $\vec{g}_{\vec{k}}$ as a small perturbation.

We choose one dominant pairing channel and study behavior of the transition temperature when the symmetry-lowering term is turned on. Technically it is most straightforward to use the Green's function formalism as is shown in the Appendix. For simplicity we assume here that always one of the two symmetries is conserved, such that the relation holds $\vec{g}_{-\vec{k}} = \pm\vec{g}_{\vec{k}}$.

Even-parity spin-singlet pairing

First we assume even-parity pairing to be dominant, represented by $\psi(\vec{k}) = \psi_a(\vec{k})$. The critical temperature is determined by the equation,

$$\ln\left(\frac{T_c}{T_{c0}}\right) = \left\langle |\psi_a(\vec{k})|^2 \left\{1 + \hat{g}_{\vec{k}}\cdot\hat{g}_{-\vec{k}}\right\} f(\rho_{\vec{k}})\right\rangle_{\vec{k}} \tag{21}$$

where the function $f(\rho)$ is defined as

$$f(\rho) = Re\sum_{n=1}^{\infty}\left(\frac{1}{2n-1+i\rho} - \frac{1}{2n-1}\right) \tag{22}$$

and

$$\rho_{\vec{k}} = \frac{|\vec{g}_{\vec{k}}|}{\pi k_B T_c} \tag{23}$$

with the following limiting behaviors:

$$f(\rho) = \begin{cases} -\dfrac{7}{8}\zeta(3)\rho^2 , & \rho \ll 1 \\[2ex] -\dfrac{\ln\rho}{2} - \dfrac{\gamma}{2} - \dfrac{\ln 2}{2} - \dfrac{1}{12\rho^2} + \cdots , & \rho \gg 1 \end{cases} \tag{24}$$

with $\gamma = 0.5772157$ as the Euler constant and $\zeta(3) = 1.202$ the zeta function. Moreover, T_{c0} is the original transition temperature, obtained from

$$k_B T_{c0} = 1.14 \varepsilon_c e^{-1/N(0)v_a} \tag{25}$$

with $N(0)$ as the density of states at the Fermi surface for $\vec{g}_{\vec{k}} = 0$ and ε_c as a cutoff energy characteristic for the pairing interaction.

As is obvious from Eq.(21), removing inversion symmetry $\hat{g}_{\vec{k}} = -\hat{g}_{-\vec{k}}$ does not lead to a reduction of the transition temperature T_c, consistent with Anderson's theorem. On the other hand, violating time reversal symmetry, e.g. by applying a magnetic field $\vec{g}_{\vec{k}} = -\mu_B \vec{H}$, leads to a reduction of T_c following the equation,

$$\ln\left(\frac{T_c}{T_{c0}}\right) = 2f\left(\frac{\mu_B H}{\pi k_B T_c}\right) . \tag{26}$$

For small fields $\mu_B H \ll k_B T_{c0}$ we find

$$\frac{T_c}{T_{c0}} \approx 1 - \frac{7\zeta(3)}{4\pi^2}\left(\frac{\mu_B H}{k_B T_{c0}}\right)^2 . \tag{27}$$

The critical value of the magnetic field for the complete suppression of superconductivity is obtained through the condition $T_c \to 0 \quad \Rightarrow \quad \rho_{\vec{k}} \to \infty$, such that

$$\ln\left(\frac{T_c}{T_{c0}}\right) \approx -\ln\left(\frac{2e^{\gamma}\mu_B H}{\pi k_B T_c}\right) \quad \Rightarrow \quad \mu_B H_p' = \frac{\pi}{e^{\gamma}} k_B T_{c0} = 3.53 k_B T_{c0} . \tag{28}$$

This destructive effect is known as the *paramagnetic limiting* and is based on the destruction of Cooper pairs through the spin polarization. If the field is large enough to the break up the spin-singlet Cooper pair in order to gain energy through spin polarization. This analysis suggest a continuous transition as the field is increased. However, the comparison of the condensation energy of the superconducting state and the spin polarization energy of the normal phase,

$$E_{cond} = -\frac{N(0)}{2}|\Delta|^2 \qquad \text{and} \qquad E_{spin} = -\frac{\chi_P}{2}H^2 \tag{29}$$

gives a critical field

$$\mu_B H_p = \frac{|\Delta|}{\sqrt{2}} = \frac{1.764}{\sqrt{2}} k_B T_{c0} = 1.248 k_B T_{c0} < \mu_B H_p' . \tag{30}$$

This transition is first order and the critical field lower. Therefore the real suppression occurs as a first order transition at a lower critical field.

The paramagnetic limiting effect is different from the orbital depairing which destroys Cooper pairs, if the electrons are confined on a length smaller than the magnetic length ℓ smaller than the extension of the Cooper pairs, given by the coherence length ξ_0:

$$\ell^2 = \frac{\hbar c}{eH} \sim \xi_0^2 \quad \Rightarrow \quad H_{c2} = \frac{\Phi_0}{2\pi\xi_0^2} \tag{31}$$

with $\Phi_0 = \frac{hc}{2e}$ as the flux quantum. The field H_{c2} is generally called the upper critical field. Only, if the coherence length is very short, H_{c2} is large enough, such that paramagnetic depairing plays a role.

Odd-parity spin-triplet pairing

Next we consider the case of a dominant odd-parity pairing state with the gap function $\vec{d}_b(\vec{k})$. The critical temperature T_c obeys the equation,

$$\ln\left(\frac{T_c}{T_{c0}}\right) = \left\langle \left\{ 2\left(\vec{d}_b^*(\vec{k})\cdot\hat{g}_{\vec{k}}\right)\left(\vec{d}_b(\vec{k})\cdot\hat{g}_{-\vec{k}}\right) + \left|\vec{d}_b(\vec{k})\right|^2\left(1-\hat{g}_{\vec{k}}\cdot\hat{g}_{-\vec{k}}\right)\right\} f(\rho_{\vec{k}}) \right\rangle_{\vec{k}} \tag{32}$$

where $f(\rho)$ is given by Eq.(22) and $T_{c0} = 1.14\varepsilon_c \exp(-1/N(0)v_b)$.

First we consider the effect of removing inversion symmetry, $\vec{g}_{\vec{k}} = -\vec{g}_{-\vec{k}}$ and obtain

$$\begin{aligned} \ln\left(\frac{T_c}{T_{c0}}\right) &= -2\left\langle \left|\vec{d}_b(\vec{k})\cdot\hat{g}_{\vec{k}}\right|^2 - \left|\vec{d}_b(\vec{k})\right|^2 f(\rho_{\vec{k}}) \right\rangle_{\vec{k}} \\ &= 2\left\langle \left|\vec{d}_b(\vec{k})\times\hat{g}_{\vec{k}}\right|^2 f(\rho_{\vec{k}}) \right\rangle_{\vec{k}} . \end{aligned} \tag{33}$$

The critical temperature T_c is bound to shrink, whenever the right hand side of Eq.(33) is finite. The condition $\vec{d}_b(\vec{k} \parallel \vec{g}_{\vec{k}}$, however, yields a case for which T_c remains unaffected. Such an odd-parity state is protected against the loss of inversion symmetry. In order to see the general behavior of T_c we use again Eq.(24). For $\langle|\vec{g}_{\vec{k}}|\rangle_{\vec{k}} \ll k_B T_{c0}$ we find

$$\frac{T_c}{T_{c0}} = 1 - \frac{7\zeta(3)}{4}\frac{\left\langle |\vec{d}_b(\vec{k})\times\vec{g}_{\vec{k}}|^2\right\rangle_{\vec{k}}}{(\pi k_B T_{c0})^2} . \tag{34}$$

For the limit $\langle|\vec{g}_{\vec{k}}|\rangle_{\vec{k}} \gg k_B T_{c0}$ we obtain

$$\begin{aligned} \ln-\left(\frac{T_c}{T_{c0}}\right) &= \left\langle \left|\vec{d}_b(\vec{k})\times\hat{g}_{\vec{k}}\right|^2 \ln(\rho_{\vec{k}}2e^{\gamma}) \right\rangle_{\vec{k}} \\ &\geq -\left\langle \left|\vec{d}_b(\vec{k})\times\hat{g}_{\vec{k}}\right|^2 \right\rangle_{\vec{k}} \ln\left(\langle\rho_{\vec{k}}\rangle_{\vec{k}}2e^{\gamma}\right) . \end{aligned} \tag{35}$$

This leads to

$$\frac{T_c}{T_{c0}} \geq \left(\frac{2e^{\gamma}\langle|\vec{g}_{\vec{k}}|\rangle_{\vec{k}}}{\pi k_B T_c}\right)^{-a} . \tag{36}$$

with $a = \left\langle |\vec{d}_b(\vec{k})\times\hat{g}_{\vec{k}}|^2\right\rangle_{\vec{k}} \leq 1$. If $a = 1$ then we find a critical value $\langle|\vec{g}_{\vec{k}}|\rangle_{\vec{k}c}$:

$$\langle|\vec{g}_{\vec{k}}|\rangle_{\vec{k}c} \geq \frac{\pi}{2e^{\gamma}} k_B T_{c0} = 0.882 k_B T_{c0} \tag{37}$$

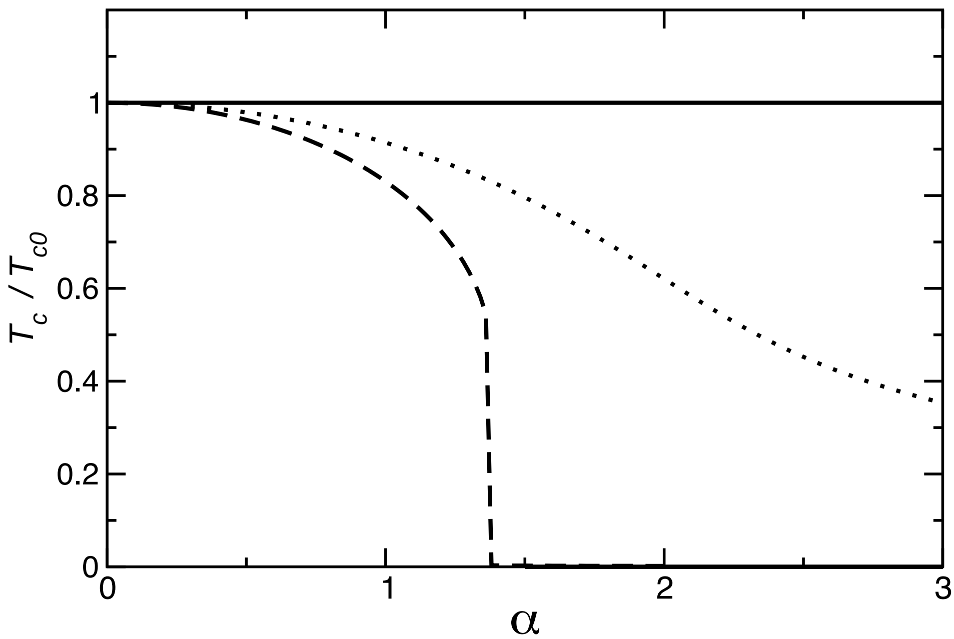

FIGURE 3. Numerically determined transition temperatures for odd-parity states. The horizontal axis is given by α in units of $\pi k_B T_{c0}$. The following pairing states are included: $\vec{d}(\vec{k}) = \hat{x}k_y - \hat{y}k_x$ (solid line) with $a = 0$; $\vec{d}(\vec{k}) = \hat{x}k_x - \hat{y}k_y$ (dotted line) with $a = 1/2$; $\vec{d}(\vec{k}) = \hat{x}k_x + \hat{y}k_y + \hat{z}k_z$ (dashed line) with $a = 1$ [22]. Note that in the last case the transition is not continuous.

On the other hand, if $a < 1$ then no critical value exists and the T_c decreases asymptotically to zero:

$$T_c \geq T_{c0} \left(\frac{\pi k_B T_{c0}}{2e^{\gamma} \langle |\vec{g}_{\vec{k}}| \rangle_{\vec{k}}} \right)^{\frac{a}{1-a}} . \tag{38}$$

The case $a = 1$ corresponds to the situation when $\vec{d}_b(\vec{k}) \cdot \vec{g}_{\vec{k}} = 0$ strictly for all $\vec{k}$. While in all other cases $0 < \alpha < 1$. Obviously, for $\alpha = 0$ there is no reduction of T_c which corresponds to $\vec{d}_b(\vec{k} \parallel \vec{g}_{\vec{k}}$. In Fig.3 typical examples of the behavior T_c as a function of α is depicted using $\vec{g}_{\vec{k}} = \alpha(\hat{z} \times \vec{k})/k_F$. It is important to see that T_c is reduced on energy scales of the order of $\alpha \sim k_B T_c$, except for $\vec{d}(\vec{k}) = \hat{x}k_y - \hat{y}k_y \parallel \vec{g}_{\vec{k}}$.

Next we turn to the case of broken time reversal symmetry, by applying a uniform magnetic field, $\vec{g}_{\vec{k}} = -\mu_B \vec{H}$. This leads to

$$\ln\left(\frac{T_c}{T_{c0}}\right) = \frac{2}{H^2} \left\langle \left| \vec{d}_b(\vec{k}) \cdot \vec{H} \right|^2 \right\rangle_{\vec{k}} f\left(\frac{\mu_B H}{\pi k_B T_c}\right) . \tag{39}$$

The superconducting transition remains unaffected, if $\vec{H} \perp \vec{d}_b(\vec{k})$ for all $\vec{k}$. This corresponds to the case of equal-spin pairing, where the spin lies also parallel to the applied magnetic field. In all other cases, a reduction occurs and can be described in analogous way as in the previous calculation. For $\mu_B H \ll k_B T_{c0}$,

$$\frac{T_c}{T_{c0}} \approx 1 - \frac{7\zeta(3)}{4\pi^2} \frac{\mu_B^2 \left\langle \left| \vec{d}_b(\vec{k}) \cdot \vec{H} \right|^2 \right\rangle_{\vec{k}}}{(k_B T_{c0})^2} \tag{40}$$

and for $\mu_B H \gg k_B T_{c0}$ we obtain a critical (paramagnetic limiting) field for $\vec{d}_b(\vec{k}) \parallel \vec{H}$ with the same value as in the spin-singlet pairing case (Eq.(28)). Otherwise we obtain

$$\mu_B H_p(T) = \frac{\pi k_B T_{c0}}{2e^\gamma} \left(\frac{T_{c0}}{T} \right)^{\frac{1-a'}{a'}} \tag{41}$$

for $0 < a' < 1$ with $a' = \langle |\vec{d}_b(\vec{k}) \cdot \vec{H}|^2 \rangle_{\vec{k}} / H^2$.

Our discussion confirms the basic statements of Anderson's theorem. However, it gives also a more detailed overview on the way different pairing states are suppressed when symmetries such as time reversal and inversion are removed. In the case of odd-parity states a rather diverse behavior is found for both types of perturbations. It is important to notice that all even-parity are on this perturbative level unchanged and for the odd-parity channel there remains one "protected" state which is determined by the structure of the antisymmetric spin-orbit coupling. It is the state which perfectly adapts its spin structure to the split band structure. For magnetic fields violating time reversal symmetry all even-parity states are severely vulnerable. Additionally, all odd-parity states suffer depairing which are not equal-spin pairing states with their spin-orientation parallel to the magnetic field.

