Symmetry properties of triplet superconductors

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I give a rigorous discussion of the group theory applicable to triplet superconductors and a list of possible symmetries and order parameters. It is "vanishingly improbable" to have curves of vanishing gap on the Fermi surface.

The unusual properties of the so-called "heavy-fermion" superconductors $CeCu_2Si_2$ (Ref. 1), UBe_{13} (Ref. 2), and UPt_3 (Ref. 3) led Varma,[4] Ott *et al.*,[5] and Anderson[6] to suggest the possibility that the pairing could be triplet or "p-wave."[7–10] Anderson[11] emphasized the need to take into account both spin-orbit coupling and the crystalline potential and listed the possible irreducible representations of the "p-wave" states, basically assuming that the order parameter could be treated as a spin field in $\mathbf{k}$ space. Volovik and Gor'kov[12] have listed a few of the possible symmetries. [See note (i) of *Notes added in proof*.]

In this paper, I give a rigorous treatment of the group theory of pairing in a crystal with strong crystalline potential and spin-orbit coupling. It will be seen that the assumption that the order parameter can be treated as an axial vector is justified, but for somewhat unexpected reasons. I shall also show all the symmetries that can be reached from the normal state by a second-order transition.

The problem of defining an order parameter is significantly more complicated in a crystal with spin-orbit coupling than in an isotropic liquid like ^{3}He.[6] In the latter, there are two readily apparent approaches to state labeling. In the first, one uses the same axis of quantization for spin whatever the momentum is. In the second, possibly more appealing aesthetically, the spin is quantized along the direction of the momentum—the spin quantum number is helicity. In this case, all proper rotations preserve helicity, while all improper operations reverse it. The trouble with this method is that the double-valued nature of the spin-rotation group intrudes—a rotation of 2π about any axis changes the sign of the wave function. It is then necessary to introduce a branch cut on the Fermi surface, across which the sign of the wave function changes. This introduces discontinuities in the matrices representing rotations, destroys the manifestness of spherical symmetry, and generally is more complicated and less appealing. The first method does not encounter these difficulties and is, so far as I know, always used for ^{3}He.

Unfortunately, that method is not available in our problem, because we do not have independent spin and space rotations. Additional problems may arise from singularities in band structure which can occur at points or lines of additional (more than Kramers) degeneracy. Such lines are particularly apt to appear in nonsymmorphic crystals—and all known heavy-fermion superconductors are nonsymmorphic. It will be seen below that the transformation behavior of the pair wave functions depends on the transformation properties of the wave function at $-\mathbf{k}$ as well as at $\mathbf{k}$. The relation between the two can become messy when there are screw axes or symmetry elements which do not pass through the inversion centers. It is undoubtedly possible to take all these problems into account, but it is much easier to sidestep them with the method we introduce in Eq. (17). This involves introducing a new notation where the old one is firmly established, but it is very easy, if desired, to return to the standard notation at the end. We shall be able to express the order parameter in ways independent of the choice of basis vectors—which is very desirable considering that the latter are defined only to within arbitrary 2×2 unitary transformations[13] at each point of $\mathbf{k}$ space.

We start by establishing notation and writing elementary results. For most purposes, we are interested in using the Bloch functions $\{\psi_{\mathbf{k}\alpha}\}$ as a basis; almost everywhere α is a two-valued index distinguishing, according to some convention, the two wave functions degenerate at $\mathbf{k}$. (We need not use an additional band index, because we are interested in what goes on near the Fermi surface. Adding it would only create a writing problem.) It is easier for the writer to use a single index μ, and the results so written will be valid for an arbitrary basis of one-electron functions. When desirable the form with $\mathbf{k}\alpha$ will also be used.

Under an operation $\mathscr{R}$ of the space group, ψ_μ is transformed according to

$$\mathscr{R}\psi_\mu=\psi_{\mu'}D_{\mu'\mu}(\mathscr{R})\ , \tag{1}$$

where the matrices $D(\mathscr{R})$ constitute a representation of the space group and we use the summation convention. Furthermore,

$$\mathscr{R}\psi^\dagger_\mu=\psi^\dagger_{\mu'}D^*_{\mu'\mu}(\mathscr{R})=D^\dagger_{\mu\mu'}(\mathscr{R})\psi^\dagger_{\mu'}\ . \tag{2}$$

The ψ_μ are also transformed by time reversal $\mathscr{K}$ according to the rule

$$\mathscr{K}\psi_\mu=\psi_{\mu'}K_{\mu'\mu}\ . \tag{3}$$

K is a unitary matrix, but a typical vector in the Hilbert space is transformed as

$$\mathscr{K}(\psi_\mu a_\mu)=(\mathscr{K}\psi_\mu)a^*_\mu=\psi_\lambda K_{\lambda\mu}a^*_\mu\ . \tag{4}$$

This characteristic of $\mathcal{K}$ is called antiunitarity. In particular,

$$\mathcal{K}^2\psi_\mu=\mathcal{K}(\psi_\lambda K_{\lambda\mu})=(\mathcal{K}\psi_\lambda)K^*_{\lambda\mu}=\psi_\kappa K_{\kappa\lambda}K^*_{\lambda\mu}\ . \tag{5}$$

For fermions $\mathcal{K}^2\psi_\mu=-\psi_\mu$, so that

$$KK^*=-1,\quad K=-\tilde{K}\ . \tag{6}$$

Furthermore,

$$\mathcal{K}^2\psi_\mu=K^\dagger_{\mu'}\mathcal{K}\psi_\lambda,\quad \mathcal{K}\psi^\dagger_\mu=K^\dagger_{\mu\mu'}\psi^\dagger_{\mu'}\ . \tag{7}$$

Since $\mathcal{K}$ commutes with all space-group operations $\mathcal{R}$,

$$\mathcal{R}\mathcal{K}\psi_\mu=\mathcal{K}\mathcal{R}\psi_\mu=(\mathcal{K}\psi_\nu)D^*_{\nu\mu}(R)=D^\dagger_{\mu\nu}\mathcal{K}\psi_\nu\ , \tag{8}$$

$$\mathcal{R}\mathcal{K}\psi^\dagger_\mu=\mathcal{K}\psi^\dagger_\nu D_{\nu\mu}\ . \tag{9}$$

In summary, $\mathcal{K}\psi_\mu$ and $\psi^\dagger_\mu$ behave identically under $\mathcal{K}$ and all $\mathcal{R}$. It is also convenient to define the operator which I shall call conjugation:[14]

$$\mathcal{C}\equiv\mathcal{J}\mathcal{K}=\mathcal{K}\mathcal{J}\ , \tag{10}$$

where $\mathcal{J}$ is inversion. $\mathcal{C}$ is also antiunitary and has the property $\mathcal{C}^2=-1$; it operates on basis vectors by

$$\mathcal{C}\psi_\mu=\psi_{\mu'}C_{\mu'\mu} \tag{11}$$

and, as with $\mathcal{K}$, $CC^*=-1$, $CC^\dagger=1$. $C=-\tilde{C}$. If the basis states are Bloch functions $\psi_{\mathbf{k}\alpha}$, C connects only the two Bloch functions degenerate at $\mathbf{k}$ and takes the form $e^{i\phi}i\sigma_2$, where σ_2 is of course the antisymmetric Pauli matrix.

