Conventional mechanisms for exotic superconductivity

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We consider the pairing state due to the usual BCS mechanism in substances of cubic and hexagonal symmetry where the Fermi surface forms pockets around several points of high symmetry. We find that the symmetry imposed on the multiple pocket positions could give rise to a multidimensional nontrivial superconducting order parameter. The time-reversal symmetry in the pairing state is broken. We suggest several candidate substances where such ordering may appear, and discuss means by which such a phase may be identified. [S0163-1829(99)00942-X]

Most conventional superconductors are described very well by the BCS theory.[1] The electron-phonon interaction mediates an attraction between electrons that is stronger than the Coulomb repulsion. This gives rise to the Cooper instability of the normal state leading to the appearance of a condensate of pairs. The order parameter (the anomalous function $\mathcal{F}$; Ref. 2) in this case belongs to the "s-wave" type, *i.e.*, it is invariant with respect to the transformations of $G \otimes R$, where G is the crystal point group and R is time-reversal operation. As a result the quasiparticle spectrum has a gap, which leads to well-known experimental consequences. A variety of materials: ^{3}He,[3] UBe_{13},[4] UPt_3,[5] high-T_c materials,[6] and Sr_2RuO_4,[7] have been discovered that potentially break the $G\otimes R$ symmetry of the normal state. A well-known example is the A phase of ^{3}He,[3] which is not rotationally or time-reversal invariant (note that the B phase of ^{3}He is both rotation and time-reversal invariant). Such non-s-wave superconductors are usually expected to have a gapless excitation spectrum and arise when the interaction itself depends upon the superconducting ground state (in the case of ^{3}He the BCS ground state is the B phase and the spin-fluctuation feedback effect is required to stabilize the A phase[8]). All the possible symmetry classes of the superconducting state in crystalline materials were enumerated in Ref. 9 (for a review, see Refs. 10 and 11).

We show below that exotic superconductivity can be a much more common phenomenon and does not require unusual mechanisms. The electron-phonon and Coulomb interactions are enough to give rise to a multidimensional order parameter which would have lower symmetry than the normal state — including the breaking of time-reversal invariance. The effects we consider are possible in metals with several pockets which are centered at or around some symmetry points of the Brillouin zone (BZ). A BCS approximation generalized to the multiband case (see, e.g., Ref. 12) will be used. The point here is that since the form of the interaction parameters describing the two electron scattering on and between the different pockets of the Fermi surface (FS) is fixed by symmetry, the resulting superconducting state need not be s wave. Below we consider three cases in detail: (a) three FS pockets centered about the X-points of a simple cubic lattice; (b) three FS pockets at the M points of the hexagonal lattice; (c) four FS pockets at the L points in the face-centered-cubic lattice. A complete analysis of all other high-symmetry points is possible, and will be published elsewhere.[13]

We emphasize that this FS structure is not unusual. Indeed, superconductivity with pockets as in case (a) and $T_c \sim 0.1$ K is found in LaB_6.[14] Another example is given by the superconducting semiconductors such as PbTe, SnTe, or $SrTiO_3$.[15] Many materials exist where such FS sheets coexist with other nonsymmetry related FS sheets and some of these materials have anomalous superconducting properties. One example is $CeCo_2$;[16,17] Fig. 1 shows some of the FS sheets of $CeCo_2$ $(T_c=1.6$ K). We will return to this later.[13]