STRUCTURE OF THE PAIRING STATES

We turn now away from small perturbations which leads to small band splittings only, and study the superconducting states in systems which do not have time reversal or inversion symmetry. The band splitting shall be much larger than the superconducting energy scales. The corresponding Hamiltonian can be given in the respective quasiparticle basis,

$$\mathscr{H} = \sum_{\vec{k},\lambda} \xi_{\vec{k},\lambda} a^\dagger_{\vec{k}\lambda} a_{\vec{k},\lambda} + \frac{1}{2} \sum_{\vec{k},\vec{k}'} \sum_{\lambda,\lambda'} V_{\lambda,\lambda'}(\vec{k},\vec{k}') a^\dagger_{\vec{k}\lambda} a^\dagger_{-\vec{k},\lambda} a_{-\vec{k}'\lambda'} a_{\vec{k}'\lambda'} \tag{42}$$

where the energy dispersion $\xi_{\vec{k}\lambda}$ for the two spin-split bands is labeled by λ and is measured relative to the chemical potential μ. Assuming that paired electrons reside on the same Fermi surface allows us to restrict to zero-momentum Cooper pairs. This aspect is implemented in the pairing interaction of Eq.(42) which includes for Cooper pair scattering within and between the bands, but does not contain any terms describing inter-band pairing. For the ordinary decoupling of the pairing interaction we introduce the gap function of the band λ as

$$\Delta_{\vec{k},\lambda} = - \sum_{\vec{k}',\lambda'} V_{\lambda\lambda'}(\vec{k},\vec{k}') \langle a_{-\vec{k}'\lambda'} a_{\vec{k}'\lambda'} \rangle \, . \tag{43}$$

which yields straightforwardly the Bogolyubov quasiparticle spectrum

$$E_{\vec{k}\lambda} = \sqrt{\xi_{\vec{k}\lambda}^2 + |\Delta_{\vec{k}\lambda}|^2} \,. \tag{44}$$

In this formulation the self-consistence equation has the standard form with the minor extension to two bands,

$$\Delta_{\vec{k}\lambda} = -\sum_{\vec{k}',\lambda'} V_{\lambda\lambda'}(\vec{k},\vec{k}') \frac{\Delta_{\vec{k}'\lambda'}}{2E_{\vec{k}'\lambda'}} \tanh\left(\frac{E_{\vec{k}'\lambda'}}{2k_bT}\right) \,. \tag{45}$$

The linearized gap equation can be derived to discuss the superconducting instability,

$$\begin{aligned}
\Delta_{\vec{k}\lambda} &= -\sum_{\lambda'} \langle V_{\lambda\lambda'}(\vec{k},\vec{k}')\Delta_{\vec{k}'\lambda'}\rangle_{\vec{k}'\lambda'} N_{\lambda'}(0) \int_{-\varepsilon_c}^{+\varepsilon_c} d\xi \frac{1}{2\xi} \tanh\left(\frac{\xi}{2k_bT}\right) \\
&= -\sum_{\lambda'} \langle V_{\lambda\lambda'}(\vec{k},\vec{k}')\Delta_{\vec{k}'\lambda'}\rangle_{\vec{k}'\lambda'} N_{\lambda'}(0) \underbrace{\ln\left(\frac{1.14\varepsilon_c}{k_BT_c}\right)}_{=\gamma}
\end{aligned} \tag{46}$$

where we introduce the density of states $N_\lambda(0)$ on the two Fermi surfaces, and the cutoff energies ε_c is taken to be the same for both bands. The average $\langle\ldots\rangle_{\vec{k}}$ runs over momenta $\vec{k}$ on the Fermi surface of band λ. Then the eigenvalue γ yields the transition temperature,

$$k_BT_c = 1.14\varepsilon_c e^{-1/\gamma} \,. \tag{47}$$

The Cooper pairs on the two Fermi surfaces are coupled via the inter-band pair scattering term included in $V_{+-}(\vec{k},\vec{k}')$ and $V_{-+}(\vec{k},\vec{k}')$. In this way one single transition temperature results.

Superconducting phase in a ferromagnetic material

The first concrete situation we will examine, is a metal with ferromagnetic spin polarization, characterized by

$$\vec{g}_{\vec{k}} = \vec{m} \tag{48}$$

with $\vec{m} = -\mu_B\vec{M}$ denoting the magnetization. The paired states are now connected via inversion symmetry, still valid here. Without loss of generality we choose $\vec{m} \parallel \hat{z}$, such that

$$\begin{aligned}
|\vec{k}+\rangle = |\vec{k}\uparrow\rangle \quad &\Leftrightarrow \quad a_{\vec{k}+} = c_{\vec{k}\uparrow} \,, \\
|\vec{k}-\rangle = |\vec{k}\downarrow\rangle \quad &\Leftrightarrow \quad a_{\vec{k}-} = c_{\vec{k}\downarrow} \,.
\end{aligned} \tag{49}$$

Therefore the state paired with $|\vec{k}\lambda\rangle$ is given by

$$\mathscr{I}|\vec{k}s\rangle = |-\vec{k}s\rangle \quad \Rightarrow \quad \mathscr{I}|\vec{k},\lambda\rangle = |-\vec{k}\lambda\rangle \,. \tag{50}$$

The pairing matrix elements can be expanded in spectral form,

$$V_{\lambda\lambda'}(\vec{k},\vec{k}') = \sum_a v^{(a)}_{\lambda\lambda'} \phi^*_{\lambda,a}(\vec{k}) \phi_{\lambda',a}(\vec{k}') \ . \tag{51}$$

The basis functions $\phi_\lambda(\vec{k})$ possess the symmetries of the pairing amplitude $\langle a_{-\vec{k}\lambda} a_{\vec{k}\lambda} \rangle$ combining to two electrons connected by inversion symmetry. The Fermion sign under exchange of the two electrons yields

$$\begin{aligned} \langle a_{-\vec{k}\lambda} a_{\vec{k}\lambda} \rangle \quad &\stackrel{\text{exchange}}{\longrightarrow} \quad \langle a_{\vec{k}\lambda} a_{-\vec{k}\lambda} \rangle = -\langle a_{-\vec{k}\lambda} a_{\vec{k}\lambda} \rangle \\ \Rightarrow \qquad & V_{\lambda\lambda'}(\vec{k},\vec{k}') = -V_{\lambda\lambda'}(-\vec{k},\vec{k}') = -V_{\lambda\lambda'}(\vec{k},-\vec{k}') \ , \end{aligned} \tag{52}$$

which implies that $\phi_\lambda(-\vec{k}) = -\phi_\lambda(\vec{k})$ has to be an odd function of $\vec{k}$ with

$$\langle \phi^*_{\lambda,a}(\vec{k}) \phi_{\lambda,a'}(\vec{k}) \rangle_{\vec{k}\lambda} = \delta_{aa'} \ . \tag{53}$$

We now address the symmetry of the gap function and the pairing state which is given by the dominant pairing channel as

$$\Delta_{\vec{k}\lambda} = \Delta_\lambda \phi_{\lambda,a}(\vec{k}) \tag{54}$$

In spin space this is given by

$$\Delta_{\vec{k}ss'} = \sum_\lambda \frac{1}{2} \left\{ \hat{\sigma}^0 + \lambda \hat{m} \cdot \hat{\vec{\sigma}} \right\}_{ss'} \Delta_{\vec{k}\lambda} = \left\{ [\psi(\vec{k}) + \vec{d}(\vec{k}) \cdot \hat{\vec{\sigma}}] i \hat{\sigma}^y \right\}_{ss'} \tag{55}$$

which leads to the identification

$$\psi(\vec{k}) = d_z(\vec{k}) = 0 \quad \text{and} \quad \left\{ \begin{array}{l} d_x(\vec{k}) = \dfrac{1}{2}(\Delta_{\vec{k}-} - \Delta_{\vec{k}+}) \\ \\ d_y(\vec{k}) = \dfrac{1}{2i}(\Delta_{\vec{k}-} + \Delta_{\vec{k}+}) \end{array} \right. . \tag{56}$$

This state is a so-called non-unitary pairing state. Unitary pairing states satisfy the condition the gap matrix $\Delta_{ss'}$ in spin space satisfies the condition $\hat{\Delta}_{\vec{k}} \hat{\Delta}^\dagger_{\vec{k}} \propto \hat{\sigma}^0$. Here we obtain

$$\hat{\Delta}_{\vec{k}} \hat{\Delta}^\dagger_{\vec{k}} = (\vec{d}(\vec{k}) \cdot \hat{\vec{\sigma}}) i \hat{\sigma}^y (-i \hat{\sigma}^y)(\vec{d}^*(\vec{k}) \cdot \hat{\vec{\sigma}}) = |\vec{d}(\vec{k})|^2 \hat{\sigma}^0 + i\{\vec{d}(\vec{k}) \times \vec{d}^*(\vec{k})\} \cdot \hat{\vec{\sigma}} \ , \tag{57}$$

where the second term is

$$i\{\vec{d}(\vec{k}) \times \vec{d}^*(\vec{k})\} = \frac{\hat{z}}{2}(\Delta^2_{\vec{k}+} - \Delta^2_{\vec{k}-}) \quad \parallel \ \vec{m} \ , \tag{58}$$

a measure for the imbalance of the condensation of the two spin orientations (↑ and ↓).

A famous example for such a pairing state is the superfluid phase A_1 of ^{3}He which nucleates under pressure in a high enough field. The phase nucleated is characterized by $\Delta_{\vec{k}+} \neq 0$ and $\Delta_{\vec{k}-} = 0$ [3]. As temperature is lowered there is a first order phase transition to the A-phase $\vec{d}(\vec{k}) = \hat{z}(k_x \pm ik_y)$. Other cases are superconducting phases coexisting with ferromagnetism, such as observed in the heavy Fermion superconductors UGe_2[13], URhGe[14] and UCoGe [16]. Detailed studies on the superconducting phases in ferromagnetic metals has been given by Mineev [25, 26, 27].

Superconducting phase in a non-centrosymmetric metal

The situation of pairing in a non-centrosymmetric metal is slightly more complicated through the fact that we have to join electrons in states connected by time reversal operation. In the helicity basis time reversal operation is not trivial as is shown in Appendix B. In this basis the relation

$$\mathscr{K}|\vec{k}\lambda\rangle = t_\lambda(\vec{k})|-\vec{k}\lambda\rangle \tag{59}$$

implies that the pair scattering matrix element in Eq.(42) can be written in the form,

$$V_{\lambda\lambda'}(\vec{k},\vec{k}') = \tilde{V}_{\lambda\lambda'}(\vec{k},\vec{k}')t^*_\lambda(\vec{k})t_{\lambda'}(\vec{k}') \ . \tag{60}$$

Here $\tilde{V}_{\lambda,\lambda'}(\vec{k},\vec{k}')$ is invariant under point group operations g in a simple way,

$$\tilde{V}_{\lambda,\lambda'}(\vec{k},\vec{k}') = \tilde{V}_{\lambda,\lambda'}(g\vec{k},g\vec{k}') \ . \tag{61}$$

Like in the last section we may now represent $\tilde{V}_{\lambda\lambda'}(\vec{k},\vec{k}')$ in a spectral form of Eq.(51). The symmetry of $\phi_\lambda(\vec{k})$ is given by the particle exchange symmetry:

$$\begin{aligned} t_\lambda(\vec{k})\langle a_{-\vec{k}\lambda}a_{\vec{k}\lambda}\rangle \quad &\xrightarrow{\text{exchange}} \quad t_\lambda(\vec{k})\langle a_{\vec{k}\lambda}a_{-\vec{k}\lambda}\rangle = -t_\lambda(-\vec{k})\langle a_{-\vec{k}\lambda}a_{\vec{k}\lambda}\rangle = t_\lambda(\vec{k})\langle a_{-\vec{k}\lambda}a_{\vec{k}\lambda}\rangle \\ \Rightarrow \quad & \tilde{V}_{\lambda\lambda'}(\vec{k},\vec{k}') = \tilde{V}_{\lambda\lambda'}(-\vec{k},\vec{k}') = \tilde{V}_{\lambda\lambda'}(\vec{k},-\vec{k}') \ , \end{aligned} \tag{62}$$

and leads to the result that $\phi_\lambda(\vec{k})$ is an even function of $\vec{k}$.

It is now possible to write the gap function in the spin basis again using $\Delta_{\vec{k}\lambda} = \tilde{\Delta}_{\vec{k}\lambda}t_\lambda(\vec{k}) = \Delta_\lambda\phi_\lambda(\vec{k})t_\lambda(\vec{k})$ using

$$\Delta_{\vec{k}ss'} = \sum_\lambda t_\lambda(\vec{k})u_{\lambda s}(-\vec{k})u_{\lambda s'}(\vec{k})\tilde{\Delta}_{\vec{k}\lambda} \tag{63}$$

which can also be represented as

$$\hat{\Delta}_{\vec{k}} = \sum_\lambda \hat{\Pi}_{\vec{k}\lambda}(\vec{k})\tilde{\Delta}_{\vec{k}\lambda} \quad \Rightarrow \quad \hat{\Pi}_{\vec{k}\lambda} = \frac{1}{2}\left\{\hat{\sigma}^0 + \lambda\hat{g}_{\vec{k}}\cdot\hat{\vec{\sigma}}\right\}i\hat{\sigma}^y \ . \tag{64}$$

It is now obvious that the pairing state contains two components, an even- and an odd-parity part:

$$\begin{aligned}\psi(\vec{k}) &= \frac{1}{2}\left\{\tilde{\Delta}_{\vec{k}+}+\tilde{\Delta}_{\vec{k}-}\right\} = \frac{1}{2}\left\{\phi_+(\vec{k})+\phi_-(\vec{k})\right\} \\ \vec{d}(\vec{k}) &= \frac{1}{2}\left\{\tilde{\Delta}_{\vec{k}+}-\tilde{\Delta}_{\vec{k}-}\right\}\hat{g}_{\vec{k}} = \frac{1}{2}\left\{\phi_+(\vec{k})-\phi_-(\vec{k})\right\}\hat{g}_{\vec{k}} \, .\end{aligned} \tag{65}$$

We call this a *mixed-parity* state whose gap function on the two Fermi surfaces can be written

$$\tilde{\Delta}_{\vec{k}\lambda} = \psi(\vec{k}) + \lambda\left\{\hat{g}_{\vec{k}}\cdot\vec{d}(\vec{k})\right\} \, , \tag{66}$$

as the sum and difference, respectively, of the even- and odd-parity component. Note, that the odd-parity part corresponds to the protected state, following from Eq.(32), because

$$|\vec{d}(\vec{k})\cdot\hat{g}_{\vec{k}}|^2 - |\vec{d}(\vec{k})|^2 = 0 \qquad \Rightarrow \qquad T_c = T_{c0} \, . \tag{67}$$

Also this pairing state is non-unitary,

$$\hat{\Delta}_{\vec{k}}\hat{\Delta}^{\dagger}_{\vec{k}} = \left\{|\psi(\vec{k})|^2+|\vec{d}(\vec{k})|^2\right\}\hat{\sigma}^0 + \left\{\psi^*(\vec{k})\vec{d}(\vec{k})+\psi(\vec{k})\vec{d}^*(\vec{k})\right\}\cdot\hat{\vec{\sigma}} + i\left\{\vec{d}(\vec{k})\times\vec{d}^*(\vec{k})\right\}\cdot\hat{\vec{\sigma}} \, . \tag{68}$$

The third term is identical to the one we found in the previous section for superconducting state in a time reversal symmetry breaking environment. It vanishes here. The second term is genuine for a non-centrosymmetric superconductor and is a measure for the difference of the superconducting gaps of the two Fermi surfaces,

$$\psi^*(\vec{k})\vec{d}(\vec{k})+\psi(\vec{k})\vec{d}^*(\vec{k}) = \frac{1}{2}\left\{|\phi_+(\vec{k})|^2-|\phi_-(\vec{k})|^2\right\}\hat{g}_{\vec{k}} = \frac{1}{2}\left\{|\tilde{\Delta}_{\vec{k}+}|^2-|\tilde{\Delta}_{\vec{k}-}|^2\right\}\hat{g}_{\vec{k}} \, . \tag{69}$$

This term is directed along $\hat{g}_{\vec{k}}$ reflecting the broken inversion symmetry.

MICROSCOPIC PAIRING INTERACTION

From now on we will concentrate on various aspects of non-centrosymmetric superconductors. In a first step we analyze the structure of the pairing interaction and the relation to microscopic mechanisms. It is helpful therefore to compare representations of Cooper pair scattering in both the spin and the helicity basis. The former allows us to express the interaction in terms of charge density and spin density coupling, which are familiar, for instance, from electron-phonon and spin fluctuation mediated interaction. As an example we will then consider the case of $CePt_3Si$ and construct a pairing interaction based on spin exchange in order to discuss the possible pairing state.

