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Structure of "triplet" superconducting energy gaps

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Application of group theory to the "triplet" superconducting states in metals is discussed with special attention to the explanation of experimental phenomena on "heavy-electron" superconductors. It is shown that naive extrapolation from the case of ^3He is not justifiable.

In recent months several additional "heavy-fermion" compounds have joined CeCu_2Si_2 (Ref. 1) as superconductors: UBe_{13} ,² UPt_3 ,³ and UPt_2C ,⁴ at least. For a number of reasons given in a previous paper,⁵ these are likely to be unconventional so-called "triplet" superconductors, with odd-parity pair functions. Some theoretical speculations on such materials (e.g., Ref. 6) have based their study on the theory of ^3He ; however, there are two major differences. First, as in the 3P_2 state of neutron matter,⁷ there is strong spin-orbit coupling and the spin and orbital variables may not be freely rotated independently; second, there is an underlying crystal structure and hence, the orbital variables—and through them the spins—have only a discrete rotation symmetry. Thus, it is essential to formulate the theory including the effects of spin-orbit coupling and crystal symmetry on the band electrons. At a later stage we shall also have to include their effects on the interactions, especially on the Brinkman-Anderson feedback mechanism via the anisotropic susceptibility which will undoubtedly play an important role; but we will focus here primarily on the possible states near T_c and their degeneracies, which will be controlled by simple symmetry considerations.

In the presence of spin-orbit coupling, spin labels can no longer be given to the Bloch states in a metal.⁸ Each Bloch state will contain spin-up and spin-down components, just as the Wannier functions on individual ions will be, in general, admixtures of up and down spin. For example, the Wannier function for the first f band in cerium will be like

$$\Psi_{M=5/2}^{J=5/2} = \frac{1}{\sqrt{2}} \phi_2^3 \chi_{1/2}^{1/2} - \sqrt{3} \phi_3^3 \chi_{-1/2}^{1/2} ,$$

where the ϕ 's are orbital and χ 's are spin functions of labels L, M_L, S, M_S . We can expect that insofar as the band quasi-particles admix with the f band, they too will be thoroughly mixed in their spin directions.

We assume that the crystal has parity symmetry; otherwise there will be only one possible form of superconductivity since the bands are then nondegenerate. Then for every \vec{k} and every band there will necessarily be four degenerate states, which by Kramers's theorem cannot be

identical:

$$\vec{k}, P\vec{k}, T\vec{k}, \text{ and } PT\vec{k} .$$

(P is the parity operator; T is the time-reversal operator.) These correspond to $\vec{k} \uparrow$, $-\vec{k} \uparrow$, $-\vec{k} \downarrow$, and $\vec{k} \downarrow$ in the conventional theory. P does not reverse either spin or orbital angular momentum, only \vec{k} , and T reverses all three. To define states in the degenerate manifold $\vec{k}, PT\vec{k}$, we pick the state with maximum moment in the z direction. It can be shown that this defines a continuous sheet in \vec{k} space.

Conventional "singlet" superconductivity involves only a pairing operator $\langle C_{\vec{k}}^\dagger C_{T\vec{k}}^\dagger \rangle = b_{\vec{k}}^\dagger$ and multiplies this by an even—often, isotropic—function of \vec{k} . Then $b_{\vec{k}}^\dagger$ is even under parity. This pair wave function is an eigenstate of parity = +1. It does not mix at all with the odd parity pairings

$$\langle C_{\vec{k}}^\dagger C_{P\vec{k}}^\dagger \rangle , \quad (1)$$

and

$$\langle C_{T\vec{k}}^\dagger C_{PT\vec{k}}^\dagger \rangle , \quad (2)$$

each of which is automatically $P = -1$. We may construct a third $P = -1$ pairing,

$$\langle C_{\vec{k}}^\dagger C_{T\vec{k}}^\dagger - C_{P\vec{k}}^\dagger C_{PT\vec{k}}^\dagger \rangle , \quad (3)$$

which corresponds to the third spin component of $S = 1$, for the conventional system.