We will use the generalized Ginsburg-Landau (GL) functional to identify possible nontrivial superconducting phases. The Hamiltonian for several separate pieces of the FS can be written in the following form:

$$H=\sum_{\alpha\sigma\mathbf{p}} \epsilon(\mathbf{p}) a^{\dagger}_{\alpha\sigma}(\mathbf{p}) a_{\alpha\sigma}(\mathbf{p}) + \frac{1}{2}\sum_{\mathbf{k},\mathbf{k}',\mathbf{q}} \sum_{\alpha\beta\sigma\sigma'} \times \lambda_{\alpha\beta}(\mathbf{q}) a^{\dagger}_{\alpha\sigma}(\mathbf{k}+\mathbf{q}) a^{\dagger}_{\beta\sigma'}(\mathbf{k}'-\mathbf{q}) a_{\alpha\sigma'}(\mathbf{k}') a_{\beta\sigma}(\mathbf{k}), \tag{1}$$

where σ and σ' are spin indices, $\lambda_{\alpha\beta}(\mathbf{q})$ includes the interaction for scattering two electrons from the pocket α into pocket β which is due to both Coulomb and electron-phonon terms. Introducing the anomalous Green's function $\hat{\mathcal{F}}_\alpha(x-x')$ for each FS sheet α, the corresponding Gor'kov equations[18] can be used to obtain the following solution at finite temperatures for the case of singlet pairing:

$$\mathcal{F}^{\dagger}_{\alpha}(\omega_n,\mathbf{p}) = \frac{\Delta^*_\alpha(\mathbf{p})}{\omega_n^2+\xi^2+|\Delta_\alpha(\mathbf{p})|^2}, \tag{2}$$

where

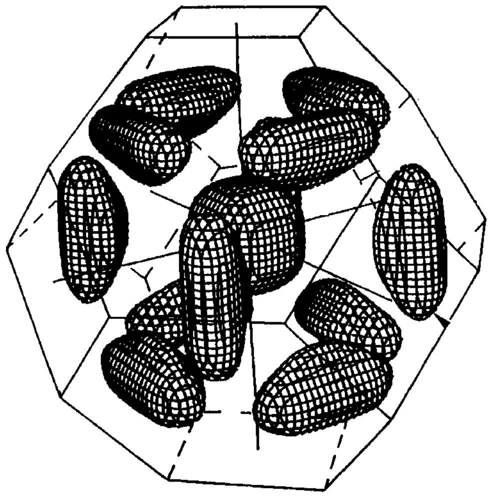

FIG. 1. Some FS sheets of $CeCo_2$ (from Ref. 17).

$$\Delta^*_\alpha(\mathbf{p}) = -\frac{T}{(2\pi)^3}\sum_\beta \sum_n \int d\mathbf{k}\lambda_{\beta\alpha}(\mathbf{p}-\mathbf{k})F^\dagger_\beta(\omega_n,\mathbf{k}). \tag{3}$$

Equation (2) being expanded in $|\Delta_\alpha|$ up to the third order, Eq. (3) becomes a variation of the GL functional with respect to the vector order parameter $\Delta_\alpha(\mathbf{p})$.[19,20] For simplicity we assume that each $\Delta_\alpha(\mathbf{p})$ is constant along the corresponding FS, and to fourth order in Δ_α we can write

$$F_s - F_n = -\Delta^*_\alpha\left[(\hat{\lambda}^{-1})_{\alpha\beta} - \delta_{\alpha\beta}\frac{mp_0}{2\pi^2}\ln\left(\frac{2\gamma\omega_D}{\pi T}\right)\right]\Delta_\beta + \frac{7\zeta(3)mp_0}{32\pi^4T^2}\sum_\beta |\Delta_\beta|^4, \tag{4}$$

where $\hat{\lambda}^{-1}$ is the matrix inverse to the interaction $\lambda_{\alpha\beta}$, ω_D is the cutoff (Debye) frequency.

We now analyze three different cases for multiple FS sheets.