General interactions

We begin with the derivation of the structure of the pairing interaction in spin space by transforming the pair scattering matrix element from the helicity back to the spin representation. Our starting point is the matrix element $\tilde{V}_{\lambda\lambda'}(\vec{k},\vec{k}')$ which we transform in the following way:

$$\begin{aligned} V_{s_1 s_2 s_2' s_1'}(\vec{k},\vec{k}') &= \sum_{\lambda,\lambda'} \tilde{V}_{\lambda\lambda'}(\vec{k},\vec{k}') t^*_{\lambda}(\vec{k}) u^*_{\lambda s_1}(\vec{k}) u^*_{\lambda s_2}(-\vec{k}) t_{\lambda'}(\vec{k}') u_{\lambda' s_2'}(-\vec{k}') u_{\lambda' s_1'}(\vec{k}') \\ &= \sum_{\lambda,\lambda'} \tilde{V}_{\lambda\lambda'}(\vec{k},\vec{k}') \, \{\hat{\Pi}^{\dagger}_{\vec{k}\lambda}\}_{s_1 s_2} \{\hat{\Pi}_{\vec{k}'\lambda'}\}_{s_2' s_1'} \, . \end{aligned} \tag{70}$$

This form can be decomposed into matrix element for intra-parity and inter-parity pair scattering,

$$\begin{aligned} V_{s_1 s_2 s_2' s_1'}(\vec{k},\vec{k}') &= \sum_{a} \sum_{\lambda,\lambda'} v^{(a)}_{\lambda\lambda'} \phi_{\lambda,a}(\vec{k}) \phi^*_{\lambda',a}(\vec{k}') \\ &\quad \times \Big\{ (i\hat{\sigma}^y)_{s_1 s_2} (i\hat{\sigma}^y)^{\dagger}_{s_2' s_1'} + (i\hat{g}_{\vec{k}} \cdot \hat{\vec{\sigma}} \hat{\sigma}^y)_{s_1 s_2} (i\hat{g}_{\vec{k}'} \cdot \hat{\vec{\sigma}} \hat{\sigma}^y)^{\dagger}_{s_2' s_1'} \\ &\qquad + \lambda (i\hat{g}_{\vec{k}} \cdot \hat{\vec{\sigma}} \hat{\sigma}^y)_{s_1 s_2} (i\hat{\sigma}^y)^{\dagger}_{s_2' s_1'} + \lambda' (i\hat{\sigma}^y)_{s_1 s_2} (i\hat{g}_{\vec{k}'} \cdot \hat{\vec{\sigma}} \hat{\sigma}^y)^{\dagger}_{s_2' s_1'} \Big\} \end{aligned} \tag{71}$$

The basis functions $\phi_{\lambda,a}(\vec{k})$ are even functions of $\vec{k}$, as can be easily verified. The inter-parity scattering contributions are essential to obtain a sizable mixing between even- and odd-parity states.

In order to explore the origin of the different terms of the pairing interaction we consider a general form based on the electron-electron coupling,

$$\mathcal{H}_{int} = \frac{1}{2} \sum_{\vec{q}} \Big\{ \Gamma_{\rho}(\vec{q}) \rho_{\vec{q}} \rho_{-\vec{q}} + \Gamma_s(\vec{q}) \vec{S}_{\vec{q}} \cdot \vec{S}_{-\vec{q}} + i \vec{\Gamma}_g(\vec{q}) \cdot (\vec{S}_{\vec{q}} \times \vec{S}_{-\vec{q}}) \Big\} \tag{72}$$

where

$$\rho_{\vec{q}} = \sum_{\vec{k},s} c^{\dagger}_{\vec{k}+\vec{q},s} c_{\vec{k}s} \quad \text{and} \quad \vec{S}_{\vec{q}} = \frac{1}{2} \sum_{\vec{k},s} c^{\dagger}_{\vec{k}+\vec{q},s} \vec{\sigma}_{ss'} c_{\vec{k}s'} \, . \tag{73}$$

The first two terms are the usual charge density-charge density and spin density-spin density coupling, respectively. Their coefficient is an even function of $\vec{q}$ ($\Gamma_{\rho,s}(-\vec{q}) = \Gamma_{\rho,s}(\vec{q})$). The third term describes a special spin density-spin density coupling for a non-centrosymmetric metal and has the structure of a Dzyaloshinsky-Moriya interaction [28]. The coefficient $\vec{\Gamma}_g(\vec{q})$ has the same symmetry as $\vec{g}_{\vec{k}}$ and is an odd function of $\vec{q}$ in order to maintain the proper symmetry ($\vec{\Gamma}_g(\vec{q}) = -\vec{\Gamma}_g(-\vec{q})$). It is now straightforward to express the pair scattering matrix element in the decomposition of intra- and inter-parity components, as done in Eq.(71),

$$
\begin{aligned}
&V_{s_1 s_2 s_2' s_1'}(\vec{k},\vec{k}') \\
&= \frac{1}{2}\left[\left\{\Gamma_\rho(\vec{k}-\vec{k}')+\Gamma_\rho(\vec{k}+\vec{k}')\right\}-\frac{3}{2}\left\{\Gamma_s(\vec{k}-\vec{k}')+\Gamma_s(\vec{k}+\vec{k}')\right\}\right](i\hat{\sigma}^y)_{s_1s_2}(i\hat{\sigma}^y)^\dagger_{s_2's_1'} \\
&+\frac{1}{2}\left[\left\{\Gamma_\rho(\vec{k}-\vec{k}')-\Gamma_\rho(\vec{k}+\vec{k}')\right\}+\frac{1}{2}\left\{\Gamma_s(\vec{k}-\vec{k}')-\Gamma_s(\vec{k}+\vec{k}')\right\}\right]\sum_\mu(i\hat{\vec{\sigma}}^\mu\hat{\sigma}^y)_{s_1s_2}(i\hat{\vec{\sigma}}^\mu\hat{\sigma}^y)^\dagger_{s_2's_1'} \\
&+\frac{1}{8}\sum_\nu\left[\left\{\Gamma_g^\nu(\vec{k}-\vec{k}')-\Gamma_g^\nu(\vec{k}+\vec{k}')\right\}(i\hat{\sigma})_{s_1s_2}(i\hat{\sigma}^\nu\hat{\sigma}^y)^\dagger_{s_2's_1'}\right. \\
&\qquad\left.+\left\{\Gamma_g^\nu(\vec{k}-\vec{k}')+\Gamma_g^\nu(\vec{k}+\vec{k}')\right\}(i\hat{\sigma}^\nu\hat{\sigma}^y)_{s_1s_2}(i\hat{\sigma})^\dagger_{s_2's_1'}\right]
\end{aligned}
\tag{74}
$$

The symmetry properties of the coefficients of Eq.(71) and (74) are identical, as can be easily verified. Obviously the inter-parity term appears as a spin-fluctuation mediated exchange term in the microscopic Hamiltonian.

Toy model for pairing interaction in $CePt_3Si$

We consider now the example of $CePt_3Si$ in order to construct a toy model for the pairing interaction based on spin fluctuations and to discuss the possible pairing states. For this purpose we use a simple lattice model whose band structure is given within a nearest neighbor tight binding approximation and also the interaction terms are restricted to nearest-neighbor coupling only. The compound $CePt_3Si$ shows a phase transition to an antiferromagnetically ordered state at a temperature only slight above the superconducting phase transition. Upon pressure the antiferromagnetic phase can be suppressed with a quantum critical point around $p_c^{(AF)} \approx 0.6GPa$. Superconductivity survives only up to slightly higher pressure of $p_c^{(SC)} \approx 1.5GPa$, suggesting that the pairing interaction is caused by magnetic fluctuations. In the tetragonal crystal lattice the antiferromagnetic order is of A-type nature, i.e. ferromagnetic in the x-y-plane and staggered along the z-axis. The crystal lattice has the point group C_{4v} which leads in a single-band picture to the following tight-binding Hamiltonian with nearest-neighbor hopping:

$$
\mathscr{H}_{kin} = -\sum_{i,\vec{a},s} t_{\vec{a}} c^\dagger_{\vec{r}_i+\vec{a}s} c_{\vec{r}_is} + \sum_{i,\vec{a}}\sum_{s,s'} \vec{\lambda}_{\vec{a}} \cdot c^\dagger_{\vec{r}_i+\vec{a}s} \vec{\sigma}_{ss'} c_{\vec{r}_is'} \tag{75}
$$

where the antisymmetric spin-orbit coupling is given by a Rashba term with $\vec{\lambda}_{\vec{a}} = i\alpha(\hat{z}\times\hat{a})$ and $\vec{a}$ denotes the lattice basis vectors ($\hat{a} = \vec{a}/|\vec{a}|$). The transformation into momentum space leads to

$$
\mathscr{H}_{kin} = \sum_{\vec{k},s,s'} \left\{\varepsilon_{\vec{k}}\hat{\sigma}^0 + \vec{g}_{\vec{k}}\cdot\hat{\vec{\sigma}}\right\}_{ss'} c^\dagger_{\vec{k}s} c_{\vec{k}s'} \tag{76}
$$

with

$$\varepsilon_{\vec{k}} = -2\sum_{\vec{a}} t_{\vec{a}} \cos(\vec{k}\cdot\vec{a}) = -2t'[\cos(k_x a)+\cos(k_y a)] - 2t'\cos(k_z c) \,, \\ \vec{g}_{\vec{k}} = 2\alpha(\hat{x}\sin(k_y a) - \hat{y}\sin(k_x a)) \,. \tag{77}$$

Next we introduce a spin exchange Hamiltonian in the real space representation. The non-centrosymmetric crystal structure leads to besides the ordinary spin-isotropic Heisenberg exchange also a Dzyaloshinsky-Moriya type interaction. Thus, we can write

$$\mathscr{H}_{ss} = \sum_{i,\vec{a}} \left\{ J_{\vec{a}} \vec{S}_{\vec{r}_i+\vec{a}} \cdot \vec{S}_{\vec{r}_i} + \vec{D}_{\vec{a}} \cdot (\vec{S}_{\vec{r}_i+\vec{a}} \times \vec{S}_{\vec{r}_i}) \right\} \tag{78}$$

where for the A-type antiferromagnetic correlation we choose $J_x = J_y = J < 0$ and $J_z = J' > 0$. The Dzyaloshinsky-Moriya coupling is parametrized as $\vec{D}_{\vec{a}} = D(\hat{z}\times\hat{a})$. In momentum space we use

$$\vec{S}_{\vec{r}_i} = \frac{1}{\sqrt{N}} \sum_{\vec{q}} \vec{S}_{\vec{q}}\, e^{i\vec{q}\cdot\vec{r}_i} \tag{79}$$

and obtain

$$\mathscr{H}_{ss} = \sum_{\vec{q}} \left\{ \tilde{J}_{\vec{q}} \vec{S}_{\vec{q}} \cdot \vec{S}_{-\vec{q}} + \vec{G}_{\vec{q}} \cdot (\vec{S}_{\vec{q}} \times \vec{S}_{-\vec{q}}) \right\} \tag{80}$$

with

$$\tilde{J}_{\vec{q}} = 2J\{\cos(q_x a)+\cos(q_y a)\} + 2J'\cos(q_z c) \,, \\ \vec{G}_{\vec{q}} = 2D\,(-\sin(q_y a), \sin(q_x a), 0) \,, \tag{81}$$

where a and c are the lattice constants in the basal plane and along the z-axis, respectively. With the use of Eq.(71) and (74) we decompose $\mathscr{H}_{ss}$ into its spectral form defining the possible pairing channels,

$$\begin{aligned} & V_{s_1 s_2 s_2' s_1'}(\vec{k},\vec{k}') \\ & = \left\{ v_s \phi_s(\vec{k})\phi_s^*(\vec{k}') + v_d \phi_d(\vec{k})\phi_d^*(\vec{k}') + v_{s'} \phi_{s'}(\vec{k})\phi_{s'}^*(\vec{k}') \right\} (i\hat{\sigma}^y)_{s_1 s_2} (i\hat{\sigma}^y)^\dagger_{s_2' s_1'} \\ & + \left\{ v_p \phi_x(\vec{k})\phi_x^*(\vec{k}') + v_p \phi_y(\vec{k})\phi_y^*(\vec{k}') + v_{p'} \phi_z(\vec{k})\phi_z^*(\vec{k}') \right\} \sum_\mu (i\hat{\vec{\sigma}}^\mu \hat{\sigma}^y)_{s_1 s_2} (i\hat{\vec{\sigma}}^\mu \hat{\sigma}^y)^\dagger_{s_2' s_1'} \\ & + v_D \sum_\nu \left\{ \phi_s(\vec{k}) g_s^\nu(\vec{k}') - \phi_d(\vec{k}) g_d^\nu(\vec{k}') \right\} (i\hat{\sigma}^y)_{s_1 s_2} (i\hat{\sigma}^\nu \hat{\sigma}^y)^\dagger_{s_2' s_1'} \\ & + v_D \sum_\nu \left\{ g_s^\nu(\vec{k})\phi_s^*(\vec{k}') + g_d^\nu(\vec{k})\phi_d^*(\vec{k}') \right\} (i\hat{\sigma}^\nu \hat{\sigma}^y)_{s_1 s_2} (i\hat{\sigma}^y)^\dagger_{s_2' s_1'} \,. \end{aligned} \tag{82}$$

The coefficients are given as

$$v_s = v_d = -3J \,,\ \ v_{s'} = -3J' \,,\ \ v_p = J \,,\ \ v_{p'} = J' \,,\ \ v_D = -\frac{D}{4} \tag{83}$$

The pairing channels are characterized by the basis functions

$$\begin{array}{ll} \phi_s(\vec{k}) = \cos(k_x a) + \cos(k_y a) & \text{extended s-wave} \\ \phi_{s'}(\vec{k}) = \cos(k_z c) & \text{extended s-wave} \\ \phi_d(\vec{k}) = \cos(k_x a) - \cos(k_y a) & \text{d-wave} \end{array} \tag{84}$$

for the even-parity channels and

$$\left. \begin{array}{l} \phi_x(\vec{k}) = \sin(k_x a) \\ \phi_y(\vec{k}) = \sin(k_y a) \\ \phi_z(\vec{k}) = \sin(k_z c) \end{array} \right\} \quad \text{p-wave} \tag{85}$$

for the odd-parity channel. The vectors $\vec{g}_{s,d}(\vec{k})$ describe the inter-parity scattering which for the extended s-wave state is given by

$$\vec{g}_s(\vec{k}) = \hat{x}\sin(k_y z) - \hat{y}\sin(k_x a), 0) \tag{86}$$

and for the d-wave state by

$$\vec{g}_d(\vec{k}) = \hat{x}\sin(k_y z) + \hat{y}\sin(k_x a) \; . \tag{87}$$

Note that $\vec{g}_s(\vec{k})$ has the same symmetry as $\vec{g}_{\vec{k}}$. On the other hand, $\vec{g}_d(\vec{k})$ is has the symmetry $\phi_d(\vec{k})\vec{g}_{\vec{k}}$.

Within this restricted model the leading pairing channel is inplane p-wave pairing. According to our previous discussion of the Anderson theorem spin-orbit coupling only allows for the pairing state with

$$\vec{d}(\vec{k}) = \hat{x}\sin(k_y a) - \hat{y}\sin(k_x a) \tag{88}$$

which combines in the mixed-parity phase with the extended s-wave state,

$$\psi(\vec{k}) = \cos(k_x a) + \cos(k_y a) \; . \tag{89}$$

It is interesting to notice that despite the unconventional nature for the dominant state, within the point group C_{4v} this state belongs to the most symmetric representation and, consequently, is continuously connected with the conventional superconducting phase. Other competing phases would require spin-spin interaction beyond nearest-neighbor coupling. The complete table of states is given here. Note that it is necessary that the odd-parity component is represented by $\vec{d}$-vector which is parallel to $\vec{g}_{\vec{k}}$.

Γ	even-parity $\psi(\vec{k})$	odd-parity $\vec{d}(\vec{k})$
A_1	$\cos(k_x a) + \cos(k_y a)$	$\vec{g}_{\vec{k}}$
A_2	$\sin(k_x a)\sin(k_y a)(\cos(k_x a) - \cos(k_y a))$	$\sin(k_x a)\sin(k_y a)(\cos(k_x a) - \cos(k_y a))\vec{g}_{\vec{k}}$
B_1	$\cos(k_x a) - \cos(k_y a)$	$(\cos(k_x a) - \cos(k_y a))\vec{g}_{\vec{k}}$
B_2	$\sin(k_x a)\sin(k_y a)$	$\sin(k_x a)\sin(k_y a)\vec{g}_{\vec{k}}$
E	$\{\sin(k_z c)\sin(k_x a), \sin(k_z c)\sin(k_y a)\}$	$\{\sin(k_z c)\sin(k_x a), \sin(k_z c)\sin(k_y a)\}\vec{g}_{\vec{k}}$

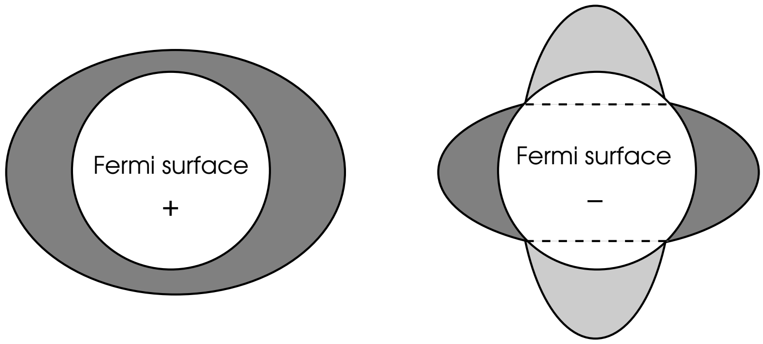

FIGURE 4. Gap structure on the two Fermi surfaces (projection on the k_y-k_z-plane): On the Fermi surface $\lambda = +$ we find the sum of the even- and odd-parity part of the gap yielding full (anisotropic gap) while on the Fermi surface $\lambda = -$ it is the difference yielding tow horizontal line nodes (dashed lines).