Now the pair "wave function" Ψ is the expectation value of an operator product $\langle\psi_\mu\psi_\nu\rangle$ in an ensemble characterized by some density matrix P. If we subject the ψ's and P to some symmetry operation, we find a new object equal to $\langle\psi_\mu\psi_\nu\rangle$:

$$\begin{aligned}\Psi_{\mu\nu}=\langle\psi_\mu\psi_\nu\rangle&=\langle\mathcal{R}\psi_{\mu'}\mathcal{R}\psi_\nu\rangle_{\mathcal{R}}\\&=\tilde{D}_{\mu\mu'}(\mathcal{R})\Psi_{\mu'\nu'}(\mathcal{R})D_{\nu'\nu}(\mathcal{R})\ ,\end{aligned} \tag{12}$$

when the subscript $\mathcal{R}$ and $\Psi(\mathcal{R})$ remind us that P must also be transformed. If we transform with $\mathcal{K}$, we get

$$\Psi^*_{\mu\nu}=\langle\mathcal{K}\psi_\mu\mathcal{K}\psi_\nu\rangle_{\mathcal{K}}=\tilde{K}\Psi K\ . \tag{13}$$

In the case where the ψ_μ are Bloch functions, these equations take the form

$$\begin{aligned}&\langle\psi_{-\mathbf{k}\alpha}\psi_{\mathbf{k}\beta}\rangle=\tilde{D}_{-\mathbf{k}\alpha,-\mathbf{k}'\alpha'}(\mathcal{R})\langle\psi_{-\mathbf{k}'\alpha'},\psi_{\mathbf{k}'\beta'}\rangle_R D_{\mathbf{k}'\beta',\mathbf{k}\beta}(\mathcal{R})\ ,\\&\langle\psi_{-\mathbf{k}\alpha}\psi_{\mathbf{k}\beta}\rangle^*=\tilde{K}_{-\mathbf{k}\alpha,\mathbf{k}\alpha'}\langle\psi_{\mathbf{k}\alpha}\psi_{-\mathbf{k}\beta'}\rangle_{\mathcal{K}}K_{-\mathbf{k}\beta'\mathbf{k}\beta}\ .\end{aligned} \tag{14}$$

The problems mentioned in the introduction to this paper appears here in two ways: If we start at some $\mathbf{k}_0$ with a pair of Bloch function $(\psi_{\mathbf{k}_0\alpha'},\psi_{\mathbf{k}_0\beta})$, we can in the first place take arbitrary linear combinations of these. These combinations constitute a four-parameter family. In general, they have no direction that we can attribute to spin. If we calculate similar wave functions at a nearby point, we have no prescription to define uniquely the particular pair we use there. It is not obvious that there is a workable way to guarantee that after following the wave functions along a closed contour in $\mathbf{k}$ space, we will come back to precisely the same pair we started with, as opposed to linear combinations of them. It is similarly difficult to assure that there is a simple relation between $D_{-\mathbf{k}\alpha,-\mathbf{k}'\alpha'}(\mathcal{R})$ and $D_{\mathbf{k}\alpha,\mathbf{k}'\alpha'}(\mathcal{R})$. Actually dealing with these problems is, in any case, much more difficult than what we shall now do.

The one-electron density matrix ρ transforms according to

$$\begin{aligned}&\rho_{\mu\nu}=\langle\psi^\dagger_\mu\psi_\nu\rangle=\langle\mathcal{R}\psi^\dagger_\mu,\mathcal{R}\psi_\nu\rangle_{\mathcal{R}}=D^\dagger_{\mu\mu'}\rho_{\mu'\nu'}(\mathcal{R})D_{\nu'\nu}\ ,\\&\rho^*_{\mu\nu}=\langle\mathcal{K}\psi^\dagger_\mu\mathcal{K}\psi_\nu\rangle_{\mathcal{K}}=K^\dagger_{\mu\mu'}\rho_{\mu'\nu'}\mathcal{K}_{\nu'\nu}\ .\end{aligned} \tag{15}$$

When the ψ's are Bloch functions, we write

$$\begin{aligned}&\rho_{\alpha\beta}(\mathbf{k})=D_{\mathbf{k}\alpha,\mathbf{k}'\alpha'}\rho^\dagger_{\alpha\beta}(\mathbf{k}',\mathcal{R})D_{\mathbf{k}'\beta',\mathbf{k}\beta}\ ,\\&\rho^*_{\alpha\beta}(\mathbf{k})=K^\dagger_{\mathbf{k}\alpha,-\mathbf{k}\alpha'}\rho_{\alpha'\beta'}(\mathbf{k},\mathcal{K})K_{-\mathbf{k}\beta',\mathbf{k}\beta}\ .\end{aligned} \tag{16}$$

Thus, ρ and Ψ do not transform identically, and Ψ involves matrices connecting $-\mathbf{k}$ to $\mathbf{k}$, which involve the more global properties of the representation, and which lead to unpleasant complications as mentioned earlier.

If on the other hand, we define new objects

$$\chi_{\mu\nu}=\langle\mathcal{K}\psi_\mu,\psi_\nu\rangle=\tilde{K}_{\mu\mu'}\Psi_{\mu'\nu}\ , \tag{17}$$

we find, Eqs. (8) and (9),

$$\chi_{\mu\nu}=D^\dagger_{\mu\mu}\chi_{\mu'\nu'}(\mathcal{R})D_{\nu'\nu},\quad \chi^*_{\mu\nu}=K^\dagger_{\mu\mu'}\chi_{\mu'\nu'}(\mathcal{K})K_{\nu'\nu} \tag{18}$$

and in the Bloch function case,

$$\begin{aligned}&\chi_{\alpha\beta}(\mathbf{k})=D_{\mathbf{k}\alpha,\mathbf{k}'\alpha'}\chi^\dagger_{\alpha'\beta'}(\mathbf{k}';\mathcal{R})D_{\mathbf{k}'\beta',\mathbf{k}\beta}\ ,\\&\chi^*_{\alpha\beta}(\mathbf{k})=K_{\mathbf{k}\alpha,-\mathbf{k}\alpha'}\chi^\dagger_{\alpha'\beta'}(-\mathbf{k};\mathcal{K})K_{-\mathbf{k}\beta',k\beta}\ .\end{aligned} \tag{19}$$

Although χ also involves wave functions at $-\mathbf{k}$, they now have been so defined that they transform according to the way $\psi_\mathbf{k}$ transforms

Thus, the χ's transform in a manner entirely familiar to us, which is also the way the matrix elements of an operator in this basis set transform:

$$\begin{aligned}&\langle\psi^*_\mu\mid\mathcal{O}\mid\psi_\nu\rangle=D^\dagger_{\mu\mu'}\langle\psi^\dagger_{\mu'}\mid\mathcal{O}(\mathcal{R})\mid\psi_{\nu'}\rangle D_{\nu'\nu}\ ,\\&\langle\psi^\dagger_\mu\mid\mathcal{O}\mid\psi_\nu\rangle^*=K^*_{\mu\mu'}\langle\psi^*_{\mu'}\mid\mathcal{O}(\mathcal{K})\mid\psi_{\nu'}\rangle K_{\nu'\nu}\ ,\end{aligned} \tag{20}$$

where $\mathcal{O}(\mathcal{R})$ $[\mathcal{O}(\mathcal{K})]$ is the operator obtained from $\mathcal{O}$ by the transformation $\mathcal{R}(\mathcal{K})$.

We have now eliminated some of the unpleasantness I mentioned above, but we are still left with the fact that the Bloch functions at a single $\mathbf{k}$ are subject to a large indeterminancy—a four-parameter family of unitary transformations. This means that the χ's and particularly their k dependence are highly undetermined. Making sense out of their $\mathbf{k}$ dependence would be very difficult. We shall start dealing with this problem after introducing the gap function.