In ^3He , these three pairings are totally independent except for very weak interactions as far as quadratic terms in the free energy are concerned, because they are not connected by any normal linear, spin-independent interaction. They quite literally have $M_S = 1, 0$, and -1 , and an interaction term such as

$$V \langle C_{\vec{k}_1}^\dagger C_{-\vec{k}_1}^\dagger \rangle \langle C_{-\vec{k}'_1} C_{\vec{k}'_1} \rangle ,$$

is forbidden by spin symmetry. They couple at the level of quartic terms, especially because of the nonlinear feedback effect of anisotropic spin susceptibility. But it is the qua-

dratic term which determines T_c , and so all $L=1$ states have exactly the same T_c . This is why, for instance, the A_1 phase appears near T_c , and why the equilibria are so sensitive to the small quartic effects. As far as I can see, in the presence of spin-orbit coupling this degeneracy need no longer be present and the "spin" functions can be coupled at quadratic level, hence, greatly reducing the degenerate manifold of possible "triplet" states. Therefore it becomes a matter for group-theoretical investigation to determine what kinds of states are possible in a given crystal structure.

There are a number of possible ways to describe the appropriate group. For instance, one may observe that the general pairing function may be written as

$$\langle \psi(\bar{r}, \sigma) \psi(\bar{r}', \sigma') \rangle = F(\bar{r}, \bar{r}'; \sigma, \sigma'), \quad (4)$$

where (translational) periodicity, parity, antisymmetry, and time-reversal invariance are the fundamental requirements so that

$$F(\bar{r} + \bar{\tau}, \bar{r}' + \bar{\tau}; \sigma, \sigma') = F(\bar{r}, \bar{r}'; \sigma, \sigma'), \quad (5)$$

$$F(-\bar{r}, -\bar{r}'; \sigma, \sigma') = \pm F(\bar{r}, \bar{r}'; \sigma, \sigma'), \quad (6)$$

$$F(\bar{r}', \bar{r}; \sigma', \sigma) = -F(\bar{r}, \bar{r}'; \sigma, \sigma'), \quad (7)$$

and, as well,

$$TF = F^*(\bar{r}, \bar{r}', -\sigma, -\sigma'), \quad (8)$$

must also be a solution, but not necessarily linearly independent of F .

A simple way to understand the implications of group theory is to specialize to the case in which $\bar{r}' = -\bar{r}$. Then clearly we have two possible ways to satisfy (6), (7), and

$$f_{++}(\bar{r}, \sigma; \bar{r}' \sigma') = \int d\Omega_{\bar{k}} \exp i \bar{k}(\bar{r} - \bar{r}') u_+(-\bar{r}) u_+(\bar{r}'), \quad (13a)$$

$$f_{--}(\bar{r}, \sigma; \bar{r}' \sigma') = \int d\Omega_{\bar{k}} \exp i \bar{k}(\bar{r} - \bar{r}') u_-^*(\bar{r}) u_-^*(-\bar{r}'), \quad (13b)$$

$$f_{+-}(\bar{r}, \sigma; \bar{r}' \sigma') = \int d\Omega_{\bar{k}} \exp i \bar{k}(\bar{r} - \bar{r}') \{u_+(-\bar{r}) u_-^*(-\bar{r}') - u_-^*(\bar{r}) [u_+(+\bar{r}')]\}. \quad (13c)$$

Either way it is clear how we are to interpret the action of one of the rotations or other transformations of the crystal point group (identical with the group at point Γ) on the pair function: It rotates \bar{r} or \bar{k} and the quantization axis of spin together. Thus the group for which the pair amplitudes should provide a basis consists of the crystal point group rotation operators acting on odd-parity space functions times spin functions from the $S=1$ manifold. Neither space nor spin is free to rotate independently.

I remind the reader that as in ${}^3\text{He}$ the most complete freedom of choice for the f exists only with respect to the quadratic terms in $F(\psi)$, and that already at the level of quartic terms the system picks, in case of degeneracy of ψ , one particular type of structure which breaks some or all of the extra freedom permitted by the symmetry-determined degeneracy of ψ . Thus, for instance, ${}^3\text{He}$ has the A_1 phase in a magnetic field near T_c , since, although A_1 is quite unfavorable for the quartic terms in the superconducting free energy, the quadratic terms leave the T_c 's of all possible pairings the same. Whatever part of the point-group symmetry is broken by the choice of state is restored by the possibility of reorienting the state.