We list here the odd-parity states which are equivalent in symmetry to the one given above, but constructed entirely on the basis of nearest-neighbor pairing:

Γ	equivalent $\vec{d}(\vec{k})$
A_2	$\hat{x}\sin(k_x a) + \hat{y}\sin(k_y a)$
B_1	$\hat{x}\sin(k_y a) + \hat{y}\sin(k_x a)$
B_2	$\hat{x}\sin(k_x a) - \hat{y}\sin(k_y a)$

It was found, looking at the spin fluctuation induced pairing interaction, that the only serious competitor among the states listed here belongs to the representation E and with the dominant pairing interaction being inter-plane spin singlet without any intra-plane pairing component [43]. This state needs next-nearest-neighbor coupling and does not appear in the decomposition of Eq.(82). Like most of the other pairing states such a state would have more nodes in gap than the A_1-state, and has, therefore, a disadvantage in gaining condensation energy on weak-coupling approximation level.

Nevertheless, also the A_1-state has nodes, if the odd-parity component is dominant. The mixed parity state has the following gap function

$$\hat{\Delta}_{\vec{k}} = \left\{\Delta_s[\cos(k_x a) + \cos(k_y a)] + \Delta_p[\hat{\sigma}^x \sin(k_y a) - \hat{\sigma}^y \sin(k_x a)]\right\}(i\hat{\sigma}^y) \qquad (90)$$

which yields for the gaps on the two bands

$$\tilde{\Delta}_{\vec{k}\lambda} = \Delta_s[\cos(k_x a) + \cos(k_y a)] + \lambda\Delta_p\sqrt{\sin^2(k_x a) + \sin^2(k_y a)}\,. \qquad (91)$$

Assuming both Δ_s and Δ_p being real and positive and the band is less than half-filled we find an (accidental) node on the gap $\tilde{\Delta}_{\vec{k}-}$ under certain conditions. For $\vec{k} \parallel \hat{z}$ the gap is obviously positive: $\tilde{\Delta}_{\vec{k}-} = 2\Delta_s$, while for $\vec{k}$ in the basal plane find $\tilde{\Delta}_{\vec{k}-} < 0$, if Δ_p is large compared to Δ_s. Generally, a line node is expected to occur, which winds around the z-axis.

This property can be seen more easily assuming a spherical Fermi surface on which the even-parity component is isotropic (Δ_s) and the odd-parity component has the form

$\vec{d}(\vec{k}) = \Delta_p(\hat{x}k_y - \hat{y}k_x)$. The moduli of the two gaps are then given by

$$|\tilde{\Delta}_{\vec{k}\lambda}| = |\Delta_s + \lambda\Delta_d|\sin\theta_{\vec{k}}|| \tag{92}$$

where $\theta_{\vec{k}}$ is the angle of $\vec{k}$ on the Fermi surface with the c-direction . In this case we obtain on the band $\lambda = -$ a horizontal line node for the condition $\Delta_s \leq \Delta_p$ at the angle $\sin\theta_{\vec{k}} = \Delta_s/\Delta_p$ (see Fig.4). Note that for $\Delta_s = \Delta_p$ there is single (broad) node at the equator ($k_z = 0$), while for $\Delta_s \ll \Delta_p$ the nodes shrink to points at the two poles ($k_x = k_y = 0$).

Experiments on $CePt_3Si$ show low-temperature powerlaw behavior in the London penetration depth $\Delta\lambda \propto T$[29, 30], the NMR relaxation time $(TT_1)^{-1} \propto T^2$ [31], heat conductance $\kappa \propto T^2$ [38] and specific heat [32]. These results are consistent with the nodes suggested here. However, the coexistence with antiferromagnetism complicates the situation and it has been suggested that the magnetic order may additionally influence the low-energy quasiparticle excitation spectrum in the superconducting phase [39, 40]. Moreover, it was found that the NMR-T_1^{-1} has a Hebel-Slichter peak at T_c which is generally viewed as a sign of conventional s-wave type pairing [41]. Also this feature is consistent with the pairing state belonging to the A_1-representation as it promotes a coherence effect [42].

SPIN SUSCEPTIBILITY

Since via the spin splitting of the electron band the lack of inversion symmetry has a strong influence on the spin structure of Cooper pairs, the spin polarizability through a magnetic field is affected in a characteristic way [33, 34, 35, 36]. Before addressing the situation in the superconducting state we consider first the normal state spin susceptibility.

The Zeeman coupling to the spin introduces an additional contribution to the spin dependent part of the kinetic energy,

$$\mathscr{H}_{kin} = \sum_{\vec{k},s,s'} \left\{ \xi_{\vec{k}}\hat{\sigma}^0 + (\vec{g}_{\vec{k}} - \mu_B\vec{H}) \cdot \hat{\vec{\sigma}} \right\}_{ss'} c^{\dagger}_{\vec{k}s} c_{\vec{k}s'} \tag{93}$$

with $\xi_{\vec{k}} = \varepsilon_{\vec{k}} - \mu$. We expand the energy of the eigenstates for small magnetic fields,

$$\begin{aligned} \tilde{\xi}_{\vec{k},\lambda}(\vec{H}) &= \xi_{\vec{k}} + \lambda\sqrt{(\vec{g}_{\vec{k}} - \mu_B\vec{H})^2} \\ &\approx \tilde{\xi}_{\vec{k}\lambda} - \lambda\mu_b\hat{g}_{\vec{k}} \cdot \vec{H} - \lambda\frac{\mu_B^2}{|\vec{g}_{\vec{k}}|}\{\vec{H}^2 - (\hat{g}_{\vec{k}} \cdot \vec{H})^2\} \\ &= \tilde{\xi}_{\vec{k}\lambda} - \lambda A_{\vec{k}} - \lambda B_{\vec{k}} \end{aligned} \tag{94}$$

with $A_{\vec{k}} = -A_{-\vec{k}}$ and $B_{\vec{k}} = B_{-\vec{k}}$. We then calculate the thermodynamic potential of the electrons

$$\Omega_n(\vec{H},T) = -k_BT\sum_{\vec{k},\lambda}\ln\left(1 + e^{-\tilde{\xi}_{\vec{k}\lambda}(\vec{H})/k_BT}\right) \tag{95}$$

from which we deduce the susceptibility by means of the second derivative,

$$\chi_{\mu\nu} = - \left. \frac{\partial^2 \Omega_n}{\partial H_\mu \partial H_\nu} \right|_{\vec{H}=0} = \mu_B^2 \sum_{\vec{k},\lambda} \left[\frac{\partial f(\tilde{\xi}_{\vec{k}\lambda})}{\partial \tilde{\xi}_{\vec{k},\lambda}} \hat{g}^\mu_{\vec{k}} \hat{g}^\nu_{\vec{k}} + \lambda \frac{f(\tilde{\xi}_{\vec{k}\lambda})}{|\vec{g}_{\vec{k}}|} (\delta_{\mu\nu} - \hat{g}^\mu_{\vec{k}} \hat{g}^\nu_{\vec{k}}) \right] . \tag{96}$$

The first term describes the intraband contribution to susceptibility, while the second term originates from the interband effects, similar to a van Vleck contribution. Assuming that the temperature is much lower than the band splitting, i.e. $\langle |\vec{g}_{\vec{k}}| \rangle_{\vec{k}} \gg k_B T$ and that the density of states is weakly energy dependent over the range of the band splitting, we obtain

$$\begin{aligned} \chi_{\mu\nu} &= \mu_B^2 \sum_\lambda N_\lambda \langle \hat{g}^\mu_{\vec{k}} \hat{g}^\nu_{\vec{k}} \rangle_{\vec{k},\lambda} + N(0) \mu_B^2 \sum_\lambda \langle \delta_{\mu\nu} - \hat{g}^\mu_{\vec{k}} \hat{g}^\nu_{\vec{k}} \rangle_{\vec{k},\lambda} \\ &\approx \chi_P \left\{ \langle \hat{g}^\mu_{\vec{k}} \hat{g}^\nu_{\vec{k}} \rangle_{\vec{k}} + \langle \delta_{\mu\nu} - \hat{g}^\mu_{\vec{k}} \hat{g}^\nu_{\vec{k}} \rangle_{\vec{k}} \right\} = \chi_P \delta_{\mu\nu} \end{aligned} \tag{97}$$

with the Pauli susceptibility defined as $\chi_P = 2\mu_B^2 N(0)$ with the averaged density of states $N(0) = (N_+ + N_-)/2$. The bracket $\langle \ldots \rangle_{\vec{k},\lambda}$ denotes the average over the Fermi surface λ. Eventually we define $\langle \ldots \rangle_{\vec{k}} = \sum_\lambda \langle \ldots \rangle_{\vec{k},\lambda}$ and find that within this approximation the susceptibility is isotropic. The anisotropy which is found in a more extended calculation is irrelevant for our further discussion such that our approximation does not obscure any of the important aspects.

Now we turn to the superconducting phase. The quasiparticle spectrum of the band λ is derived from the eigenvalues of the particle-hole matrix

$$\begin{pmatrix} \tilde{\xi}_{\vec{k}\lambda}(\vec{H}) & \Delta_{\vec{k}\lambda} \\ \Delta^*_{\vec{k}\lambda} & -\tilde{\xi}_{-\vec{k}\lambda}(\vec{H}) \end{pmatrix} = \begin{pmatrix} \tilde{\xi}_{\vec{k}\lambda} - \lambda A_{\vec{k}} - \lambda B_{\vec{k}} & \Delta_{\vec{k}\lambda} \\ \Delta^*_{\vec{k}\lambda} & -\tilde{\xi}_{-\vec{k}\lambda}(\vec{H}) - \lambda A_{\vec{k}} + \lambda B_{\vec{k}} \end{pmatrix} . \tag{98}$$

The two terms, $\lambda A_{\vec{k}}$ (intra-band) and $\lambda B_{\vec{k}}$ (inter-band), enter $E_{\vec{k}\lambda}$ in a different way. The first one is already diagonal in this matrix, while the second one enters in a more complicated way. The thermodynamic potential is given by

$$\Omega_s(\vec{H},T) = -k_B T \sum_{\vec{k},\lambda} \ln \left(1 + e^{-E_{\vec{k}}(\vec{H})} \right\} + \sum_{\vec{k},\lambda} \left\{ \tilde{\xi}_{\vec{k}\lambda}(\vec{H}) - E_{\vec{k}\lambda}(\vec{H}) \right\} + const. \tag{99}$$

First we consider the intra-band contribution which yields a shift of the quasiparticle spectrum,

$$\tilde{\xi}_{\vec{k}\lambda} - \lambda A_{\vec{k}} \quad \Rightarrow \quad E_{\vec{k}\lambda}(\vec{H}) = E_{\vec{k}\lambda} - \lambda A_{\vec{k}} = \sqrt{\tilde{\xi}^2_{\vec{k}\lambda} + |\Delta_{\vec{k}\lambda}|^2} - \lambda A_{\vec{k}} . \tag{100}$$

It is straightforward to obtain the susceptibility

$$\chi^{intra}_{\mu\nu} = \mu_B^2 \sum_{\vec{k},\lambda} \frac{\partial f(E_{\vec{k},\lambda})}{\partial E_{\vec{k}\lambda}} \hat{g}^\mu_{\vec{k}} \hat{g}^\nu_{\vec{k}} = \mu_B^2 \sum_\lambda N_\lambda \langle Y_\lambda(\vec{k},T) \hat{g}^\mu_{\vec{k}} \hat{g}^\nu_{\vec{k}} \rangle_{\vec{k},\lambda} \tag{101}$$

with the Yosida functions on the two bands defined by

$$Y_\lambda(\vec{k},T) = \int d\xi \, \frac{1}{4k_BT\cosh^2(E_{\vec{k},\lambda}/2k_BT)} \, . \tag{102}$$

Now we turn to the inter-band contribution with

$$\tilde{\xi}_{\vec{k}\lambda} - \lambda B_{\vec{k}} \quad \Rightarrow \quad E_{\vec{k}\lambda}(\vec{H}) = \sqrt{[\tilde{\xi}_{\vec{k}\lambda} - \lambda B_{\vec{k}}]^2 + |\Delta_{\vec{k}\lambda}|^2} \, . \tag{103}$$

The susceptibility takes the form

$$\chi^{inter}_{\mu\nu} = \mu_B^2 \sum_{\vec{k},\lambda} \lambda \left[\frac{\tilde{\xi}_{\vec{k}\lambda}}{E_{\vec{k}\lambda}} f(E_{\vec{k}\lambda}) + \left\{ 1 - \frac{\tilde{\xi}_{\vec{k}\lambda}}{E_{\vec{k}\lambda}} \right\} \right] \frac{\delta_{\mu\nu} - \hat{g}^\mu_{\vec{k}} \hat{g}^\nu_{\vec{k}}}{|\vec{g}_{\vec{k}}|} \, . \tag{104}$$

The first term gives a negligible contribution while from the second we obtain

$$\begin{aligned} \chi^{inter}_{\mu\nu} &= \mu_B^2 \sum_{,\lambda} \lambda \int d\tilde{\xi}_\lambda \, N_\lambda \left\langle \left\{ 1 - \frac{\tilde{\xi}_\lambda}{\sqrt{\tilde{\xi}^2_\lambda + |\Delta_{\vec{k}\lambda}|^2}} \right\} \frac{\delta_{\mu\nu} - \hat{g}^\mu_{\vec{k}} \hat{g}^\nu_{\vec{k}}}{|\vec{g}_{\vec{k}}|} \right\rangle_{\vec{k},\lambda} \\ &\approx 2\mu_B^2 N(0) \langle \delta_{\mu\nu} - \hat{g}^\mu_{\vec{k}} \hat{g}^\nu_{\vec{k}} \rangle_{\vec{k},\lambda} + O\left(\left\langle \frac{|\Delta_{\vec{k}\pm}|^2}{|g_{\vec{k}}|^2} \right\rangle_{\vec{k}\pm} \right) \, . \end{aligned} \tag{105}$$

The correction due to superconductivity is small assuming that the band splitting is much larger than the superconducting gap. In this interband contribution the quasiparticle gap does not play a role, since the band gap is much larger. Collecting the two terms we obtain an expression for the susceptibility

$$\begin{aligned} \chi_{\mu\nu} &= \chi^{intra}_{\mu\nu} + \chi^{inter}_{\mu\nu} = \chi_P \left\{ \delta_{\mu\nu} - \langle \hat{g}^\mu_{\vec{k}} \hat{g}^\nu_{\vec{k}} \rangle_{\vec{k}} + \sum_\lambda \frac{N_\lambda}{N(0)} \langle Y_\lambda(\vec{k},T) \hat{g}^\mu_{\vec{k}} \hat{g}^\nu_{\vec{k}} \rangle_{\vec{k},\lambda} \right\} \\ &\approx \chi_P \left\{ \delta_{\mu\nu} - \left\langle \hat{g}^\mu_{\vec{k}} \hat{g}^\nu_{\vec{k}} (1 - Y(\vec{k},T)) \right\rangle_{\vec{k}} \right\} \end{aligned} \tag{106}$$

where we introduce the Yosida function averaged over the two bands,

$$Y(\vec{k},T) = \sum_\lambda \frac{N_\lambda}{N(0)} Y_\lambda(\vec{k},T) \, . \tag{107}$$

The resulting susceptibility does only weakly depend on the symmetry of the superconducting state. It is formally very similar to the susceptibility obtained for a spin-triplet superconductor with $\vec{d}(\vec{k}) \parallel \vec{g}_{\vec{k}}$. However, it should be noticed that the spin polarizability does not depend on the relative strength of the odd-parity component in the Cooper pairing state.

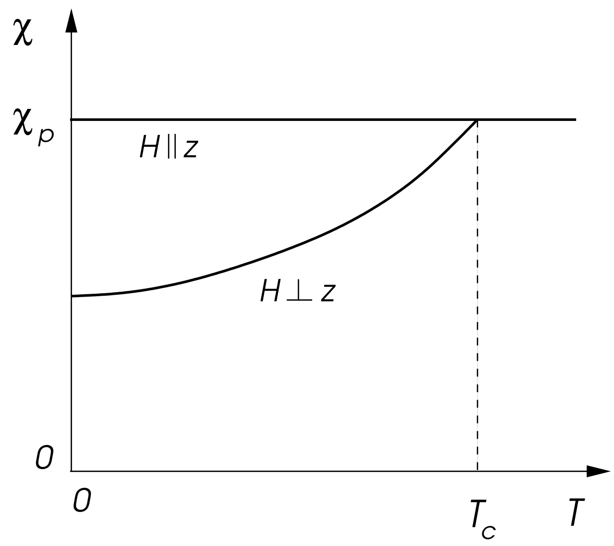

FIGURE 5. Spin susceptibility for a non-centrosymmetric superconductor with $\vec{g}_{\vec{k}} = \alpha(\vec{k} \times \hat{z})$. No suppression of $\chi(T)$ occurs for fields along the z-axis. However, $\chi(T)$ decreases continuously to $\chi_P/2$ for field perpendicular to the z-axis. Note that this property does not include corrections due to the change of the superconducting condensate by so-called magneto-electric contributions for $\vec{H} \perp \hat{z}$.