Precisely the same reasoning can be applied to the self-consistent Hamiltonian including the gap function Δ:

$$i\dot{\psi}_\mu=\psi_{\mu'}H_{\mu'\mu}+\psi^\dagger_{\mu'}\Delta_{\mu'\mu}\ . \tag{21}$$

This Δ transforms like Ψ, and we can rewrite the equation in the form

$$i\dot{\psi}_\mu = \psi_{\mu'} H_{\mu'\mu} + (\mathscr{K}\psi^\dagger_{\mu'})\mathscr{D}_{\mu'\mu} , \tag{22}$$

where $\mathscr{D}_{\mu\nu} = \tilde{K}_{\mu\mu'}\Delta_{\mu'\nu}$ now transforms like $\chi_{\mu\nu}$, like $H_{\mu\nu}$, and like $\mathscr{O}$ in Eq. (20). Here, I must emphasize that $\mathscr{K}\psi$ is to be interpreted as the Heisenberg operator $e^{-i\mathscr{K}t}(\mathscr{K}\psi_\mu)e^{i\mathscr{K}t}$, not as $\mathscr{K}(e^{-i\mathscr{K}t}\psi_\mu e^{i\mathscr{K}t})$.

Now if we suppose that for some operator $\mathscr{O}$, $\mathscr{D}_{\mu\nu} = \langle \psi^\dagger_\mu \mid \mathscr{O} \mid \psi_\nu \rangle$, the two sides are, respectively, equal to

$$D^\dagger_{\mu\mu'}\mathscr{D}_{\mu'\nu'}(\mathscr{R})D_{\nu'\nu} = D^\dagger_{\mu\mu'}\langle \psi^\dagger_{\mu'} \mid \mathscr{O}(\mathscr{R}) \mid \psi_{\nu'} \rangle D_{\nu'\nu} ,$$
$$\mathscr{D}_{\mu\nu}(\mathscr{R}) = \mathscr{O}(\mathscr{R})_{\mu\nu} . \tag{23}$$

If, to be more specific, we can write $\mathscr{D}_{\mu\nu} = \sum_i a_i \mathscr{O}^i_{\mu\nu}$, where the $\mathscr{O}^i$ transform as a representation $\hat{D}$ (not necessarily irreducible) of the symmetry group, we have

$$\mathscr{D}_{\mu\nu}(\mathscr{R}) = \sum_i a_i(\mathscr{R})\mathscr{O}^i_{\mu\nu} ,$$

but also

$$\mathscr{D}_{\mu\nu}(\mathscr{R}) = \sum_i a_i \hat{D}^{ij}\mathscr{O}^j_\mu \tag{24}$$

or

$$a_i(\mathscr{R}) = \sum_j a_j \hat{D}^{ji} .$$

Similarly,

$$\mathscr{D}_{\mu\nu}(\mathscr{K}) = [\mathscr{O}(\mathscr{K})]_{\mu\nu} ,$$
$$\mathscr{O}(\mathscr{K}) = a_i^* \mathscr{O}^i(\mathscr{K}) = \sum_i a_i^*(-1)^{t_i}\mathscr{O}^i , \tag{25}$$
$$a_i(\mathscr{K}) = (-1)^{t_i} a_i^* ,$$

where t_i characterizes the behavior of $\mathscr{O}^i$ under time reversal. Thus, the symmetry properties of the $\mathscr{D}$ are expressed through the coefficients a_i which are independent of the representation $\{\psi_\mu\}$.

More useful for most purposes is a related argument, appropriate to the case where the basis set consists of the Bloch functions, and the pairing is only between states at some $\mathbf{k}$ and its negative:

$$\chi_{\alpha\beta}(\mathbf{k}) = \langle \mathscr{K}\psi_{\mathbf{k}\alpha}, \psi_{\mathbf{k}\beta} \rangle \tag{26}$$

and $\mathscr{D}_{\alpha\beta}(\mathbf{k}) = \mathscr{D}_{\mathbf{k}\alpha,\mathbf{k}\beta}$ connects $\psi_{\mathbf{k}\beta}$ only with the time-reversed adjoints $\mathscr{K}\psi^\dagger_{\mathbf{k}\alpha}$. Suppose now that

$$\mathscr{D}_{\alpha\beta}(\mathbf{k}) = \sum_i a_i(\mathbf{k})\mathscr{O}^i_{\alpha\beta}(\mathbf{k}) . \tag{27}$$

Then, as before Eq. (24), the two sides are, respectively, equal to

$$D^\dagger_{\mathbf{k}\alpha,\mathbf{k}'\alpha'}(\mathscr{R})\mathscr{D}_{\alpha'\beta'}(\mathscr{R};\mathbf{k}')D_{\mathbf{k}'\beta',\mathbf{k}\beta}(\mathscr{R})$$
$$= \sum_i a_i(\mathbf{k})D^\dagger_{\mathbf{k}\alpha,\mathbf{k}'\alpha'}(\mathscr{R})\mathscr{O}^i_{\alpha'\beta'}(\mathscr{R}\mathbf{k}')\mathscr{D}_{\mathbf{k}'\beta'\mathbf{k}\beta}(\mathscr{R}) , \tag{28}$$

where $\mathbf{k}' = \mathscr{R}\mathbf{k}$. Multiplying on the left and right by D and $D^\dagger$, respectively, and removing primes, we are left with

$$\mathscr{D}_{\alpha\beta}(\mathscr{R},\mathscr{R}\mathbf{k}) = \sum_i a_i(k)\mathscr{O}^i_{\alpha\beta}(\mathscr{R};R\mathbf{k}) . \tag{29}$$

If the $\mathscr{O}^i$ transform as a representation $\hat{D}_{ij}$ of the point group, we have

$$\mathscr{D}_{\alpha\beta}(\mathscr{R},\mathscr{R}\mathbf{k}) = \sum_i a_i(k)\hat{D}_{ij}\mathscr{O}^i_{\alpha\beta}(\mathscr{R}\mathbf{k}) . \tag{30}$$

On the other hand, $\mathscr{D}(\mathscr{R})$ is a gap function in its own right:

$$\mathscr{D}_{\alpha\beta}(\mathscr{R},\mathscr{R}\mathbf{k}) = \sum_i a_i(\mathscr{R},\mathscr{R}\mathbf{k})\mathscr{O}^i_{\alpha\beta}(\mathscr{R}\mathbf{k}) \tag{31}$$

and finally

$$a_i(\mathscr{R},\mathscr{R}\mathbf{k}) = \sum_j a_j(\mathbf{k})\hat{D}^{ji}(\mathscr{R}) . \tag{32}$$

The transformation properties of $\mathscr{D}$ are expressed through the $a_i(k)$, which are independent of the representation. We have buried the arbitrariness of the $\mathscr{K}$'s and $\mathscr{D}$'s in matrix elements of the $\mathscr{O}$'s, where, for many purposes they will not concern us. Also, under $\mathscr{K}$,

$$a_i(\mathscr{K},-\mathbf{k}) = a_i^*(\mathbf{k})(-1)^{t_i} , \tag{33}$$

where $t_i = (0,1)$ characterizes the time-reversal behavior of $\mathscr{O}$.

To express a 2×2 matrix in terms of matrix elements of operators $\mathscr{O}^i$, we need four $\mathscr{O}$'s. Faced with this problem, one usually uses the Pauli matrices, but in the present case they have no representation-free meaning. That is, if we subject the Bloch states at $\mathbf{k}$ to a 2×2 unitary transformation, the σ_i becomes a linear combination of σ's. Put another way, the matrix represented by $\sum_i a_i\sigma_i$ in one representation has different a_i after such a transformation. The a_i, especially their $\mathbf{k}$ dependence, cannot be interpreted in a simple way. Their apparent symmetry properties may be misleading.