(8): first, the odd-parity or triplet case,

$$F(\bar{r}, -\bar{r}, +, +) = -F(-\bar{r}, \bar{r}, +, +), \quad (9a)$$

$$F(\bar{r}, -\bar{r}, -, -) = -F(-\bar{r}, \bar{r}, -, -), \quad (9b)$$

$$F(\bar{r}, -\bar{r}, +, -) = -F(-\bar{r}, \bar{r}, +, -) \\ = -F(-\bar{r}, \bar{r}, -, +), \quad (9c)$$

or second, the ordinary "singlet", even-parity case,

$$F(\bar{r}, -\bar{r}, +, -) = +F(-\bar{r}, \bar{r}, +, -) \\ = -F(-\bar{r}, \bar{r}, -, +). \quad (10)$$

It is also true of (10), but not of (9), that TF may be chosen to be $-F$. The triplet case does not necessarily retain T symmetry except in the nondegenerate cases; where T symmetry remains we have the "unitary" case as in ${}^3\text{He}$ where the spectrum of quasiparticles remains doubly degenerate.

Now when we combine (9) with crystal symmetry, we arrive at a somewhat simpler version of the "double-group" arguments which are used to classify bands with spin-orbit splitting: One might call it a "triplet group." One may base this group on operations on the special \bar{r} , $-\bar{r}$ functions of (5), etc., which one might call $f_{++}(\bar{r})$, $f_{--}(\bar{r})$, and $f_{+-}(\bar{r})$, or on the set of pair amplitudes as a function of \bar{k} :

$$\langle C_{P\bar{k}} C_{\bar{k}} \rangle = f_1(\bar{k}), \quad (11a)$$

$$\langle C_{T\bar{k}} C_{PT\bar{k}} \rangle = f_2(\bar{k}), \quad (11b)$$

$$\frac{1}{2} (\langle C_{P\bar{k}} C_{TP\bar{k}} \rangle - \langle C_{T\bar{k}} C_{\bar{k}} \rangle) = f_3(\bar{k}). \quad (11c)$$

The orbital wave functions are

$$b_{\bar{k}}(\bar{r}, \sigma) = e^{i\bar{k}\cdot\bar{r}} u_{\sigma}(\bar{r}), \quad (12)$$

and then the function F of (4) is proportional to

Possible representations using as basis functions $\Psi(S=1) \times$ (odd-parity functions of \bar{k}) are in fact just the same as those for functions of \bar{k} . There are two physical cases of interest: cubic point group, as in UBe_{13} ; and axial symmetry (e.g., hexagonal) as in UPt_3 or CeCu_2Si_2 .

In the cubic point group it is easy to generalize the "cubic harmonics," polynomials of a given degree, to include $S=1$ functions by noting what J values can be made up from them. For example, the $L=1$ cubic harmonics $\bar{k}_x, \bar{k}_y, \bar{k}_z$ can combine to make $J=0, 1$, or 2 . These, in fact, give almost all the possible representations.

(i) Γ_1^- : $\bar{k}_x S_x + \bar{k}_y S_y + \bar{k}_z S_z$ (from $J=0$), where symbolically $S_x = \frac{1}{2}(\uparrow\uparrow + \downarrow\downarrow)$, $S_y = \frac{1}{2}i(\uparrow\uparrow - \downarrow\downarrow)$, $S_z = \frac{1}{2}(\uparrow\downarrow + \downarrow\uparrow)$. This is the most boring possibility, a "B" or Balian-Werthamer (BW) phase with uniform gap. A state of the same symmetry may easily be made up from $J=3$ as well, as, e.g., $2(\bar{k}_x^3 S_x + \bar{k}_y^3 S_y + \bar{k}_z^3 S_z) - (\bar{k} \cdot \bar{S})$, in which case the gap is by no means uniform but has nodes on 110 lines. A possible state for UBe_{13} could be this one.