We consider again the example of $CePt_3Si$ with the point group C_{4v}. With $\vec{g}_{\vec{k}} = \alpha(\hat{z} \times \vec{k})$ the susceptibility below T_c remains constant as for fields along the z-axis and is deduced to half of the Pauli susceptibility for inplane fields:

$$\chi_{zz}(T) = \chi_P \quad \text{and} \quad \chi_{xx} = \chi_{yy} \approx \frac{\chi_P}{2}(1 - Y(T)) \tag{108}$$

where $Y(T)$ represents an averaged Yosida function with $Y(T_c) = 1$ and $Y(0) = 0$ (see Fig.5).

The behavior of the spin susceptibility can be experimentally observed using NMR-Knight shift, i.e. the shift of the NMR resonance lines due to the internal magnetization relative to the external field. This measurement is performed in the mixed superconducting phase where the magnetic field penetrates the superconductor through a vortex lattice. If the vortex cores (the region of suppressed superconducting order parameter) is small compared to their mutual distance and the London penetration depth, the field experienced by the electron spins and the superconducting condensate are essentially uniform. The experimental Knight-shift data for $CePt_3Si$ are not consistent with the expected behavior found in our simple calculation [37]. One reason for this discrepancy could be the coexistence of superconductivity with antiferromagnetism in $CePt_3Si$ as pointed out in Ref.[43, 40].

Paramagnetic limiting effects provides a further opportunity to test the characteristics of the spin susceptibility. It only plays a role for the upper critical field, if usual orbital depairing due to the magnetic field is weak which is true for superconductors with very short coherence lengths. As the coherence length is essentially proportional to the Fermi velocity ($\xi_0 = \hbar v_V F/\pi\Delta_0$), heavy Fermion superconductors show generally a rather weak orbital depairing effect. A rough estimate of the paramagnetic limiting field at

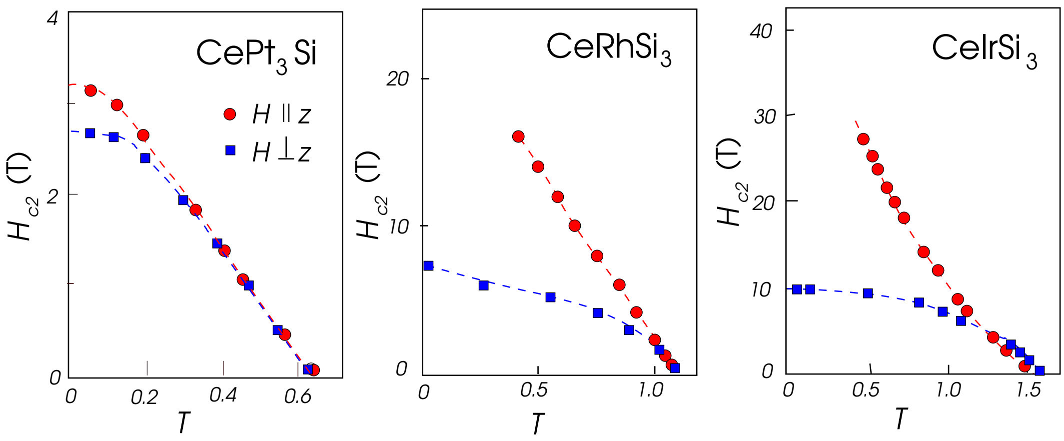

FIGURE 6. Upper critical fields H_{c2} for inplane fields and along the z-axis: CePt$_3$Si at ambient pressure (isotropic H_{c2}) [44]; CeRhSi$_3$ [45] and CeIrSi$_3$ [46] at pressure $p = 2.6 GPa$. The latter two compounds show a strong anisotropy of H_{c2} with a temperature dependence which suggests paramagnetic limiting for $\vec{H} \perp \hat{z}$ while there is a strongly enhanced H_{c2} along the z-axis without any sign of limiting. Data adapted from the Ref. [44, 45, 46].

zero temperature is obtained by comparing the superconducting condensation energy with the difference in the spin polarization energy of the normal and superconducting phase:

$$\begin{aligned} E_{cond} &= -\frac{1}{2}\sum_{\lambda} N_\lambda |\Delta_\lambda(0)|^2 \approx -\frac{1}{2} N(0)(1.764 k_B T_c)^2 \\ E_{spin} &= -\tfrac{1}{2}(\chi(0)_{\mu\mu} - \chi_P) H_\mu^2 \,. \end{aligned} \tag{109}$$

Setting the two energies equal we obtain the paramagnetic limiting field as

$$\mu_B H_{p\mu} = \frac{1.764 k_B T_c}{\sqrt{\chi_{\mu\mu}/\chi_p - 1}} = \begin{cases} \infty & \mu = z \\ 1.764 \times \sqrt{2} k_B T_c & \mu = x, y \end{cases} \,. \tag{110}$$

There is no paramagnetic limiting for fields along the z-axis while for inplane fields the paramagnetic limiting field would be enhanced by a factor $\sqrt{2}$ compared to a spin singlet superconductor (see Eq.(30)).

The measurements of the upper critical fields in CePt$_3$Si are also here inconsistent with the expectations. H_{c2} is surprisingly isotropic although slightly enhanced above the standard paramagnetic limiting. This is, in principle, consistent with the isotropy of the susceptibility found in the Knight shift experiments, but overall it is inconclusive on the intrinsic behavior of the spin polarizability in the superconducting phase. Fortunately, there are other heavy Fermion superconductors with the same point group C_{4v} and, therefore, with the same predictions for the susceptibility. The compounds CeIrSi$_3$ and CeRhSi$_3$ become superconducting only under pressure around an antiferromagnetic quantum critical point. By pressure it is possible to suppress antiferromagnetism and having a purely superconducting phase uncontaminated by other orders. Indeed the observed upper critical fields H_{c2} give a picture qualitatively consistent with our result of the spin susceptibility (see Fig. 6). Actually the upper critical field in these two superconductors takes extraordinarily high values extrapolating in the zero-temperature limit to $\sim 25T$ for $CeRhSi_3$ and to $\sim 40T$ for $CeIrSi_3$ for given pressures [45, 46]. The highest values of the z-axis H_{c2} has been measured for pressures at quantum critical point [46]. It has been suggested by Tada et al. that this may be related to a quantum fluctuation effects important for the pairing interaction [47].

MAGNETO-ELECTRIC PHENOMENA

Magneto-electric effects are a well-known feature in so-called multi-ferroic systems, which show both magnetic and ferroelectric properties, combining time reversal and inversion symmetry breaking [53]. Among other phenomena magnetic field driven ferroelectricity belong to the intriguing manifestations of the interplay between the two kinds of orders. In the case of non-centrosymmetric superconductors magnetic fields yield unusual properties of the superconducting phase. We will consider here two examples: the helical superconducting phase and the spin current carrying surface states.

Helical superconducting phase

In the discussion of the spin susceptibility and the paramagnetic limiting we had been "careless" in some way, since we ignored the influence of the magnetic field on the superconducting condensate. Usually this aspect is not necessary as the effects are not appearing in linear order of the applied field. In non-centrosymmetric superconductors the situation is different. In the last section we neglected the important fact that for magnetic fields with $\vec{H}\cdot\vec{g}_{\vec{k}} \neq 0$ the band centers are generally shifted. This is immediately obvious, if we analyze again Eq.(94) ignoring, however, the $B_{\vec{k}}$-term. We use

$$\tilde{\xi}_{\vec{k}\lambda}(\vec{H}) = \tilde{\xi}_{\vec{k},\lambda} - \lambda\mu_B\vec{H}\cdot\vec{g}_{\vec{k}} \tag{111}$$

and ask the question of where lies the center of the Fermi surface which we define it by

$$\vec{k}_{c\lambda} = \langle \vec{k}\tilde{\xi}_{\vec{k}\lambda}(\vec{H})\rangle_{\vec{k},\lambda} = -\lambda\mu_B\langle(\vec{H}\cdot\vec{g}_{\vec{k}})\vec{k}\rangle_{\vec{k},\lambda} \tag{112}$$

Since $\vec{g}_{\vec{k}}$ is an odd function of $\vec{k}$ this is generally not zero, if $\vec{H}\cdot\vec{g}_{\vec{k}} \neq 0$. Let us consider again the case $\vec{g}_{\vec{k}} = \alpha(\hat{z}\times\vec{k})$, which leads to

$$\vec{k}_{c\lambda} = -\lambda\alpha\frac{k_{F\lambda}^2}{3}\mu_B(\vec{H}\times\hat{z}) \tag{113}$$

assuming essentially spherical Fermi surfaces. The center of the Fermi surface shifts perpendicular to the magnetic field and the z-axis. This behavior contrasts the situation found in a centrosymmetric materials under a magnetic field, where the Fermi surface splits into a majority (parallel) and a minority (antiparallel to the field) spin Fermi surface.

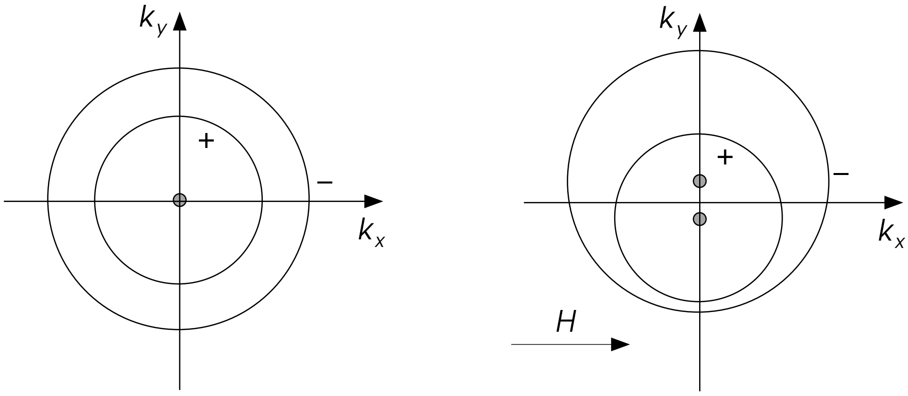

FIGURE 7. The Fermi surface center is shifted proportional to $\vec{H} \times \hat{z}$ in opposite direction for the two sheets. Here depicted for the k_x-k_y-plane.

The question arises now, how the superconducting phase would nucleate under these conditions. Indeed it is more advantageous to form Cooper pairs on the Fermi surface whereby they would necessarily have a finite total momentum, rather than insisting on zero-momentum Cooper pairs which would consist mostly of quasiparticles away from the Fermi surfaces. A gap function with finite momentum would then have a phase factor $\Delta_{\vec{k}} \rightarrow \Delta_{\vec{k}} e^{i\vec{q}_\lambda \cdot \vec{r}}$. Such a phase is called "helical" [48, 49, 50]. In order to discuss these states we turn now to the Ginzburg-Landau formulation.

Ginzburg-Landau discussion

We introduce independent order parameters, η_λ, for both Fermi surfaces. These two components are, however, coupled as to yield a common coherent phase. The free energy expansion contains the following terms:

$$F = F_+ + F_- + F_{+-} + F_{me} + F_{pl} + F_B \tag{114}$$

with

$$
\begin{aligned}
F_\lambda &= \int d^3r \left[a_\lambda(T)|\eta_\lambda|^2 + b_\lambda|\eta_\lambda|^4 + K_\lambda|\vec{D}\eta_\lambda|^2\right] , \\
F_{+-} &= \int d^3r\, c(\eta_+^*\eta_- + \eta_-^*\eta_+) , \\
F_{me} &= \int d^3r \sum_\lambda iK_{me,\lambda}(\vec{H}\times\hat{z})\cdot\left\{\eta_\lambda^*(\vec{D}\eta_\lambda) - \eta_\lambda(\vec{D}\eta_\lambda)^*\right\} , \\
F_{pl} &= \int d^3r \sum_{\lambda,\mu} Q_{\mu\lambda}|\eta_\lambda|^2 H_\mu^2 , \\
F_B &= \int d^3r \frac{\vec{B}^2}{8\pi} .
\end{aligned}
\tag{115}
$$

The first term has the standard form of a Ginzburg-Landau form with $a_\lambda(T) = a'_\lambda(T - T_{c\lambda})$ and $\vec{D} = \vec{\nabla} - \frac{2ei}{\hbar c}\vec{A}$. The second term is a coupling between the order parameters on the two Fermi surfaces on second order, such that their phase is identical ($c < 0$ by definition). The term F_{me} describes the magneto-electric behavior. It represents a Lifshitz invariant, allowed by symmetry to this order. Note that this term exists due to the lack of inversion symmetry (absence of mirror symmetry $z \to -z$), while it conserves time reversal symmetry. Its microscopic origin suggests that the two coefficients K_{me+} and K_{me-} have opposite sign. The term F_{pl} includes the effect of superconductivity on spin polarizability, with $Q_{z\lambda} = 0$, since for fields along the z-axis there is no change of the spin susceptibility according to our previous discussion. Finally the last term includes the magnetic field energy. On the other hand, $Q_{x\lambda} = Q_{y\lambda} > 0$. All coefficients are real. Despite the fact that generally the "critical temperatures" $T_{c\lambda}$ are different for the two Fermi surfaces there is only one transition due to the order parameter coupling in F_{+-}.

We first study the superconducting instability in the absence of a magnetic field which can be obtained through the linearized Ginzburg-Landau equations,

$$
\left.\begin{aligned} a_+\eta_+ + c\eta_- &= 0 \\ c\eta_- + a_-\eta_- &= 0 \end{aligned}\right\} \Rightarrow \quad a_+a_- - c^2 = 0 \tag{116}
$$

leads to the transition temperature

$$
T_c = \frac{1}{2}\left\{T_{c+} + T_{c-} + \sqrt{(T_{c+} - T_{c-})^2 + 4c^2/a'_+a'_-}\right\} . \tag{117}
$$

Below T_c the ratio of the two order parameter components changes as a function of temperature continuously, such that the even- and odd-parity part of the pairing state also vary

$$
\psi(\vec{k}) = \eta_+\tilde{\Delta}_{\vec{k}+} + \eta_-\tilde{\Delta}_{\vec{k}-} \quad \text{and} \quad \vec{d}(\vec{k}) = (\eta_+\tilde{\Delta}_{\vec{k}+} - \eta_-\tilde{\Delta}_{\vec{k}-})\hat{g}_{\vec{k}} . \tag{118}
$$

where we consider $\tilde{\Delta}_{\vec{k}\lambda}$ as renormalized basis function and η_λ determines the magnitude of the gap.