We do, however, have a convenient set of $\mathscr{O}$'s available, consisting of the following:

(1) m^0, a multiple of $\delta_{\alpha\beta}$ which is a scalar and invariant under $\mathscr{K}$.

(2) The magnetic moment operators m^i.[15] These transform among themselves like an axial vector and change sign under $\mathscr{K}$.

These operators are given in the 2×2 subspaces by combinations of the Pauli matrixes

$$m^i_{\alpha\beta}(\mathbf{k}) = g^{i\mu}(\mathbf{k})\sigma^\mu_{\alpha\beta} , \tag{34}$$

but only $G^{ij}(\mathbf{k}) = g^{i\mu}\tilde{g}^{\mu j}$ will appear in physical expressions. $G^{ij}(\mathbf{k})$ is the tensor which determines the splitting of the band energies at $\mathbf{k}$ when a magnetic field is present. The splitting is given by $(B_i G^{ij} B_j)^{1/2}$.

Making this choice, we call the coefficients of these operators d_i: (1) d_0 is a scalar, invariant under $\mathscr{K}$, and (2) d^i $(i=1,2,3)$ constitute an axial vector which changes sign under time reversal:

$$d_0(\mathscr{R},\mathscr{R}\mathbf{k}) = d_0(\mathbf{k}), \quad d_i(\mathscr{R},\mathscr{R}\mathbf{k}) = d_j(\mathbf{k})\hat{D}^{ji}(\mathscr{R}) ,$$
$$d_0(\mathscr{K},-\mathbf{k}) = d_0^*(\mathbf{k}), \quad d_i(\mathscr{K},-\mathbf{k}) = -d_i^*(\mathbf{k}) . \tag{35}$$

We now consider the consequences of the fact that the

ψ's are fermion operators. This implies immediately that $\Psi=-\tilde{\Psi}$, $\tilde{\Delta}=-\Delta$, and we find

$$\mathscr{D}=\tilde{K}\Delta=-\tilde{K}\tilde{\Delta}=-\tilde{K}\tilde{\mathscr{D}}K^{\dagger}=K\tilde{\mathscr{D}}K^{\dagger} \tag{36}$$

and likewise for χ.

These relations do not depend on the presence of $\mathscr{K}$ symmetry, but follow directly from the definition of $\mathscr{D}$ and χ. If the ψ's are Bloch functions, this equation relates $\mathscr{D}(\mathbf{k})$ to $\tilde{\mathscr{D}}(-\mathbf{k})$, since K connects $\mathbf{k}$ to $-\mathbf{k}$. In terms of the d's this translates to

$$d_0(\mathbf{k})=d_0(-\mathbf{k}),\quad d_i(\mathbf{k})=-d_i(-\mathbf{k})\ . \tag{37}$$

Thus, d_0 can be expressed as an even function of $\mathbf{k}$, while d_i will be odd.

Let us now take the time-reversed adjoint of Eq. (22), obtaining

$$\begin{aligned} i\mathscr{K}\dot{\psi}^{\dagger}_{\mu}&=-i\dot{\psi}^{\dagger}_{\mu'}K^{*}_{\mu'\mu}\\ &=-(\mathscr{K}\psi)\mathscr{D}^{*}K^{*}-\psi^{\dagger}H^{*}K^{*}\\ &=-\psi K\mathscr{D}^{*}K^{*}-(\mathscr{K}\psi^{\dagger})\tilde{K}H^{*}K^{\dagger}\\ &=\psi\mathscr{D}^{\dagger}=(\mathscr{K}\psi^{\dagger})H(\mathscr{K})\ , \end{aligned} \tag{38}$$

where we use Eq. (36) and the fundamental property of time reversal

$$H^{*}=K^{\dagger}H(\mathscr{K})K\ , \tag{39}$$

and $H(\mathscr{K})$ is the matrix of the time reverse of the self-consistent Hamiltonian.

Considering now the actual application of $\mathscr{K}$, we find from Eq. (36)

$$\mathscr{D}(\mathscr{K})=\mathscr{D}^{\dagger},\quad \chi(\mathscr{K})=\chi^{\dagger},\quad H^{*}=K^{\dagger}H(\mathscr{K})K\ . \tag{40}$$

If the state is time-reversal symmetric, then

$$\mathscr{D}=\mathscr{D}^{\dagger},\quad \chi=\chi^{\dagger},\quad H^{*}=K^{\dagger}HK\ . \tag{41}$$

The first of these means that all d's are real.

A related idea is that of "unitarity."[10] A "unitary" $\mathscr{D}$ is one for which $\mathscr{D}^{\dagger}\mathscr{D}$ is a multiple of the identity. If $d_0=0$, a unitary $\mathscr{D}$ is equal to a phase factor times a Hermitian $\mathscr{D}$, but if both d_0 and d_i differ from 0, this is not the case. (For a unitary $\mathscr{D}$, d_i/d_0 is imaginary.) Either property simplifies the diagonalization of $\mathscr{D}$, but that is so easy anyway that it hardly matters. A more significant property of "unitary" $\mathscr{D}$'s is that the eigenvalues of $\mathscr{D}^{\dagger}\mathscr{D}$ are equal so that the quasiparticle bands are twofold degenerate as in the absence of pairing (provided, of course, that time reversal and inversion have not been otherwise violated).

If we had a Hermitian $\mathscr{D}$ and χ, and then multiplied $\mathscr{D}$ by $e^{i\phi}$, we should get a new $\chi'=\chi e^{i\phi}$, which would then self-consistently yield $\mathscr{D}e^{i\phi}$. Thus, it is not really important that $\mathscr{D}^{\dagger}=\mathscr{D}$. It is enough that it is possible through such a transformation to make it so. This is in keeping with the fact that if a wave function of some system obeys $\mathscr{K}\psi=\psi$, then $\psi'=e^{i\phi}\psi$ obeys $\mathscr{K}\psi'=e^{-i\phi}\mathscr{K}\psi=e^{-i\phi}\psi=e^{-2i\phi}\psi'$. We shall consider invariance under time reversal to apply in either case.

It is a matter of elementary algebra to show that the eigenvalues of $\mathscr{D}^{\dagger}\mathscr{D}$ are given by $d_0^2+d_i^{*}G^{ij}d_j\pm L$,

$$\begin{aligned} L^2=&(d_0^{*}\mathbf{d}+\mathbf{d}^{*}d_0)\cdot\mathbf{G}\cdot(d_0^{*}\mathbf{d}+\mathbf{d}^{*}d_0)\\ &+\mathbf{d}^{*}\times\mathbf{d}\cdot\mathbf{G}^{-1}\cdot(\mathbf{d}\times\mathbf{d}^{*})\ . \end{aligned} \tag{42}$$

An important special case of Eq. (31) concerns $\mathscr{R}=\mathscr{J}$. We find

$$d_0(\mathscr{J},-\mathbf{k})=d_0(\mathbf{k}),\quad d_i(\mathscr{J},-\mathbf{k})=d_i(\mathbf{k})\ . \tag{43}$$

Combining this with Eq. (37),

$$d_0(\mathscr{J},\mathbf{k})=d_0(\mathbf{k}),\quad d_i(\mathscr{J},\mathbf{k})=-d_i(\mathbf{k})\ . \tag{44}$$

Thus, the singlet pairing has positive parity and the triplet, negative. All these relations Eqs. (35), (37), and (44), are the same as in the isotropic case.