(*a*) *Three X points in a cubic lattice*. The interaction matrix $\hat{\lambda}$ for three X points takes the following general form

$$\lambda_{\alpha\beta} = \lambda\,\delta_{\alpha\beta} + \mu(1-\delta_{\alpha\beta}). \tag{5}$$

Here λ is the interaction on the same pocket, μ couples any two different pockets. Consider first the linearized gap equation Eqs. (2) and (3) to determine T_c:

$$\Delta^*_\alpha\frac{2\pi^2}{mp_0} = -\sum_\beta \lambda_{\alpha\beta}\Delta^*_\beta\ln\left(\frac{2\gamma\omega_D}{\pi T_c}\right). \tag{6}$$

The three Δ_α transform among each other at cubic symmetry transformations forming a three-dimensional (3D) reducible representation of the cubic group O_h, which *is split* into a 1D A_{1g} and a 2D E_g irreducible representation. These two representations correspond to different order parameters with two critical temperatures:

$$T_{c,E} = \frac{2\gamma\omega_D}{\pi}\exp\left(\frac{2\pi^2}{mp_0(\lambda-\mu)}\right) \quad (2\text{D}), \tag{7}$$

$$T_{c,A} = \frac{2\gamma\omega_D}{\pi}\exp\left(\frac{2\pi^2}{mp_0(\lambda+2\mu)}\right) \quad (1\text{D}) \tag{8}$$

(the terms in the exponents must be negative for the Cooper effect to take place). The basis wave function for 1D identical representation is

$$l = (\Delta_1+\Delta_2+\Delta_3)/\sqrt{3} \tag{9}$$

and the basis wave functions for the 2D representation can be chosen as

$$\eta_1 = (\Delta_1+\epsilon\Delta_2+\epsilon^2\Delta_3)/\sqrt{3},$$
$$\eta_2 = (\Delta_1+\epsilon^2\Delta_2+\epsilon\Delta_3)/\sqrt{3}, \tag{10}$$

where $\epsilon=\exp(2\pi i/3)$. From Eq. (8) if $\lambda-\mu<0$ and $\mu>0$ then superconductivity will belong to the nontrivial 2D E_g representation, i.e., if the interaction *between two* different FS pockets is dominated by Coulomb repulsion. Let us consider the latter case in detail. Rewriting the Landau functional Eq. (4) in terms of l, η_1, and η_2, we obtain, for temperatures T *near* $T_{c,E}$:

$$\frac{2\pi^2}{mp_0}\delta F = \frac{T-T_{c,E}}{T_{c,E}}(|\eta_1|^2+|\eta_2|^2) + \ln(T_{c,E}/T_{c,A})|l|^2 + \frac{7\zeta(3)}{48\pi^2T^2_{c,E}}(|\eta_1|^4+|\eta_2|^4+4|\eta_1|^2|\eta_2|^2+F^{(4)}_{l\eta}), \tag{11}$$

where $F^{(4)}_{l\eta}$ is the fourth-order term in the GL functional which may admix the 1D representation l:

$$F^{(4)}_{l\eta} = 2l(\eta_1^*)^2\eta_2 + 2l\eta_1(\eta_2^*)^2 + \text{H.c.} \tag{12}$$

With $T_{c,A}<T_{c,E}$ the superconducting instability will correspond to the 2D representation E_g of the cubic point group. The fourth-order coefficients in Eq. (11) indicate that the class $O(D_2)$ is the most preferable energetically.[9] This class corresponds to a phase with $\eta_2=0$, $\eta_1\neq 0$ in Eq. (11). The symmetry properties of this class are known[9]. Time-reversal symmetry is broken and allows for antiferromagnetic domains and for fractional vortices to appear (see, e.g., (11)). In principle point nodes should appear where the FS intersects the cube diagonals. This would lead to the *electronic* contribution in the T^3 behavior for the heat capacity at low temperatures. In our case, however, there is no FS along the diagonals of the cube and the low-temperature thermodynamic properties will be determined by the gap of the same magnitude for all three FS sheets. In the presence of another FS, for example, at the Γ point, the nontrivial order $O(D_2)$ will be induced on it. In this case the point nodes will exist and power laws in thermodynamic properties due to the superconductivity should be seen experimentally. The anisotropy of the upper critical field (H_{c2}) (Ref. 21) *near* T_c for this class also requires that (at least) two vortex lattice phases (with a second-order transition between them) exists when the magnetic field is applied along the (1,1,0) and equivalent directions. Note from Eq. (12) that the terms linear in l identically disappear for this class, i.e., there will be no admixture of the s-wave component.