(ii) Γ_{12}^- (from $J=1$): $F_a = \epsilon_{abc} \bar{k}_b S_c$, i.e., essentially $\bar{k} \times \bar{S}$. The same representation can be obtained from $L=3$. The symmetries of the three components are like

$\bar{k}_x \bar{k}_y \bar{k}_z (S_x, S_y, S_z)$.

(iii) Γ_{25}^- : This two-dimensional representation can be obtained from $L=1, J=2$, and one of the two degenerate functions is

$$(k_x S_x - k_y S_y) .$$

(iv) Γ_{15}^- : Again we have the $L=1, J=2$ example:

$$\bar{k}_x S_y + \bar{k}_y S_x, \bar{k}_x S_z + k_z S_x, \bar{k}_y S_z + \bar{k}_z S_y .$$

Note that the apparently similar symmetric combination Γ_{12}^- and the antisymmetric one Γ_{15}^- are nondegenerate, since they have different spin-orbit coupling.

(v) Γ_{17}^- : Finally, we have the one-dimensional representation which transforms like xyz : This here becomes

$$\begin{aligned} \bar{k}_x \bar{k}_y (\bar{k}_x S_y - \bar{k}_y S_x) + \bar{k}_y \bar{k}_z (\bar{k}_y S_z - \bar{k}_z S_y) \\ + \bar{k}_z \bar{k}_x (\bar{k}_z S_x - \bar{k}_x S_z) . \end{aligned}$$

In the axial case the whole story is much simpler. Here the only non-Abelian feature of the group is the mirror plane or 180° rotation perpendicular to the axis, and all representations are either onefold or twofold degenerate. The simple LS -coupling analog stands us in good stead here: We get only $M_J=0$ or $\pm M_J$ representations, the former nondegenerate and the latter doubly degenerate.

Let me emphasize that each group representation has its specific associated T_c , and that normally only one representation will be relevant. Thus, if the "boring" Γ_1 is it, there is actually only one state, with no free parameters except one overall phase. The same will tend to be true of the nondegenerate " $M=0$ " axial case, which may only be an axial distortion of the cubic one. On the other hand, it can be fully anisotropic, especially if the pairing is based more on an $L=3$ orbital state. Such states, though nondegenerate, could have as anisotropic χ 's and ρ_S 's as the A phases of ^3He . We should emphasize that these anisotropies may be such as to *oppose* the Brinkman-Anderson feedback

mechanism,⁹ which could account for the small specific heat in UPt_3 .

More interesting is the possibility of degenerate states. As far as we can see, none of these are lacking gap function zeros, for instance. Also, we will, in general, see *complex* linear combinations of the different substates, which means that we can have orbital currents and extra phase angles in the gap functions. On the other hand, in some cases there will be little or no freedom. For instance, in an axial $M_J = \pm 1$ case, the conventional arguments suggest that the system will pick one or the other of $M_J = \pm 1$, not the real combinations $\psi_M \pm \psi_{-M}$, and the axis of quantization is no longer free. More interesting would be a threefold degeneracy, where the real and imaginary parts may be any two orthogonal linear combinations of three functions, which does define a direction. It is not clear to me, however, that high-order terms will leave a continuous symmetry.

Any degeneracy leaves open the possibility—in fact, almost the certainty—of the existence of A_1 type states near T_c . This can give enormous χ anisotropies, and as a result, large H_{c2} anisotropy.

Further investigation will have to await more microscopic understanding of the states, as well as experimental indications of their thermodynamics and anisotropic response functions. So far no data are inconsistent with expectations from some one or another of these possibilities. UBe_{13} looks like a "boring" Γ_1 case, but may have the $L=3$ version which has gap-function zeros. UPt_3 suggests the highly anisotropic axial, either $\pm M_J$ or $M=0$. CeCu_2Si_2 seems suspiciously of the $M=0$, BW type. All show definite evidence of strong Fermi-liquid corrections, which must be unfolded before any quantitative comparisons with experiment can be made.

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