So far we have considered the nature of the order parameter and found a representation-independent form for it. This can be done more simply and directly if we consider only symmorphic space groups—that is, if the apparent point-group symmetry is present in a true group, rather than involving screw axes and glide planes. The present procedure, however, greatly simplifies the discussion for nonsymmorphic groups. Indeed, it has not been necessary to make any special provision for them in the preceding discussion. I also find the present approach aesthetically pleasing.

We have also found an explicit form for the order parameter which clearly reduces, in the absence of spin-orbit coupling to the standard form used for ^{3}He—the magnetic-moment operator goes continuously to the spin.

We can now address a question which has assumed some importance in the discussion of heavy-fermion superconductivity. It is the possibility of surfaces in $\mathbf{k}$ space (curves on the Fermi surface) where the gap vanishes. The condition for a zero gap is

$$d_0^2-\mathbf{d}\cdot\mathbf{G}\cdot\mathbf{d}=0\ . \tag{45}$$

(If $|d_0|^2+\mathbf{d}^{*}\cdot\mathbf{G}\cdot\mathbf{d}=0$, both gaps vanish.) Specializing to the pure triplet state $d_0=0$, we have two real equations in three variables, which can normally be satisfied only on curves in $\mathbf{k}$ space. It is "vanishingly improbable," in the sense of Herring,[16] for them to be satisfied on a surface. On the other hand, symmetry may force an increase in the size of the region of vanishing gap.

The symmetry in question is the subgroup (of the original space group) which characterizes the condensed state. We take this to consist of all elements of the original group that change the order parameter by a phase factor. Thus, a mirror plane which changes the sign of $\mathscr{D}$ would be included and only components of $\mathscr{D}$ that are reversed by the mirror could be nonvanishing. An alternative approach is to enlarge the space group to include the "gauge" group $e^{i\phi}$ (where ϕ is a constant) and consider the subgroup to include all products of space-group elements and phase factors which leave $\mathscr{D}$ invariant.

We are then led to consider whether a mirror plane could result in such a region. Now a mirror plane affects the parallel and perpendicular components of an axial vector differently, leaving one invariant and changing the sign of the other. There are then two possibilities:

(1) The parallel components vanish on the plane. There

can then be a curve on the plane where the perpendicular component vanishes, along with the gap for both branches.

(2) The perpendicular component vanishes on the plane. There may then be a point in the plane where Eq. (45) is satisfied and the gap vanishes for one branch.

Any larger region of zero gap is vanishingly improbable.

Now, in ^{3}He,[10] it is known that there is such a solution, called the "polar" solution, in which the vector $\mathbf{d}$ is in the z direction and vanishes on the equator. This solution, however, has much higher symmetry due to the independent spin and momentum symmetries. The group of this state consists of (1) the group $C_{\infty v}$ in real space containing the full two-dimensional rotation group and all vertical mirror planes, and (2) the two-dimensional rotation group in spin space plus all vertical mirrors, each combined with time reversal. This group is more than enough to make the vector $\mathbf{d}$ point in the z direction and vary only in that direction. Specifically, the two-dimensional rotation group in spin space kills both horizontal components of $\mathbf{d}$. [See note (ii) of *Notes added in proof*.]

In the preceding discussion, we quietly chose a representation in terms of magnetic-moment operators, and found a simple story which connected seamlessly with the isotropic case. There was, however, no compelling reason to choose those operators or even others of the same symmetry.

Many other possibilities exist. The only absolute requirement is that for triplet pairing, the operators change sign under conjugation.[14] It is necessary in order to get the full range of possibilities that the operators constitute a faithful representation of the proper rotation group. For, if we consider Eq. (31) with $\hat{D}_{ji}=\delta_{ij}$ for some $\mathscr{R}$, $\mathscr{D}_{\alpha\beta}(\mathscr{R},\mathscr{R}\mathbf{k})=\mathscr{D}_{\alpha\beta}(\mathscr{R}\mathbf{k})$; the pairing is left unchanged. Such pairing is possible (see below), but we could not make valid proofs of general properties from such cases.

Let us consider an example, taking the $\mathscr{O}^i$ to be the components of a polar vector p^i, even under time reversal. An example would be the perturbation produced by a polar optic mode. (The displacement x itself is not very convenient.[13]) With this choice, we would have gone through the same procedure, with the order parameter represented by f_i, a polar vector even in $\mathbf{k}$ and under time reversal. The existence of two such representations requires that the same $\mathscr{D}$ be expressible in both ways:

$$f_i p^i = d_i m^i \,. \tag{46}$$

Multiplying both sides by m^j and taking the trace we get

$$d_i = \tfrac{1}{2} G_{ij}^{-1} \mathrm{Tr}(p^k m^j) f_k \,. \tag{47}$$

As long as G is not singular, we can solve for $\mathbf{d}$ in terms of $\mathbf{f}$. The possibility that G be singular is remote. There can be no symmetry requiring it, since G becomes the identity tensor at vanishing spin-orbit coupling. Of the four three-dimensional irreducible representations of the cubic group only the axial vector has matrix elements within each of the irreducible double-group representations at $\mathbf{k}=0$. This gives it some degree of preference. Even assuming that we decide to choose a set of axial-vector operators, there are many options. The principal reasons for preferring the magnetic moments are familiarity and the fact that they go smoothly to the spin operators when the spin-orbit coupling vanishes. Of course we do not need to make such a choice; we do what is convenient.

The possibility of such different representations does underscore the fact that there is no particular significance in choosing $\mathbf{d}$ to be a linear function of $\mathbf{k}$. The same representation can, and will be shown to, arise from the other choices; in the cubic case only one of the possible representations of the order parameter cannot be represented as a linear $d_i(\mathbf{k})$. Whether it is particularly unlikely to occur is not especially interesting.

The upshot is that it is possible to represent the gap function in terms of objects transforming like any representation of the point group. If you want to be able to express any gap function, you must use a faithful representation. The objects chosen must change sign under conjugation $\mathscr{C}$.[14]

Finally, we note that we can combine Eqs. (22) and (38) into one equation with four components:

$$\frac{i\partial\hat{\psi}}{\partial t} = \hat{\psi}\hat{\mathscr{H}} \,, \tag{48}$$

where $\hat{\psi}$ is the four-component vector

$$(\psi_{\mathbf{k}\alpha}, \psi_{\mathbf{k}\beta}, \mathscr{K}\psi^\dagger_{\mathbf{k}\alpha}, \mathscr{K}\psi^\dagger_{\mathbf{k}\beta}) \,.$$

The Hamiltonian $\hat{\mathscr{H}}$ has the form in 2×2 Bloch notation:

$$\hat{\mathscr{H}} = \begin{bmatrix} H & \mathscr{D} \\ \mathscr{D}^\dagger & -H(\mathscr{K}) \end{bmatrix} .$$

Using Dirac notation, the time-reversal-invariant part is $H^+\rho_3 + \mathscr{D}_r\rho_1$, while the other part is $H^-I + \mathscr{D}_i\rho_2$, where $\mathscr{D}_r$ ($\mathscr{D}_i$) is the real (imaginary) part of $\mathscr{D}$. The spin Zeeman energy appears simply as $I\mathbf{B}\cdot\boldsymbol{\sigma}$, not

$$\tfrac{1}{2}(I+\rho_3)B\cdot\sigma + \tfrac{1}{2}(I-\rho_3)\sigma_2\mathbf{B}\cdot\boldsymbol{\sigma}\sigma_2$$

as in, for instance, Maki.[17] The content is, of course, the same but the appearance and transformation properties are more familiar and intuitive.