Now we turn to the case of a finite magnetic field. In order to simplify our discussion and to restrict to the essential part we ignore here the orbital coupling ($\vec{A} = 0$ or charge $e \to 0$). Thus, only coupling of the magnetic field to the spin is taken into account here. In particular, we want to avoid the discussion of the vortex phase. However we assume that the magnetic field penetrates the superconductor uniformly in this approximation, as we have turned off the Meissner-Ochsenfeld screening. The linearized Ginzburg-Landau equations are then given by

$$\begin{aligned} (\tilde{a}_+ - K_+\vec{\nabla}^2 - 2iK_{me+}(\vec{H}\times\hat{z})\cdot\vec{\nabla})\eta_+ + c\eta_- &= 0\,, \\ (\tilde{a}_- - K_-\vec{\nabla}^2 - 2iK_{me-}(\vec{H}\times\hat{z})\cdot\vec{\nabla})\eta_- + c\eta_+ &= 0\,. \end{aligned} \tag{119}$$

with

$$\tilde{a}_\lambda = a_\lambda + \sum_\mu Q_{\mu\lambda} H_\mu^2\,. \tag{120}$$

We analyze the instability in Fourier space

$$\eta_\lambda(\vec{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\vec{q}} \eta_{\vec{q}\lambda} e^{i\vec{q}\cdot\vec{r}} \tag{121}$$

leading to the algebraic linear equation,

$$\begin{aligned} (\tilde{a}_+ + K_+\vec{q}^2 + 2K_{me+}(\vec{H}\times\hat{z})\cdot\vec{q})\eta_{\vec{q}+} + c\eta_{\vec{q}-} &= 0 \\ (\tilde{a}_- + K_-\vec{q}^2 + 2K_{me-}(\vec{H}\times\hat{z})\cdot\vec{q})\eta_{\vec{q}-} + c\eta_{\vec{q}+} &= 0 \end{aligned} \tag{122}$$

and the instability condition

$$(\tilde{a}_+ + K_+\vec{q}^2 + 2K_{me+}(\vec{H}\times\hat{z})\cdot\vec{q})(\tilde{a}_- + K_-\vec{q}^2 + 2K_{me-}(\vec{H}\times\hat{z})\cdot\vec{q}) = c^2\,. \tag{123}$$

This equation leads to $T_c(\vec{q},\vec{H})$ where $\vec{q}$ is a parameter used to maximize T_c. There is, in general, a single $\vec{q}_{max}$ such that at the onset

$$\eta_\lambda(\vec{r}) = \eta_{0\lambda} e^{i\vec{q}_{max}\cdot\vec{r}} \tag{124}$$

represents a simple *helical* state [49, 50]. It is easy to see that $\vec{q}_{max} \parallel \vec{H}\times\hat{z}$, such that $\vec{q}_{max}$ and corresponds to the direction of the Fermi surface shift. Since the two Fermi surfaces shift in opposite direction the helicity vector $\vec{q}_{max}$ does not exactly correspond to any of the two shifting wavevectors, but represents a compromise which is more in favor of the dominant Fermi surface. Due to their coupling both order parameters would follow the same helical modulation. At lower temperatures for a given field (or at lower magnetic fields for a given temperature) this single-helicity-vector phase may not remain stable anymore. Obviously, if we completely decouple the two order parameters, setting $c = 0$, we obtain two independent instabilities for η_+ and η_- with their individual wave vectors $\vec{q}_\lambda$. In this case the gap function would even be modulated in its magnitude when both components are finite,

$$\begin{aligned}
\psi(\vec{k},\vec{r}) &= e^{i(\vec{q}_+ + \vec{q}_-)\cdot\vec{r}/2} \left[\left\{ \eta_{0+}\tilde{\Delta}_{\vec{k}+} + \eta_{0-}\tilde{\Delta}_{\vec{k}-} \right\} \cos\left(\frac{(\vec{q}_+ - \vec{q}_-)\cdot\vec{r}}{2} \right) \right. \\
&\qquad \left. + i \left\{ \eta_{0+}\tilde{\Delta}_{\vec{k}+} - \eta_{0-}\tilde{\Delta}_{\vec{k}-} \right\} \sin\left(\frac{(\vec{q}_+ - \vec{q}_-)\cdot\vec{r}}{2} \right) \right] \\
\vec{d}(\vec{k},\vec{r}) &= e^{i(\vec{q}_+ + \vec{q}_-)\cdot\vec{r}/2} \hat{g}_{\vec{k}} \left[\left\{ \eta_{0+}\tilde{\Delta}_{\vec{k}+} - \eta_{0-}\tilde{\Delta}_{\vec{k}-} \right\} \cos\left(\frac{(\vec{q}_+ - \vec{q}_-)\cdot\vec{r}}{2} \right) \right. \\
&\qquad \left. + i \left\{ \eta_{0+}\tilde{\Delta}_{\vec{k}+} + \eta_{0-}\tilde{\Delta}_{\vec{k}-} \right\} \sin\left(\frac{(\vec{q}_+ - \vec{q}_-)\cdot\vec{r}}{2} \right) \right] .
\end{aligned} \tag{125}$$

Increasing the coupling c this type of phase is gradually suppressed and more complex configurations appear which are beyond our scope. Naturally, the presence of vortices in the mixed phase will modify this picture too [52]. A detailed discussion has been given in Ref.[51].

Spin susceptibility and the helical state

As mentioned above the modification of the superconducting phase through the magnetic field will have an influence on the behavior of the spin susceptibility. Again most easily this behavior is discussed in the Ginzburg-Landau formulation. For the sake of clarity we will simplify the Ginzburg-Landau for to a single-order parameter formulation. Then it takes the form

$$\begin{aligned}
F &= F_0 + \int d^3r \left[\{a(T) + \sum_\mu Q_\mu H_\mu^2\} |\eta|^2 + b|\eta|^4 + K|\vec{D}\eta|^2 \right. \\
&\qquad \left. + iK_{me}(\vec{H}\times\hat{z})\cdot(\eta^*(\vec{D}\eta) - \eta(\vec{D}\eta)^*) + \frac{\vec{B}^2}{8\pi} \right] .
\end{aligned} \tag{126}$$

For our purpose we again ignore the orbital coupling to the magnetic field, setting $e \to 0$, and restrict again to the spin coupling with

$$F_0 = -\Omega \frac{\chi_P}{2} \vec{H}^2 , \quad Q_x = Q_y = Q \neq 0 \quad \text{and} \quad Q_z = 0 , \tag{127}$$

with Ω being the sample volume. We minimize the Ginzburg-Landau free energy in a magnetic field with the ansatz $\eta(\vec{r}) = \eta_0 e^{i\vec{q}\cdot\vec{r}}$,

$$F = F_0 + \int d^3r [a + \sum_\mu Q_\mu H_\mu^2 + K\vec{q}^2 - K_{me}(\vec{H}\times\hat{z})\cdot\vec{q}] |\eta_0|^2 + b|\eta_0|^4 . \tag{128}$$

The minimization with respect to $\vec{q}$ and η_0 leads to

$$\vec{q}_m = \frac{K_{me}}{2K}(\vec{H}\times\hat{z}) \quad \text{and} \quad |\eta_0|^2 = -\frac{1}{2b}\left\{a+\sum_\mu Q_\mu H_\mu^2 - \frac{K_{me}^2}{4K}(\vec{H}\times\hat{z})^2\right\} \tag{129}$$

and the uniform free energy density is then

$$f(\vec{H},T) = -\frac{\chi_P}{2}\vec{H}^2 - \frac{1}{4b}\left\{a+\sum_\mu Q_\mu H_\mu^2 - \frac{K_{me}^2}{4K}(\vec{H}\times\hat{z})^2\right\}^2 . \tag{130}$$

The spin susceptibility is obtained through

$$\chi_{\mu\nu} = -\left.\frac{\partial^2 f}{\partial H_\mu \partial H_\nu}\right|_{\vec{H}=0} = \chi_p\delta_{\mu\nu} - \frac{|a(T)|}{2b}\left\{2Q_\mu\delta_{\mu\nu} - \frac{K_{me}^2}{2K}(\delta_{\mu\nu}-\delta_{\mu z}\delta_{\nu z})\right\} . \tag{131}$$

The second term diminishes the susceptibility in the superconducting phase for fields in the x-y-plane,

$$\chi_{xx} = \chi_{yy} = \chi_P - \frac{a'(T_c-T)}{2b}\{2Q - \frac{K_{me}^2}{2K}\} \quad \text{and} \quad \chi_{zz} = \chi_P . \tag{132}$$

The reduction for χ_{xx} and χ_{yy} we discussed in the section on the spin susceptibility is described by the term Q. The magneto-electric adaption of the superconducting order parameter is contained in the term containing K_{me} and represents a counter term to Q. Thus this term can reduce the suppression of the spin susceptibility for inplane fields and, accordingly, also diminish the paramagnetic limiting effect to some extent. The magnitude of the recovery depends on details of the band structure and pairing state [52]. So far there have been no direct experimental observations of the helical phase in any of the non-centrosymmetric superconductors.

Supercurrent and spin magnetization

Let us return to the Ginzburg-Landau free energy of Eqs.(114,115) and discuss the effect of the antisymmetric spin-orbit coupling on the magnetic properties. First, we determine the supercurrent using the relation

$$\begin{aligned}\vec{J}_s &= -\frac{1}{c}\frac{\partial F}{\partial \vec{A}} = \sum_\lambda \left[i\frac{2e}{\hbar c}K_\lambda\left\{\eta_\lambda^*(\vec{D}\eta_\lambda) - \eta_\lambda(\vec{D}\eta_\lambda)^*\right\} + \frac{2e}{\hbar c}K_{me,\lambda}|\eta_\lambda|^2(\vec{H}\times\hat{z})\right] \\ &= \vec{J}_{s0} + \Lambda_{me}(\vec{H}\times\hat{z}) .\end{aligned} \tag{133}$$

where

$$\vec{J}_{s0} = \sum_\lambda \vec{J}_{s0\lambda} = i\frac{2e}{\hbar c}K_\lambda\left\{\eta_\lambda^*(\vec{D}\eta_\lambda) - \eta_\lambda(\vec{D}\eta_\lambda)^*\right\} . \tag{134}$$

There is an additional contribution to the supercurrent which is a signature of the magneto-electric effect and originates from the Zeeman coupling to the electron spins to a magnetic field. The shift of the Fermi surface in a magnetic field lying in the basal causes an additional supercurrent perpendicular to the Zeeman field. Next we consider the spin magnetization of the superconductor,

$$\begin{aligned} M_\mu &= -\frac{\partial F_0}{\partial H_\mu} - \frac{\partial F}{\partial H_\mu} \\ &= \chi_p H_\mu - \sum_\lambda \left[Q_{\mu\lambda} |\eta_\lambda|^2 H_\mu + i K_{me,\lambda} \left(\hat{z} \times \left\{ \eta_\lambda^* (\vec{D}\eta_\lambda) - \eta_\lambda (\vec{D}\eta_\lambda)^* \right\} \right)_\mu \right] \\ &= \chi_{\mu\mu} H_\mu + \sum_\lambda \frac{\Phi_0 K_{me,\lambda}}{2\pi K_\lambda} (\hat{z} \times \vec{J}_{s0\lambda})_\mu \end{aligned} \tag{135}$$

Here the spin response is not only given by the spin susceptibility, but also by a contribution originating from supercurrents in the basal plane.

The two equations (133) and (135) provide the important relations between spin polarization and supercurrents [55, 33, 56]. Although these effects are small, it has been shown that correlation effects may give rise to a substantial enhancement and yield experimentally detectable effects [33, 56].

ANDREEV BOUND STATES AT THE SURFACE

Several unconventional superconductors possess states at surfaces or interfaces with subgap energy. This is a consequence of the non-trivial internal phase structure of gap function and can often also be attributed to topological properties of the superconducting condensates [57, 58]. A well-known example are the zero-energy states of the $d_{x^2-y^2}$-wave superconductors which appear for surfaces with normal vector $\vec{n} \parallel (1,1,0)$[59, 60, 61]. Electrons scattered at the surface connect wave vectors close to the Fermi surface where the gap function has opposite sign. This yields so-called Andreev bound states at exactly zero energy. Similarly, in the chiral p-wave superconductor ($\vec{d}(\vec{k}) = \hat{z}(k_x \pm ik_y)$) as likely realized in Sr_2RuO_4 there are chiral surface states [62].

We discuss the situation in the case on non-centrosymmetric superconductors again using the example of he mixed-parity state proposed for $CePt_3Si$. For the sake of simplicity we assume spherical Fermi surfaces and simplify our discussion by taking $k_{F\lambda} = k_{F+} = k_{F-} = k_F$ without ignoring the influence of the spin splitting on the superconducting state. The gap function is assumed to have the form

$$\tilde{\Delta}_{\vec{k},\lambda} = \Delta_s + \lambda \Delta_p |\sin\theta_{\vec{k}}| \,. \tag{136}$$

which is rotation symmetric around the z-axis. The electron dispersion close to the Fermi surface is given by

$$\tilde{\xi}_\lambda(\vec{k}) = \hbar \vec{v}_{F\lambda} \cdot (\vec{k} - \vec{k}_{F\lambda}) \,. \tag{137}$$

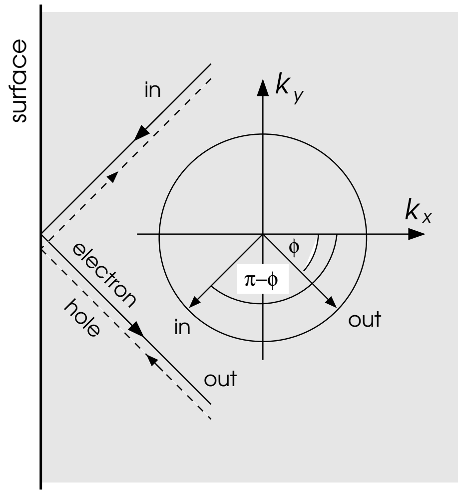

FIGURE 8.

In order to describe the surface quasiparticle bound states with their spatial dependence we introduce the Bogolyubov-de Gennes equations with the wavefunctions $u_{\vec{k}\lambda}(\vec{r})$ for the electron-like and $v_{\vec{k}\lambda}(\vec{r})$ for the hole-like part of the quasiparticles with wavevector $\vec{k}$ at the Fermi surface λ.

$$
\begin{aligned}
\tilde{\xi}_\lambda(-i\vec{\nabla})u_{\vec{k}\lambda}(\vec{r}) + \tilde{\Delta}_{\vec{k}\lambda}v_{\vec{k}\lambda} &= Eu_{\vec{k}\lambda}(\vec{r}) \\
\tilde{\Delta}^*_{\vec{k}\lambda}u_{\vec{k}\lambda} - \tilde{\xi}_\lambda(-i\vec{\nabla})v_{\vec{k}\lambda}(\vec{r}) &= Ev_{\vec{k}\lambda}(\vec{r})
\end{aligned}
\tag{138}
$$

We introduce now for the wavefunctions the ansatz

$$
u^{(\pm)}_{\vec{k}^{(\pm)}_F\lambda} = A^{(\pm)}_\lambda e^{\pm iqx + i\vec{k}^{(\pm)}_F\cdot\vec{r}} \quad \text{and} \quad v^{(\pm)}_{\vec{k}^{(\pm)}_F\lambda} = B^{(\pm)}_\lambda e^{\pm iqx + i\vec{k}^{(\pm)}_F\cdot\vec{r}}\,, \tag{139}
$$

where we distinguish between the wavefunction of particles approaching the surface $(-)$ (”in” in Fig.8) and leaving the surface $(+)$ (”out” in Fig.8), indicated by the sign of the wavevector q along the x-axis. Note, that wavevector components parallel to the surface are conserved. The slow spatial dependence of the wave function is described by the factor $e^{\pm iqx}$.

Using Eq.(137) with our ansatz we obtain the equations

$$
\begin{aligned}
\{\pm\hbar v_{Fx}q - E\}A^{(\pm)}_\lambda + \tilde{\Delta}_{\vec{k}\lambda}B^{(\pm)}_\lambda &= 0\,', \\
\tilde{\Delta}^*_{\vec{k}\lambda}A^{(\pm)}_\lambda - \{\pm\hbar v_{Fx}q + E\}B^{(\pm)}_\lambda &= 0\,,
\end{aligned}
\tag{140}
$$

which lead to

$$
\hbar v_{Fx}q_\lambda = \pm\sqrt{E^2 - \tilde{\Delta}^2_{\vec{k}\lambda}} \quad \text{and} \quad (A^{(\pm)}_\lambda, B^{(\pm)}_\lambda) = \frac{(\tilde{\Delta}_{\vec{k}\lambda}, E \mp \hbar v_{Fx}q_\lambda)}{\sqrt{2E(E \mp \hbar v_{Fx}q_\lambda)}}\,. \tag{141}
$$

Now a careful combination of the different contributions to the electron- and hole-like wavefunction is mandatory. Note also that we have to choose the solution of q_λ (imaginary for $-\tilde{\Delta}_{\vec{k}\lambda} < E < \tilde{\Delta}_{\vec{k}\lambda}$) so that the wavefunctions decay exponentially towards the bulk of the superconductor, as expected for surface bound states.