(*b*) *Three X points in a hexagonal lattice*. Calculations in this case are the same as in the previous case, i.e., Eqs. (5)–(12) apply. We only have to specify the symmetry properties and the superconducting class in this case since the symmetry of the lattice is different. The three-dimensional representation is split by the hexagonal group $D_{6h}\otimes R$ into 1D (A_{1g}) and 2D (E_{2g}). Note that the basis functions for E_{2g} can be once again chosen as given by Eq. (10). The phase with $\eta_1\neq 0,\eta_2=0$ has the lowest free energy and in this case corresponds to the nontrivial class $D_6(C_2)$. Time-reversal symmetry for this class is broken,[9] and *ferromagnetism* is allowed. Point nodes (at two points of intersection of an additional FS at the Γ point with the sixfold axis) can be seen in thermodynamic properties but again these nodes are only present if such a FS exists. The upper critical field is isotropic near T_c for this superconductivity representation. Nevertheless, it can be shown that there will also exist (at least) two distinct vortex lattice phases with a second-order transition between them for the magnetic field applied in the basal plane.[13]

(*c*) *Four L points in the fcc lattice*. The interaction and the linearized gap equation for the four L points again take the form Eqs. (5) and (6). This time the 4D representation Δ_α is split into the 1D (A_{1g}) and 3D (F_{2g}) irreducible representations. The critical temperatures for the two representations are now given by

$$T_{c,F}=\frac{2\gamma\omega_D}{\pi}\exp\left(\frac{2\pi^2}{mp_0(\lambda-\mu)}\right)\quad(3\mathrm{D}),\tag{13}$$

$$T_{c,A}=\frac{2\gamma\omega_D}{\pi}\exp\left(\frac{2\pi^2}{mp_0(\lambda+3\mu)}\right)\quad(1\mathrm{D}).\tag{14}$$

The basis functions for the 1D and 3D representations are

$$l=(\Delta_1+\Delta_2+\Delta_3+\Delta_4)/2\quad(1\mathrm{D})\tag{15}$$

and

$$\eta_x=(\Delta_1-\Delta_2-\Delta_3+\Delta_4)/2,$$
$$\eta_y=(\Delta_1+\Delta_2-\Delta_3-\Delta_4)/2\quad(3\mathrm{D})\tag{16}$$
$$\eta_z=(\Delta_1-\Delta_2+\Delta_3-\Delta_4)/2.$$

The nontrivial 3D representation is stable if $\lambda-\mu<0$ and $\mu>0$, i.e., if the interaction is *attractive* for each pocket alone, while it is *repulsive* between two different pockets. As above, we can expand Eq. (4) in terms of l and $\vec{\eta}$. Dropping the 1D identical representation, we get

$$\frac{2\pi^2}{mp_0}\delta F=\frac{T-T_{c,F}}{T_{c,F}}(\vec{\eta}\vec{\eta}^*)+\frac{7\zeta(3)}{64\pi^2T_{c,F}^2}[2(\vec{\eta}\vec{\eta}^*)^2+|\vec{\eta}^2|^2-2(|\eta_x|^4+|\eta_y|^4+|\eta_z|^4)].\tag{17}$$

The GL coefficients in Eq. (17) places the system right on the boundary of two phases, superconducting classes $D_4^{(2)}(D_2)\otimes R$ and $D_4(E)$ (see Fig. 2). This degeneracy is an artifact of the BCS theory, it is *not* lifted by higher-order terms in the GL functional. The presence of a FS at the Γ point lifts this degeneracy. As a result, the magnetic super-