We have now established the rules which govern the symmetries of the order parameter. The only rigorous restriction for triplet pairing is that the state must have negative parity. This can be achieved either with an $a_i(\mathbf{k})$ which has intrinsic positive parity, but odd-order dependence on $\mathbf{k}$ (as in the case of the $\mathbf{d}$'s in the last section), or vice versa. For the cubic and hexagonal point groups O_h and D_{6h} the character tables for the representations are shown in Table I, along with the lowest powers of $\mathbf{k}$ which produce them, in the representations using operator sets $\mathscr{O}^i$ belonging to the various three-dimensional representations of the cubic group and the axial-vector representation of the hexagonal group.

The next step is to determine the possible symmetries for minimum free energy, in states which can be reached by second-order transition from the normal state. This will be done according to the Landau theory,[18] using procedures spelled out by, for instance, Lyubarskii.[19] Since the representations have odd parity they automatically satisfy the tests imposed by Landau and Lifshitz.[18]

TABLE I. (a) The representations $\Gamma_i^{\pm}$ have $\chi(J)=\pm 1$ and operations $\mathcal{J}\mathcal{R}$ have $\chi(\mathcal{J}\mathcal{R})=\pm\chi(\mathcal{R})$. The last four columns show the lowest power n for which $\{k_i^n\}$ produces representation Γ_i^- (according to list on left) in combination with $\Gamma_j^{\pm}$ (according to the heading of the column). A polar (axial) vector transforms according to $\Gamma_4^-(\Gamma_4^+)$. (b) The same conventions are used as in (a). A polar (axial) vector transforms according to $\{H_2^- + H_5^-\}(\{H_2^+ + H_5^+\})$. The column on the right shows lowest power n for which $\{k_i^n\}$ produces the representation Γ_i^- on the left in combination with the axial-vector representation.

(a) Cubic group

	E	C_4^2	C_3	C_2	C_4	Γ_4^+	Γ_4^-	Γ_5^+	Γ_5^-
$\Gamma_1^{\pm}$	1	1	1	1	1	1	4	3	2
$\Gamma_2^{\pm}$	1	1	1	−1	−1	3	2	1	4
$\Gamma_3^{\pm}$	2	2	−1	0	0	1	2	1	2
$\Gamma_4^{\pm}$	3	−1	0	−1	1	1	0	1	2
$\Gamma_5^{\pm}$	3	−1	0	1	−1	1	2	1	0

(b) Hexagonal group

	E	C_6	C_6^2	C_6^3	$C_2^{(1)}$	$C_2^{(2)}$	$(H_2^+ + H_5^+)$
$H_1^{\pm}$	1	1	1	1	1	1	1
$H_2^{\pm}$	1	1	1	1	−1	−1	1
$H_3^{\pm}$	1	−1	1	−1	1	−1	3
$H_4^{\pm}$	1	−1	1	−1	−1	1	3
$H_5^{\pm}$	2	1	−1	−2	0	0	1
$H_6^{\pm}$	2	−1	−1	2	0	0	1

The next step is to expand the free energy in powers of the order parameter. The first term is the second-order invariant, which is always isotropic in the order-parameter space. In most cases, the fourth-order invariants will admit only a few sets of isolated directions as absolute minima, and the calculation can stop there. We assume that the isotropic fourth-order term is sufficiently positive to assure the second-order character of the transition. In the case of all the two-dimensional representations in Table I, however, the fourth-order terms are not always sufficiently isotropic, and it is necessary to use the sixth-order term to locate the minima. The fact that the order parameter may be complex introduces features not found in otherwise similar problems such as ferroelectricity. In the usual case, with real order parameters, the invariants have to be symmetric in all interchanges of indices. In the present case, with complex order parameters, it is necessary for invariants to have equal numbers of **a**'s and **a***'s and to be separately symmetric in each, and in the interchange of **a** and **a***.

When we follow this program for the representation tabulated above, it turns out that all representations of the same dimensionality present the same algebraic problem. For one-dimensional representations, this procedure is trivial. For the other cases, the algebra is carried out in Appendices A and B.

When we have reached this point, we must determine the symmetry subgroup which characterizes these order parameters. We distinguish two different groups which may be of interest: (1) the group, including time reversal, under which the order parameter is invariant as a complex (as opposed to real) vector, and (2) the group under which the order parameter behaves as a one-dimensional representation.

Table II shows these groups for all the cases under consideration. The table is to be interpreted as follows. Within the obvious divisions by cubic versus hexagonal and dimension of the irreducible representation, the left-hand column is a serial number. The next shows the type of order-parameter minimum as given in the quasitables of Appendices A and B. (There is no entry necessary for one-dimensional representations.) The next column gives the irreducible representations as shown in Table I. The fourth column shows the group under which the order parameter is truly invariant for that type of minimum and that representation. The fifth column shows the largest group under which the order parameter is a one-dimensional representation. The notation by which the groups are described is as follows:

(1) If a group is written in the form $G\times\mathcal{K}$, the order parameter is invariant (or one dimensional) under the point group G and under time reversal.

(2) If the group is written in the form (G/H), H is a subgroup of index 2 in G; the order parameter is invariant (or one dimensional) under the point group H; it is also invariant under the product of time reversal with any of the remaining elements of G. The choice of G in the fourth column is not entirely well defined. If an order parameter **d** is invariant under $\mathcal{R}\mathcal{K}$ for some $\mathcal{R}$, $e^{i\phi}\mathbf{d}$ is not, but for some choice ϕ, it may be invariant under $\mathcal{R}'\mathcal{K}$, where $\mathcal{R}'\neq\mathcal{R}$. Then for a given H, there may be more than one choice of G. These groups may be isomorphic or not. If isomorphic they may or may not be conjugate subgroups of the space group. In the fourth column, I indicate this situation only when the groups are not isomorphic. Then it is indicated by adding a second symbol on the next line.

In the sixth column are shown the forms of **d** for each phase. We single out this form because of its familiarity and its relation to the ^{3}He representations. In all cases, the given forms will be multiplied by a function of full cubic or hexagonal symmetry. It is highly likely that in a significant fraction of cases, the **k** will be measured from

TABLE II. The meanings of the columns are as follows: Column 1—a serial number, marked with an asterisk is included by Volovik and Gor'kov. Column 2—type of minimum as given in the Appendices. Column 3—irreducible representation of the order parameter. Column 4—group under which the order parameter is invariant. Column 5—group under which it behaves as a one-dimensional representation. Column 6—form of the order parameter—may be multiplied by a function ($\mathbf{k}$) with full cubic or hexagonal symmetry. Column 7—number of distinct, symmetrically equivalent order parameters of a given type. Column 8—axes in $\mathbf{k}$ space where the order parameter vanishes, indicated as threefold or fourfold. If it vanishes on only one such axis, numeral 1 is put in parentheses. Otherwise, it vanishes on all such axes. Column 9—number of components of the order parameter which vanish on those axes.