For the boundary conditions we assume that the scattering process at the surface preserves the spin. This condition may be modified by strong spin-orbit coupling. Thus, the matching between "in" (-) and "out" (+) waves has to be done in the spin basis which is defined by the spin-matrices,

$$\hat{\sigma}_\lambda(\vec{k}) = \frac{1}{2}\left\{\hat{\sigma}^0 + \lambda \hat{g}_{\vec{k}} \cdot \hat{\vec{\sigma}}\right\} = \frac{1}{2}\begin{pmatrix} 1 & -\lambda i e^{-i\phi_{\vec{k}}} \\ \lambda i e^{i\phi_{\vec{k}}} & 1 \end{pmatrix}, \tag{142}$$

defining $\vec{k}_F = k_F(\cos\phi_{\vec{k}} \sin\theta_{\vec{k}}, \sin\phi_{\vec{k}} \sin\theta_{\vec{k}}, \cos\theta_{\vec{k}})$. Note, that the angle $\phi_{\vec{k}}$ is connected with $\vec{k}_F^{(+)} \Rightarrow \phi_{\vec{k}}^{(+)}$ and $\vec{k}_F^{(-)} \Rightarrow \phi_{\vec{k}}^{(-)} = \pi - \phi_{\vec{k}}^{(+)}$ as can be seen in Fig.8. In the spin basis then we write the wavefunctions as

$$u_\uparrow(\vec{r}) = \sum_{\lambda,s=\pm} C_\lambda^{(s)} A_\lambda^{(s)} e^{-|q_\lambda|x + i\vec{k}_F^{(s)}\cdot\vec{r}} \quad \text{and} \quad u_\downarrow(\vec{r}) = \sum_{\lambda,s=\pm} C_\lambda^{(s)} A_\lambda^{(s)} \lambda i e^{i\phi_{\vec{k}}^{(s)}} e^{-|q_\lambda|x + i\vec{k}_F^{(s)}\cdot\vec{r}}, \tag{143}$$

for the electron-like component and

$$v_\uparrow(\vec{r}) = \sum_{\lambda,s=\pm} C_\lambda^{(s)} B_\lambda^{(s)} e^{-|q_\lambda|x + i\vec{k}_F^{(s)}\cdot\vec{r}} \quad \text{and} \quad v_\downarrow(\vec{r}) = \sum_{\lambda,s=\pm} C_\lambda^{(s)} B_\lambda^{(s)} \lambda i e^{i\phi_{\vec{k}}^{(s)}} e^{-|q_\lambda|x + i\vec{k}_F^{(s)}\cdot\vec{r}}, \tag{144}$$

for the hole-like component. The boundary condition requires that all the wavefunction components vanish simultaneously at the surface ($x = 0$). This leads to the equation for the energy spectrum,

$$\cos^2\phi_{\vec{k}} = \frac{2\sqrt{(\tilde{\Delta}_{\vec{k}+}^2 - E^2)(\tilde{\Delta}_{\vec{k},-}^2 - E^2)}}{E^2 - \tilde{\Delta}_{\vec{k}+}\tilde{\Delta}_{\vec{k}-} + \sqrt{(\tilde{\Delta}_{\vec{k}+}^2 - E^2)(\tilde{\Delta}_{\vec{k},-}^2 - E^2)}} \tag{145}$$

which yields bound states under the condition that $\tilde{\Delta}_{\vec{k}+}\tilde{\Delta}_{\vec{k}-} < 0$. The spectrum is then restricted to $|E| < |\tilde{\Delta}_{\vec{k}-}$ as can be seen from Eq.(145). From small momenta along the y-direction ($|\phi_{\vec{k}} \ll 1$) we find the linear dependence on the momentum k_y

$$E_{k_y} \approx \pm\sqrt{2|\tilde{\Delta}_{\vec{k}+}\tilde{\Delta}_{\vec{k}-}|}\ \frac{k_y}{k_F \cos\theta_{\vec{k}}} \tag{146}$$

and for gracing angles $\phi_{\vec{k}} \to \pm\pi/2$ the energy approaches $E \to \pm|\tilde{\Delta}_{\vec{k}-}|$ (see Fig.9). The presence of the Andreev bound state relies on the condition that $\tilde{\Delta}_{\vec{k}-} < 0$. With Eq.(136) this requires that p-wave component is dominant $\Delta_s < \Delta_p$ and $k_z < k_F \Delta_s/\Delta_p$. At $\Delta_s = \Delta_p$ the subgap mode disappears and is absent for $\Delta_s > \Delta_p$.

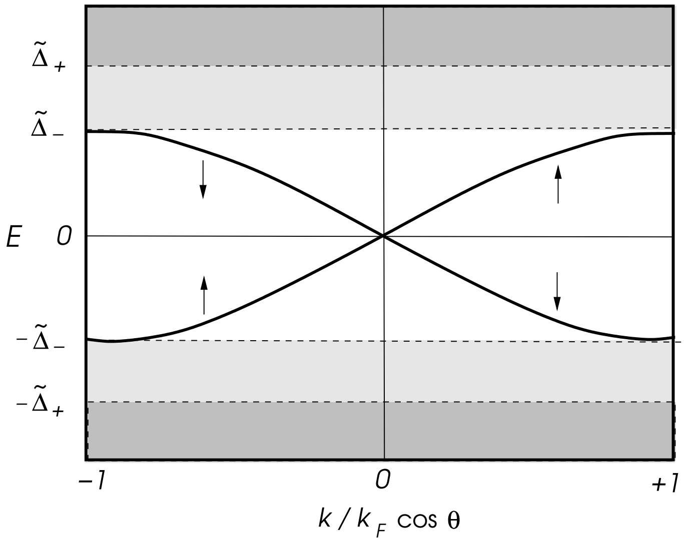

FIGURE 9. Schematic quasiparticle spectrum of the surface Andreev bound states with subgap energy. The spectrum extends in the regions between the bulk excitation continua with $|E| > \tilde{\Delta}_-$. Note that the angle $\theta_{\vec{k}}$ chosen such that $\sin\theta_{\vec{k}} < \Delta_s/\Delta_p$.

The regime of $\Delta_p > \Delta_s$ is adiabatically connected with the limit $\Delta_s = 0$ where we have pure odd-parity p-wave state with $\vec{d}(\vec{k}) = \Delta_p(\hat{x}k_y - \hat{y}k_x)$. This is an equal-spin pairing state with a gap matrix in spin space,

$$\hat{\Delta}_{\vec{k}} = \begin{pmatrix} -i(k_x + ik_y) & 0 \\ 0 & -i(k_x - ik_y) \end{pmatrix} = \begin{pmatrix} \Delta_{\vec{k}\uparrow\uparrow} & 0 \\ 0 & \Delta_{\vec{k}\downarrow\downarrow} \end{pmatrix} \tag{147}$$

which represent chiral p-wave state of opposite chirality for the two spin orientations. The spectrum in this case is much simpler and can be obtained from Eq.(145) through the limit $-\tilde{\Delta}_{\vec{k}-} \to \tilde{\Delta}_{\vec{k}+} \to \Delta_p$,

$$E(k_y, \sigma) = \sigma \Delta_p \frac{k_y}{k_F} \tag{148}$$

where $\sigma = +$ and $-$ represent the branches for the spin $\uparrow$ and $\downarrow$, respectively. These are two chiral edge states confined on a length scale of coherence length at the surface, which yield a current density of the state with (k_y, s) along the surface in opposite direction,

$$j_y(k_y, \sigma) = \frac{1}{L} v_y = \frac{1}{\hbar L} \frac{\partial E(k_y, \sigma)}{\partial k_y} = \sigma \frac{\Delta_p}{\hbar k_F} \,. \tag{149}$$

The total current is the integral over all occupied states $(n(k_y, \sigma) = \Theta(-E(k_y, \sigma))$ at $T = 0)$,

$$I_\sigma = \sum_{\vec{k}} n(k_y, \sigma) j_y(k_y, \sigma) = \frac{\Delta_p}{\hbar} \int_{\sigma k_F}^{0} \frac{dk_y}{2\pi} \frac{1}{k_F} = \sigma \frac{\Delta_p}{h} \,. \tag{150}$$

It is obvious that there is no net charge current: $I_c = \sum_{\sigma=\pm} I_\sigma = 0$, because time reversal symmetry is conserved. However, there is a finite spin current

$$I_s = \sum_{\sigma=\pm} \sigma I_\sigma = \frac{2\Delta_p}{h} \tag{151}$$

with the spin component point along the z-axis. This property survives, if we adiabatically turn on the s-wave component Δ_s again reaching the mixed-parity state. However, it disappears continuously when Δ_s approaches Δ_p.

Note that this discussion is oversimplified, if spin-orbit coupling is taken into account. Then the spin current is not preserved. The antisymmetric spin-orbit coupling term in the Hamiltonian leads to spin precession. We do not into these detailed discussion here and refer to Ref.[63].

CONCLUSIONS

In this introduction to superconductivity in non-centrosymmetric metals we have seen that inversion symmetry is one of two key symmetries for Cooper pairing. The absence of these symmetries has profound implications on the formation of Cooper pairs. In both cases we encounter a spin splitting of the electronic bands which imprints a specific spin structure on the Cooper pairs. Due to the spin splitting the pairing state end up naturally to be non-unitary, i.e. having different pairing amplitudes on the two Fermi surface sheets. These key symmetries are closely related to Anderson's two theorems [23, 24].

Concentrating on materials without inversion symmetry, non-centrosymmetric metals, we have seen that a number of novel properties appear. The symmetry classification distinguishing even- and odd-parity pairing, is obsolete, since the new states are parity-mixing. Aspects of the new conditions under which superconductivity exists in these systems, are visible in spin susceptibility in the superconducting phase, which has been verified in several heavy Fermion superconductors. Magneto-electric effects provide an intriguing coupling between orbital supercurrents and spin magnetization, which shows analogies with features known from multi-ferroic systems and may be experimentally observable. Eventually, possibility of surface Andreev bound state is a property which has experimental relevance of quasiparticle tunneling experiments. Many topics have not been discussed in this introduction, which are of imminent interest and under current investigations. This includes the mixed phase in a magnetic field [51, 64, 65], the vortex structure [66], the implication of mixed-parity for the Josephson effect [68, 69], the coexistence of magnetic order and superconductivity [40, 67] (the absence of both key symmetries) are some examples.

The number of new non-centrosymmetric superconductors is growing in recent years. There are many "conventional" non-centrosymmetric superconductors known since many years, e.g.NbReSi (C_{2v})and Mo_3Al_2C (O). With the discovery of non-centrosymmetric heavy Fermion superconductors, the prospects of having superconductivity with dominant unconventional pairing, most likely based on mechanisms involving magnetic fluctuations, is a strong driving motivation. The best studied examples in this class are $CePt_3Si$, $CeRhSi_3$ and $CeIrSi_3$, which show some most spectacular results. It is interesting to observed that these materials have non-heavy-Fermion partners which are also superconducting, if Ce is replaced by La (no f-electrons), do not display such unusual features. Very puzzling is the behavior of the two superconductors Li_2Pd_3B and Li_2Pt_3B which have the same crystal structure $P4_332$ leading to the cubic point group O. While the former has more or less usual superconducting properties like a conventional superconductor, the latter shows thermodynamic properties indicating the possibility of line nodes in the gap and the Knight shift stays constant through the superconducting transition down to lowest temperatures [70, 71]. The spin-orbit coupling strength is likely very different in the two compounds which may be responsible for the dramatic difference. However, from the normal state properties none of the two materials shows strong correlation effects which would suggest unconventional Cooper pairing. So it remains to be seen whether strong antisymmetric spin-orbit coupling would yield unconventional behavior even for nominally conventional pairing mechanisms.

APPENDIX

A. Instability conditions

In this appendix we derive the expressions to calculate the critical temperatures for time reversal and inversion symmetry breaking systems on a perturbative level. We use the kinetic energy of Eq.(6) and the pairing interaction of Eq.(18,19). For our purpose it is useful to apply the powerful Green's function technique. The Green's function of the kinetic energy is obtained from the equation

$$\{(i\omega_n - \xi_{\vec{k}})\hat{\sigma}^0 - \vec{g}_{\vec{k}} \cdot \hat{\vec{\sigma}}\}\hat{G}^0(\vec{k}, i\omega_n) = \hat{\sigma}^0 \tag{152}$$

where $\omega_n = \pi k_B T(2n+1)$ is the Fermionic Matsubara frequency. It is easy to solve this equation,

$$\hat{G}^0(\vec{k}, i\omega_n) = G^{(+)}(\vec{k}, i\omega_n)\hat{\sigma}^0 + G^{(-)}(\vec{k}, i\omega_n)\hat{\vec{\sigma}} \cdot \hat{g}_{\vec{k}} \tag{153}$$

with

$$G^{(\pm)}(\vec{k}, i\omega_n) = \frac{1}{2}\{G_+(\vec{k}, i\omega_n) \pm G_-(\vec{k}, i\omega_n)\} \quad \text{and} \quad G_\lambda = \frac{1}{i\omega_n - \tilde{\xi}_{\vec{k}\lambda}} \tag{154}$$

with $\lambda = \pm$. Using Gorkov's equations one can derive the linearized gap equation of the form [54],

$$\Delta_{s_1 s_2}(\vec{k}) = -k_B T \sum_{\vec{k}', n} \sum_{s_1', s_2', s_3', s_4'} V_{s_1 s_2 s_2' s_1'}(\vec{k}, \vec{k}') G^0_{s_2' s_3'}(\vec{k}', i\omega_n) \Delta_{s_3', s_4'}(\vec{k}') G^0_{s_1' s_4'}(-\vec{k}', -i\omega_n) \,. \tag{155}$$

We use for the gap matrix $\hat{\Delta}(\vec{k}) = \{\psi(\vec{k})\hat{\sigma}^0 + \vec{d}(\vec{k}) \cdot \hat{\vec{\sigma}}\}i\hat{\sigma}^y$. To simplify the discussion we impose the condition that one of the two symmetries is conserved such that $\vec{g}_{-\vec{k}} = \pm\vec{g}_{\vec{k}} \Rightarrow |\vec{g}_{\vec{k}}| = |\vec{g}_{-\vec{k}}|$.

First we restrict our discussion to the even parity part and use for the dominant pairing channel,

$$V_{s_1 s_2 s_2' s_1'}(\vec{k},\vec{k}') = v_a(\psi_a(\vec{k}) i\hat{\sigma}^y)_{s_1 s_2}(\psi_a(\vec{k}')\hat{\sigma}^y)^{\dagger}_{s_2' s_1'} \,. \tag{156}$$

After some algebra we obtain the two linear gap equations for $\psi(\vec{k})$,

$$\begin{aligned}\psi(\vec{k}) = k_B T \sum_{\vec{k}',n} v_a \psi_a(\vec{k}) \psi_a^*(\vec{k}') \psi(\vec{k}') \Big\{ & G^{(+)}(\vec{k}', i\omega_n) G^{(+)}(-\vec{k}', -i\omega_n) \\ & + \hat{g}_{\vec{k}'} \cdot \hat{g}_{-\vec{k}'} G^{(-)}(\vec{k}', i\omega_n) G^{(-)}(-\vec{k}', -i\omega_n) \Big\} \,.\end{aligned} \tag{157}$$

We neglect here terms which induce small odd-parity pairing components whose magnitude depends on the particle-hole asymmetry. Analogously we deal with the odd-parity pairing state with the dominant pairing interaction part,

$$V_{s_1 s_2 s_2' s_1'}(\vec{k},\vec{k}') = v_b(\vec{d}(\vec{k}) \cdot \hat{\vec{\sigma}} i\hat{\sigma}^y)_{s_1 s_2}(\vec{d}(\vec{k}') \cdot \hat{\vec{\sigma}} i\hat{\sigma}^y)^{\dagger}_{s_2' s_1'} \tag{158}$$

leading to

$$\begin{aligned}\vec{d}(\vec{k}) = k_B T \sum_{\vec{k}' n} v_b \vec{d}_b(\vec{k}) \vec{d}_b^*(\vec{k}') \Big\{ & \vec{d}(\vec{k}') G^{(+)}(\vec{k}', i\omega_n) G^{(+)}(-\vec{k}', -i\omega_n) \\ & + \Big[2(\hat{g}_{\vec{k}'} \cdot \vec{d}(\vec{k}')) \hat{g}_{-\vec{k}'} - \vec{d}(\vec{k}') \hat{g}_{\vec{k}'} \cdot \hat{g}_{-\vec{k}'} \Big] G^{(-)}(\vec{k}', i\omega_n) G^{(-)}(-\vec{k}', -i\omega_n)) \Big\} \,,\end{aligned} \tag{159}$$

also here neglecting terms which are small and depend on the particle-hole asymmetry at the Fermi surface.