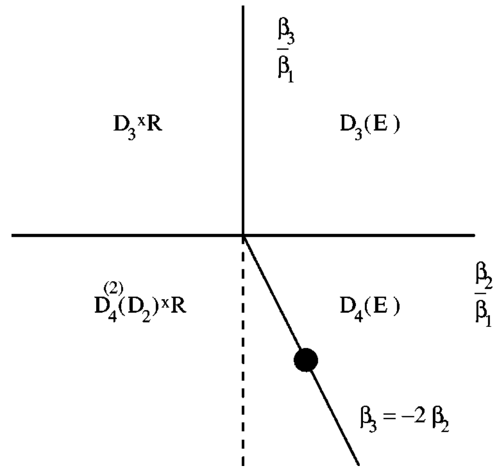

FIG. 2. Regions of existence of different superconducting phases on the basis of the three-dimensional representations of the cubic group (from Ref. 9). A point on the boundary of two phases corresponds to our BCS solution.

conducting class $D_4(E)$ is likely to appear. This class also allows ferromagnetism. Note that it has a line of nodes (at the intersection of the FS with the horizontal plane of symmetry) i.e., $C\propto T^2$ at low temperatures.[9] There are also point nodes at the intersection of the FS with the fourfold symmetry axis. This representation also exhibits an anisotropy of H_{c2} near T_c. In principle multiple vortex lattice phases can also exist for this class but they are not required by symmetry as they are for the E representations discussed above.

In the above cases, other than the standard isotropic order parameter, only multidimensional order parameters appeared. This leads to the possibility of domain walls between different equivalent superconducting states and as a possible consequence the existence of inhomogeneous magnetic order[9] (see also Refs. 10 and 11). Also in all the above cases the resulting superconducting states had gaps of equal magnitude on each of the FS sheets. In such a case a Hebel-Slichter peak in $1/T_1$ measurements may be present. The nontrivial representations were stable when the pair interaction between the different sheets was repulsive (independent of the intrasheet interaction). In many materials the Coulomb repulsion can be comparable to the attraction between electrons due to electron-phonon interactions. This is illustrated through the reduction of isotope effect due to Coulomb repulsion. It is well known that for a number of metals $T_c \propto M^{-\alpha}$, where not only $\alpha\neq 0.5$ but it may even have the opposite sign ($\alpha\simeq -2$ for $\alpha-U$; Ref. 22). The sensitivity of these exotic superconducting phases to impurities needs a more detailed analysis. However, provided the interpocket defect scattering amplitudes are much smaller than the intrapocket amplitudes, these phases will survive the presence of a considerable amount of defects (due to the ordinary BCS pairing on each sheet). This will be studied in more detail in Ref. 13.

In summary, we have shown that exotic superconductivity can appear merely as a competition of the phonon and Coulomb interactions if the FS consists of several pockets located at some symmetry points. Time-reversal symmetry is broken for the nontrivial order, meaning that the superconducting transition should be accompanied by some kind of magnetic order. The simplest methods to identify exotic order parameters are, apart from the phase-sensitive measurements, the power-law dependence of the heat capacity (due to the nodes), measurements of the upper critical field anisotropy $H_{c2}(\theta)$ at T_c,[21] or the observation of transitions between different vortex lattice phases. Note that if the FS pockets are fully isolated then the nodes are absent since the order parameter is then constant on each FS pocket and changes phase as one moves from one pocket to another. Nodes could appear, however, if there are ''necks'' connecting different sheets[14] or if superconductivity is induced on a FS centered, for example, around the Γ point. The upper critical-field anisotropy near T_c does not work as a test of nontrivial order in the hexagonal group.[21] The magnetic order, on the other hand, can be observed in μSR (muon spin-rotation) measurements or magnetization measurements in small enough samples (where the dimensions are on the order of the penetration depth). A general classification of all cases of nontrivial superconductivity of the type considered above is possible. These FS sheets are not always centered on the BZ boundary, as, for example, in some doped semiconductors[15] and $CeCo_2$.[17] We postpone a detailed analysis of the various possibilities to a future work.[13]

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