1	2	3	4	5	6	7	8	9
Cubic groups								
One-dimensional representations								
1[a]		Γ_1^-	$\mathcal{O}\times\mathcal{K}$	$\mathcal{O}_h\times\mathcal{K}$	$k_x\hat{\mathbf{x}}+k_y\hat{\mathbf{y}}+k_z\hat{\mathbf{z}}$	1	none	
2[a]		Γ_2^-	$T_d\times\mathcal{K}$	$\mathcal{O}_h\times\mathcal{K}$	$k_x(k_y^2-k_z^2)\hat{\mathbf{x}}+k_y(k_z^2-k_x^2)\hat{\mathbf{y}}+k_z(k_x^2-k_y^2)\hat{\mathbf{z}}$	1	3,4	2
Two-dimensional representations								
3	1	Γ_3^-	$D_4\times\mathcal{K}$	$D_{4h}\times\mathcal{K}$	$2k_z\hat{\mathbf{z}}-k_x\hat{\mathbf{x}}-k_y\hat{\mathbf{y}}$	3	none	
4	2	Γ_3^-	$D_{2d}\times\mathcal{K}$	$D_{4h}\times\mathcal{K}$	$k_x\hat{\mathbf{x}}-k_y\hat{\mathbf{y}}$	3	4(1)	2
5[a]	3	Γ_3^-	(D_4/D_2)	$(\mathcal{O}_h/T_h)$	$\omega k_x\hat{\mathbf{x}}+\bar{\omega}k_y\hat{\mathbf{y}}+k_z\hat{\mathbf{z}}$	2	3	1
Three-dimensional representations								
6	1	Γ_4^-	$C_{4v}\times\mathcal{K}$	$D_{4h}\times\mathcal{K}$	$k_y\hat{\mathbf{x}}-k_x\hat{\mathbf{y}}$	3	4(1)	2
7	1	Γ_5^-	$D_{2d}\times\mathcal{K}$	$D_{4h}\times\mathcal{K}$	$k_y\hat{\mathbf{x}}+k_x\hat{\mathbf{y}}$	3	4(1)	2
8[a]	2(b)	Γ_4^-	(C_{2v}/C_{1h})	(D_{4h}/C_{4h})	$ik_z\hat{\mathbf{x}}-k_z\hat{\mathbf{y}}+(k_y-ik_x)\hat{\mathbf{z}}$	6	4(1)	1
9[a]	2(b)	Γ_5^-	(C_{2v}/C_{1h})	(D_{4h}/C_{4h})	$ik_z\hat{\mathbf{x}}+k_z\hat{\mathbf{y}}+(k_y+ik_x)\hat{\mathbf{z}}$	6	4(1)	1
10	3(a)	Γ_4^-	$C_{3v}\times\mathcal{K}$	$D_{3d}\times\mathcal{K}$	$(k_y-k_z)\hat{\mathbf{x}}+(k_z-k_x)\hat{\mathbf{y}}+(k_x-k_y)\hat{\mathbf{z}}$	4	3(1)	2
11	3(a)	Γ_5^-	$D_3\times\mathcal{K}$	$D_{3d}\times\mathcal{K}$	$(k_y+k_z)\hat{\mathbf{x}}+(k_x+k_z)\hat{\mathbf{y}}+(k_x+k_y)\hat{\mathbf{z}}$	4	none	
12	3(b)	Γ_4^-	(C_{1h}/E) (C_2/E)	(D_{3d}/C_{3i})	$(\bar{\omega}k_z-k_y)\hat{\mathbf{x}}+(k_x-\omega k_z)\hat{\mathbf{y}}+(\omega k_y-\bar{\omega}k_x)\hat{\mathbf{z}}$	8	3(1)	1
13	3(b)	Γ_5^-	(C_2/E) (C_{1h}/E)	(D_{3d}/C_{3i})	$(k_y+\bar{\omega}k_z)\hat{\mathbf{x}}+(\omega k_z+k_x)\hat{\mathbf{y}}+(\bar{\omega}k_x+\omega k_y)\hat{\mathbf{z}}$	8	3(1)[b]	1
Hexagonal groups								
One-dimensional representations								
1		H_1^-	$D_6\times\mathcal{K}$	$D_{6h}\times\mathcal{K}$	$k_z\hat{\mathbf{z}},k_x\hat{\mathbf{x}}+k_y\hat{\mathbf{y}}$	1	none	
2		H_2^-	$C_{6v}\times\mathcal{K}$	$D_{6h}\times\mathcal{K}$	$k_y\hat{\mathbf{x}}-k_x\hat{\mathbf{y}}$	1	6	2
3		H_3^-	$D_{3v}\times\mathcal{K}$	$D_{6h}\times\mathcal{K}$	$k_y(k_y^2-3k_x^2)\hat{\mathbf{z}},k_z[(k_x^2-k_y^2)\hat{\mathbf{x}}-2k_xk_y\hat{\mathbf{y}}]$	1	6,2(3)	2
4		H_4^-	$D_{3v}\times\mathcal{K}$	$D_{6h}\times\mathcal{K}$	$k_x(k_x^2-3k_y^2)\hat{\mathbf{z}},k_z[(k_y^2-k_x^2)\hat{\mathbf{y}}-2k_xk_y\hat{\mathbf{x}}]$	1	6,2(3)	2
Two-dimensional representations								
5	1	H_5^-	$C_{2v}\times\mathcal{K}$	$D_{2h}\times\mathcal{K}$	$k_z\hat{\mathbf{y}},k_y\hat{\mathbf{z}}$	3	2(1)	2
6	1	H_6^-	$C_{2v}\times\mathcal{K}$	$D_{2h}\times\mathcal{K}$	$k_x\hat{\mathbf{x}}-k_y\hat{\mathbf{y}}$	1	6	2
7	2	H_5^-	$C_{2v}\times\mathcal{K}$	$D_{2h}\times\mathcal{K}$	$k_z\hat{\mathbf{x}},k_y\hat{\mathbf{z}}$	3	2(1)	2
8	2	H_6^-	$D_2\times\mathcal{K}$	$D_{2h}\times\mathcal{K}$	$k_y\hat{\mathbf{x}}+k_x\hat{\mathbf{y}}$	1	6	2
9	3	H_5^-	(C_{2v}/C_{1v})	(D_{6h}/C_{6h})	$k_z\hat{\mathbf{x}}+ik_z\hat{\mathbf{y}},(k_x+ik_y)\hat{\mathbf{z}}$	2	6	1
10	3	H_6^-	(C_{2v}/C_2) (D_2/C_2)	(D_{6h}/C_{6h})	$(k_x+ik_y)\hat{\mathbf{x}}+i(k_x+ik_y)\hat{\mathbf{y}}$	2	6	2

[a]Also given by Volovik and Gor'kov with the difference noted in the text concerning 8 and 9.
[b]Also two zeros at $(k_z=-3k_x=-3k_y)$, etc., in the case where the threefold axis is (111).

a point of high symmetry on the zone boundary rather than from the center. In metals with disconnected or multiply connected Fermi surfaces, the form will be even more different from the sample form in the table. It would really be better to use the group velocity rather than the wave numbers in these expressions, but I think most readers would find it less clear. The seventh column shows the number of distinct order parameters which are equivalent by symmetry. The eighth column shows the symmetry of the axes, e.g., threefold, along which the gap vanishes. A number in parentheses signifies the number of such axes along which this happens. If there is no such number, the vanishing occurs on all such axes. The ninth column shows whether one or both branches vanish.

Volovik and Gor'kov have given a table which they say contains "only superconducting phases in crystals with the group $O_h(UBe_{13})$ possessing the highest symmetry (in the theory of superfluid ^{3}He these phases are called inert)." I do not understand this statement. What is meant by highest symmetry? To see that the most obvious inter-

pretations do not work, consider the cases 8 and 9 in Table II. [Volovik and Gor'kov combine these into one $D_4(E)(S=1)$, presumably because they have precisely the same symmetry. I have separated them because they are derived from different representations.] The group for these cases is a proper subgroup of those for cases 6 and 7, which Volovik and Gor'kov do not include.

The term "inert" is also ambiguous. If we take the definition of Barton and Moore[20] literally, none of our cases is inert: the forms in the sixth column are multiplied by a function of full cubic (or hexagonal) symmetry—the $f(\mathbf{k})$ of Volovik and Gor'kov—which certainly depends explicitly on the physical parameters. A more reasonable view might be that inert should mean that the symmetry of the order parameter, the forms in the sixth column, have no explicit dependence on the physical parameters but then, of course, all these states are inert, with some remaining ambiguity as to how one views their state $D_4(E)$.