In these linear gap equations we have to deal with the Green's function products,

$$G^{(\pm)}(\vec{k}', i\omega_n) G^{(\pm)}(-\vec{k}', -i\omega_n) = \frac{1}{4} \sum_{\lambda=\pm} \left\{ \frac{1}{\omega_n^2 + (\xi_{\vec{k}} + \lambda |\vec{g}_{\vec{k}}|)^2} \pm \frac{1}{(\omega_n + i\lambda |\vec{g}_{\vec{k}}|)^2 + \xi_{\vec{k}}^2} \right\} \,. \tag{160}$$

When evaluating the sum over $\vec{k}'$ and n we then encounter the following terms,

$$\begin{aligned} k_B T \sum_{\vec{k}',n} \frac{1}{\omega_n^2 + (\xi_{\vec{k}'} + \lambda |\vec{g}_{\vec{k}'}|)^2} &= \frac{1}{2} \int \frac{d\Omega_{\vec{k}'}}{4\pi} \int_{-\varepsilon_c}^{+\varepsilon_c} d\xi N(\xi) \frac{\tanh)[(\xi + \lambda |\vec{g}_{\vec{k}'}|)/2k_B T)}{\xi + \lambda |\vec{g}_{\vec{k}'}|} \\ &\approx N(0) \ln\left(\frac{1.14\varepsilon_c}{k_B T}\right) \,, \end{aligned} \tag{161}$$

and

$$
\begin{aligned}
k_B T \sum_{\vec{k}',n} \frac{1}{(\omega_n + i\lambda|\vec{g}_{\vec{k}'}|)^2 + \xi_{\vec{k}'}^2} &= 2k_B T \sum_{n=0}^{\infty} \int \frac{d\Omega_{\vec{k}'}}{4\pi} \int_{-\varepsilon_c}^{+\varepsilon_c} d\xi \frac{N(\xi)}{(\omega_n + i\lambda|\vec{g}_{\vec{k}'}|)^2 + \xi_{\vec{k}'}^2} \\
&\approx 2N(0) \left\langle \sum_{n=0}^{n_c} \frac{1}{2n+1+i\rho_{\vec{k}}} \right\rangle_{\vec{k}} \\
&= N(0) \ln\left(\frac{1.14\varepsilon_c}{k_B T}\right) + 2N(0) \sum_{n=0}^{\infty} \left\langle \frac{1}{2n+1+i\rho_{\vec{k}}} - \frac{1}{2n+1} \right\rangle_{\vec{k}} \\
&= N(0) \ln\left(\frac{1.14\varepsilon_c}{k_B T}\right) + 2N(0) \langle R(i\rho_{\vec{k}}) \rangle_{\vec{k}}
\end{aligned}
\tag{162}
$$

with $\rho_{\vec{k}} = |\vec{g}_{\vec{k}}|/\pi k_B T$. Inserting these results into Eq.(157,159) we obtain

$$
\psi_a(\vec{k}) = \psi_a(\vec{k}) \left\{ N(0) v_a \ln\left(\frac{1.14\varepsilon_c}{k_B T}\right) + \frac{N(0) v_a}{2} \left\langle |\psi_a(\vec{k}')|^2 (1 + \hat{g}_{\vec{k}} \cdot \hat{g}_{-\vec{k}}) [R(i\rho_{\vec{k}}) + R(-i\rho_{\vec{k}})] \right\rangle_{\vec{k}'} \right\} . \tag{163}
$$

The relation $N(0) v_a \ln[1.14\varepsilon_c/k_B T_{c0}] = 1$ leads then to

$$
\ln\left(\frac{T_c}{T_{c0}}\right) = \left\langle |\psi_a(\vec{k}')|^2 (1 + \hat{g}_{\vec{k}} \cdot \hat{g}_{-\vec{k}}) f(\rho_{\vec{k}}) \right\rangle_{\vec{k}'} \tag{164}
$$

with $f(\rho) = ReR(i\rho)$ as in Eq.(21). Analogously we can derive Eq.(32) for the odd-parity case.

B. Time reversal operation in the helicity basis

Time reversal operation: Consider the state

$$
|\vec{k}\lambda\rangle = u_{\lambda\uparrow}(\vec{k})|\vec{k}\uparrow\rangle + u_{\lambda\downarrow}(\vec{k})|\vec{k}\downarrow\rangle . \tag{165}
$$

We apply the time reversal operator $\mathscr{K} = -i\hat{\sigma}^y K_0$ (K_0: complex conjugation):

$$
\mathscr{K}|\vec{k}\lambda\rangle = t_\lambda(\vec{k})|-\vec{k}\lambda\rangle = u_{\lambda\uparrow}^*(\vec{k})|-\vec{k}\downarrow\rangle + u_{\lambda\downarrow}(\vec{k})|-\vec{k}\uparrow\rangle \tag{166}
$$

where $t_\lambda(\vec{k})$ is a phase factor,

$$
|-\vec{k}\lambda\rangle = u_{\lambda\uparrow}(-\vec{k})|-\vec{k}\uparrow\rangle + u_{\lambda\downarrow}(-\vec{k})|-\vec{k}\downarrow\rangle . \tag{167}
$$

Thus, we find

$$
t_\lambda(\vec{k}) = \langle -\vec{k}\lambda|\mathscr{K}|\vec{k}\lambda\rangle = -u_{\lambda\uparrow}^*(-\vec{k})\, u_{\lambda\downarrow}^*(\vec{k}) + u_{\lambda\downarrow}^*(-\vec{k})\, u_{\lambda\uparrow}^*(\vec{k}) = -\lambda \frac{g_{\vec{k}x} - i g_{\vec{k}y}}{\sqrt{|\vec{g}_{\vec{k}}|^2 - g_{\vec{k}z}^2}} . \tag{168}
$$

Since $\mathscr{K}$ is an anti-unitary operator, $\mathscr{K}^2 = -1$, and we obtain

$$\mathscr{K}^2|\vec{k}\lambda\rangle = \mathscr{K} t_\lambda(\vec{k})|-\vec{k}\lambda\rangle = t^*_\lambda(\vec{k}) t_\lambda(-\vec{k})|\vec{k}\lambda\rangle = -|\vec{k}\lambda\rangle \ , \tag{169}$$

which is leads to $t_\lambda(-\vec{k}) = -t_\lambda(\vec{k})$ consistent with the fact that $\vec{g}_{\vec{k}}$ is odd in $\vec{k}$.

ACKNOWLEDGMENTS

I would like to thank my colleagues with whom I had the pleasure to work and to discuss on the subjects which have been topics of these notes: H. Adachi, D.F. Agterberg, E. Bauer, I. Bonalde, M. Eschrig, P.A. Frigeri, S. Fujimoto, N. Hayashi, C. Iniotakis, H. Kaneyasu, R.P. Kaur, N. Kimura, A. Koga, C. Miclea, I. Milat, V.P. Mineev, A.C. Mota, H. Mukuda, T. Neupert, Y. Onuki, D. Perez, T.M. Rice, K. Samokhin, L. Savary, Y. Tanaka, K. Wakabayashi, Y. Yanase S.-K. Yip, Y. Yokoyama, H. Yuan These notes are partially build upon a recent brief review I have written together with V.P. Mineev.

REFERENCES

1. M. Sigrist, AIP Conf. Proc. **789**, 165 (2005).
2. M. Tinkham, *Introduction to Superconductivity*, McGraw Hill (1996)
3. D. Vollhardt and P. Wölfle, *The superfluid phases of* ^{3}*He*, Tayler & Francis, London (1990).
4. F. Steglich, J. Aarts, C.D. Bredl, W. Lieke, D. Meschede, W. Franz and H. Schäfer, Phys. Rev. Lett. **43**, 1892 (1979).
5. H.R. Ott, H. Rudigier, Z. Fisk and J.L. Smith, Phys. Rev. Lett. **50**, 1595 (1983).
6. G.R. Stewart, Z. Fisk, J.O. Willis and J.L. Smith, Phys. Rev. Lett. **52**, 679 (1984).
7. C. Pfleiderer, Rev. Mod. Phys. to be published.
8. D. Jerome, A. Mazaud, M. Ribault and K. Bechgaard, J. Phys. Lett. (Paris) **41**, L95 (1980).
9. T. Ishiguro, K. Yamaji and G. Saito, *Organic Superconductors*, Springer (1998).
10. N.D. Mathur, G.M. Grosche, S.R. Julian, I.R. Walker, D.M. Freye, R.K.W. Haselwimmer, G.G. Lonzarich, Nature (London) **394**, 39 (1998).
11. J.D. Thompson, R. Movshovich, Z. Fisk, F. Bouquet, N.J. Cueeo, R.A. Fisher, P.C. Hammel, H. Heeger, M.F. Hundley, M. Jaime, P.G. Pagliuso, C. Petrovic, N.E. Philips, J.L. Sarrao, J. Magn. Magn. Mater. **226-230**, 5 (2001).
12. C. Petrovic, R. Movshovich, M. Jaime, P.G. Hundley, J.L. Sarrao, Z. Fisk, J.D. Thompson, Europhys. Lett. **53**, 354 (2001).
13. S.S. Saxena, P. Agarwal, K. Ahllan, F.M. Grosche, R.K.W. Haselwimmer, M.J. Steiner, E. Pugh, I.R. Walker, S.R. Julian, P. Monthoux, G.G. Lonzarich, A. Huxley, I. Shelkin, D. Braithwaite, and J. Flouquet, Nature (London) **406** , 587 (2000).
14. D. Aoki, A. Huxley, E. Ressouche, D. Braithwaite, J. Flouquet, J.-P. Brison, and E. Lhotel, Nature **413**, 613 (2001).
15. K. Ishida, Y. Nakai and H. Hosono, J. Phys. Soc. Jpn. **78**, 062001 (2009).
16. N. T. Huy, A. Gasparini, D. E. de Nijs, Y. Huang, J. C. P. Klaasse, T. Gortenmulder, A. de Visser, A. Hamann, T. Gorlach, and H. v. Lohneysen, Phys. Rev. Lett. **99**, 067006, (2007).
17. Y. Maeno, H. Hashimoto, K. Yoshida, S. Nishizaki, T. Fujita, J.G. Bednorz and F. Lichtenberg, Nature (London) **372**, 532 (1994).
18. A.P. Mackenzie and Y. Maeno, Rev. Mod. Phys. **75**, 657 (2003).
19. Y. Maeno, T.M. Rice and M. Sigrist, Physics Today **54**, 42 (2001).
20. E. Bauer, G. Hilscher, H. Michor, C. Paul, E.W. Scheidt, A. Gribanov, Y. Seropegin, H. Noel, M. Sigrist and P. Rogl, Phys. Rev. Lett. **92**, 027003 (2004).
21. K.V.Samokhin, E.S.Zijlstra, and S.K.Bose, Phys. Rev. B **69**, 094514 (2004). See also Erratum **70**, 069902(E) (2004).

22. P.A.Frigeri, D.F.Agterberg, A.Koga, and M.Sigrist, Phys.Rev.Lett. **92**, 097001 (2004). See also Erratum **93**, 099903(E) (2004).
23. P.W. Anderson, J. Phys. Chem. Solids **11**, 26 (1959).
24. P.W. Anderson, Phys. Rev. B**30**, 4000 (1984).
25. V. P. Mineev, Phys. Rev. B **66**, 134504 (2002).
26. V. P. Mineev and T. Champel, Phys. Rev. B **69**, 144521 (2004).
27. V. P. Mineev, Int. J. Mod. Phys. **18**, 2963 (2004).
28. K. Yosida, *Theory of magnetism*, Springer (1998).
29. I. Bonalde, W. Bramer-Escamilla and E. Bauer, Phys. Rev. Lett. **94**, 207002 (2005).
30. N. Hayashi, K. Wakabayashi, P. A. Frigeri and M. Sigrist, Phys. Rev. B **73**, 024504 (2006)
31. H. Mukuda, S. Nishide, A. Harada, K. Iwasaki, M. Yogi, M. Yashima, Y. Kitaoka, M. Tsujino, T. Takeuchi, R. Settai, Y. Onuki, E. Bauer, K. M. Itoh, and E. E. Haller, J. Phys. Soc. Jpn. **78**, 014705 (2009).
32. T. Takeuchi, T. Yasuda, M. Tsujino, H. Shishido, R. Settai, H. Harima, and Y. Onuki, J. Phys. Soc. Jpn. **76**, 014702(2007).
33. S.-K. Yip, Phys. Rev. B **65**, 144508 (2002).
34. P.A.Frigeri, D.F.Agterberg and M.Sigrist, New J.Phys. **6**, 115 (2004).
35. K.V.Samokhin, Phys. Rev. Lett. **94**, 027004 (2005).
36. K.V.Samokhin, Phys. Rev. B **76**, 094516 (2007).
37. M. Yogi, H. Mukuda, Y. Kitaoka, S. Hashimoto, T. Yasuda, R. Settai, T. D. Matsuda, Y. Haga, Y. Onuki, P. Rogl and E. Bauer, J. Phys. Soc. Jpn. **75**, 013709 (2006).
38. K. Izawa, Y. Kasahara, Y. Matsuda, K. Behnia, T. Yasuda, R. Settai, and Y. Onuki, Phys. Rev. Lett. **94**, 197002 (2005).
39. S. Fujimoto, J. Phys. Soc. Jpn. **75**, 083704 (2006).
40. Y. Yanase and M. Sigrist, J. Phys. Soc. Jpn. **77**, 124711 (2008).
41. M. Yogi, Y. Kitaoka, S. Hashimoto, T. Yasuda, R. Settai, T. D. Matsuda, Y. Haga, Y. Onuki, P. Rogl, and E. Bauer, Phys. Rev. Lett. **93**, 027003 (2004).
42. N. Hayashi, K. Wakabayashi, P. A. Frigeri, and M. Sigrist, Phys. Rev. B **73**, 092508 (2006).
43. Y. Yanase and M. Sigrist, J. Phys. Soc. Jpn. **76**, 043712 (2007).
44. T. Yasuda, H. Shishido, T. Ueda, S. Hashimoto, R. Settai, T. Takeuchi, T. D. Matsuda, Y. Haga, and Y. Onuki, J. Phys. Soc. Jpn. **73**, 1657 (2004).
45. N. Kimura, K. Ito, H. Aoki, S. Uji, and T. Terashima, Phys. Rev. Lett. **98**, 197001 (2007).
46. R. Settai, Y. Miyauchi, T. Takeuchi, F. Levy, I. Sheikin, and Y. Onuki, J. Phys. Soc. Jpn. **77**, 073705 (2008).
47. Y. Tada, N. Kawakami, and S. Fujimoto, Phys. Rev. Lett. **101**, 267006 (2008).
48. V.P. Mineev and K.V. Samokhin, Zh. Eksp. Teor. Fiz. **105**, 747 (1994) [Sov. Phys. JETP **78**, 401 (1994)].
49. R.P. Kaur, D.F. Agterberg and M. Sigrist, Phys. Rev. Lett. 94, 137002 (2005).
50. O.V.Dimitrova, M.V.Feigel'man, Pis'ma v ZhETF **78**,1132 (2003); Phys. Rev.B **76**,014522 (2007).
51. D. F. Agterberg and R. P. Kaur, Phys. Rev. B **75**, 064511 (2007).
52. V.P. Mineev and M. Sigrist, cond-mat/0904.2962.
53. J. van den Brink and D.I. Khomskii, J. Phys. - Condens. Matter **20**, 434217 (2008).
54. R.D. Parks, "Superconductivity", Marcel Dekker Inc. (1969).
55. V.M. Edelstein, Phys. Rev. Lett. **75**, 2004 (1995).
56. S. Fujimoto, Phys. Rev. B **72**, 024515 (2005).
57. M. Sato and S. Fujimoto, Phys. Rev. B **79**, 094504 (2009).
58. Y. Tanaka, T. Yokoyama, A.V. Balatsky and N. Nagaosa, Phys. Rev. B **79**, 060505 (2009).
59. C.-R. Hu, Phys. Rev. Lett. **72**, 1526 (1994).
60. S. Kashiwaya and Y. Tanaka, Rep. Prog. Phys. **63**, 1641 (2000).
61. M. Sigrist, Prog. Theor. Phys. **99**, 899 (1998).
62. A. Furusaki, M. Matsumoto and M. Sigrist, Phys. Rev. B **64**, 054514 (2001).
63. A. B. Vorontsov, I. Vekhter and M. Eschrig, Phys. Rev. Lett. **101**, 127003 (2008).
64. Y. Matsunaga, N. Hiasa and R. Ikeda, Phys. Rev. B **78**, 220508 (2008).
65. N. Hiasa and R. Ikeda, Phys. Rev. B **78**, 224514 (2008).
66. Y. Nagai, Y. Kato and N. Hayashi, J. Phys. Soc. Jpn. **75**, 043706 (2006).
67. S. Fujimoto, J. Phys. Soc. Jpn. **76**, 034712 (2007).

68. A. Sumiyama, K. Nakatsuji, Y. Tsuji, Y. Oda, T. Yasuda, R. Settai and Y. Onuki, J. Phys. Soc. Jpn. **74**, 3041 (2005).
69. N. Hayashi, C. Iniotakis, M. Machida and M. Sigrist, Physica C **468**, 844 (2008).
70. H. Q. Yuan, D. F. Agterberg, N. Hayashi, P. Badica, D. Vandervelde, K. Togano, M. Sigrist, M. B. Salamon, Phys. Rev. Lett. **97**, 017006 (2006).
71. M. Nishiyama, Y. Inada, and G-q. Zheng, Phys. Rev. Lett. **98**, 047002 (2007).