It seems more relevant that all the states shown in Table II are the only ones required by symmetry to be extrema, except for those arising from type 2(a) of Appendix B. [See note iii of *Notes added in proof.*]

Notes added in proof:

(i) Since this work was completed, a paper has been published [K. Ueda and T. M. Rice, Phys. Rev. B **31**, 7114 (1985)] which overlaps this one considerably. They exhibit the order parameters for all but one (No. 2) of the cubic subgroups. The omission is due to the fact that they chose to consider only symmetries which could be obtained with a linear $\mathbf{k}$ dependence. They do not indicate the symmetries of the states they find and their treatment is valid only for symmorphic space groups. On the other hand, they also discuss how to calculate the magnetic field dependence of T_c.

(ii) This prohibition against surfaces of vanishing gap depends crucially on the presence of spin-orbit coupling. Without it, we can easily imagine a state whose symmetry group contains, as in the preceding paragraph, the two-dimensional rotation group in spin space, leaving only one component of $\mathbf{d}$; there is then no difficulty in having this vanish on a surface.

To be more specific, we note that the normal state symmetry is the direct product of O(3), the three-dimensional rotation group in spin space, and G the crystalline symmetry group. The order parameter representation is then $D_l \times \Gamma_i$, where D_l is the representation of O(3) with angular momentum l and Γ_i is a negative parity representation of G. The symmetrized second order product of this representation is $[D_l \times \Gamma_i]^2 = [D_l]^2 \times [\Gamma_i]^2 + \{D_l\}^2 \times \{\Gamma_i\}^2$. Here, $[H]^2$ ($\{H\}^2$) is the symmetrized (antisymmetrized) square of H. This can now be reexpressed as $[D_l \times \Gamma_i]^2 = (D_0 + D_2) \times S_{il}\Gamma_l + D_l \times A_{il} T_l$, where $S_i(A_{il})$ is the number of times Γ_l occurs in $[\Gamma_i]^2(\{\Gamma_i\}^2)$. This results in the following number of fourth-order invariants: If the dimension d_i of Γ_i is 1, 2, or 3, the number of invariants is 2, 5, or 7, respectively.

Considering the case of $d_i = 3$, which occurs only in the cubic class, the invariants additional to those for ^{3}He (Ref. 10) are $A_6 \equiv \sum_i |(dd^+)_{ii}|^2$ and $A_7 \equiv \sum_i |(d\tilde{d})_{ii}|^2$. It is clear that if the corresponding coefficients are small, they will simply orient one of the ^{3}He states with respect to the cubic axes, at least if the ^{3}He state is inert.[20] It is certainly possible, though not, I think, entirely obvious that with larger coefficients, qualitatively different states could result.

(iii) In a very recent paper [Zh. Eksp. Teor. Fiz. **88**, 1412 (1985)], Volovik and Gor'kov have given a complete listing of the symmetries for both singlet and triplet pairing in cubic, hexagonal, and tetragonal crystals. Their basic group theoretic approach is quite different from mine, and they include some discussion of magnetism and vortices.

I want to thank C. M. Varma and P. W. Anderson for suggesting this work and for useful discussions.

APPENDIX A

In the representation $\Gamma_3^{\pm}$ of the cubic group, the operations C_4^2 are represented by the identity. The factor group is isomorphic to D_6. This makes it possible to treat all the two-dimensional representations in a parallel manner. It is convenient to write the basis function in the form $\{u+iv, u-iv\}$ where u and v may be complex and where u is chosen to be invariant and v to change sign under a twofold axis (other than C_4^2 or C_6^3). The operations C_3 and/or C_6 then multiply $(u \pm iv)$ by phase factors of the general form $\pm\omega^l$, where $\omega = e^{2\pi i/3}$.

When the free energy is expanded in powers of u,v and u^*,v^*, each term must have equal numbers of starred and unstarred quantities and the whole expression must be invariant under the interchange of u,v with u^*,v^*. In other words, the free energy is of even order in the imaginary parts of u and v.

The second-order invariant is simply $|u^2| + |v^2| \equiv I_2$. The second-order products of u,v are grouped in representations as

$$R_{21}: \; u^2+v^2 ,$$

$$R_{23}: \; \{(u+iv)^2, (u-iv)^2\} .$$

These lead to fourth-order invariants

$$I_{41} \equiv |u^2+v^2|^2 = (|u|^2+|v|^2)^2 - |uv^*-vu^*|^2 ,$$

$$I_{43} = (|u|^2+|v|^2) + |u^*v - v^*u|^2 ,$$

which enter the free energy F in the form $(A_{41}I_{41} + A_{43}I_{43})$. When this is minimized, v/u is real if $A_{41} < A_{43}$; if $A_{41} > A_{43}$, $u^2+v^2=0$. In either case, the remaining fourth-order term is $(|u|^2+|v|^2)$ and isotropic.

It is therefore necessary to consider sixth-order terms. They are formed from the third-order representations

$$R_{31}: \; u^3 - 3uv^2 ,$$

$$R_{32}: \; v^3 - 3vu^2 ,$$

$$R_{33}: \; \{(u^2+v^2)(u+iv), (u^2+v^2)(u-iv)\} .$$

The invariants are then

$$I_{61} = |u|^2 |u^2 - 3v^2|^2 ,$$

$$I_{62} = |v|^2 |v^2 - 3u^2|^2 ,$$

$$I_{63} = (|u|^2+|v|^2) |u^2+v^2|^2 .$$

If v/u is real, we call it $\tan\theta$ and the minima are at either $2l\pi/6$ or $(2l+1)\pi/6$, corresponding, respectively, to $v=0$ or $u=0$, and states equivalent by symmetry. All these points are required by symmetry to be extrema not only with respect to real (u,v) (because they lie on twofold axes or mirror planes) but also with respect to imaginary parts of (u,v) (because the free energy is even in the imaginary parts).

If, on the other hand, $u^2+v^2=0$, $I_{61}=I_{62}=\frac{1}{2}(|u|^2+|v|^2)^3$, and $I_{63}=0$. These points are also required by symmetry to be extrema by the following argument: All products of $(u\pm iv)$ can be written in the form

$$p_{ln\pm}=(u\pm iv)^l(u^2+v^2)^n .$$

The pair p_{ln+} and p_{ln-} constitute an irreducible representation unless l is divisible by 3. In that case the combinations $(p_{ln+}\pm p_{ln-})$ are the irreducible representations.

We consider the neighborhood of a point (u_0,v_0) where $iv_0=u_0$, and expand in powers of $u-iv$, intending to show that there is no linear term. We first note that $(p_{3kn+}\pm p_{3kn-})$ is equal to

$$2[(u+iv)^{3k}\pm(u-iv)^{3k}](u^2+v^2)^n .$$

This consists of a term of order $(u-iv)^n$ and one of order $n+3k$. Thus, we are concerned only with the cases $k=0$ and $n=0$ or 1.

Considering now the cases $l\neq 3k$, the invariant formed from $p_{ln\pm}$ is

$$|u^2+v^2|^{2n}(|u+iv|^{2l}+|u-iv|^{2l}) ,$$

which is of even order in $(u-iv)$. Because (u^*,v^*) must occur in each term to the same power as (u,v) we have exhausted the types of terms in the expansion. In the neighborhood of (u_0,v_0), then

$$F=F_0(u_0,v_0)+|u^2+v^2|^2F_2(u_0,v_0)$$
$$+\text{higher-order terms} .$$

Now (u_0,v_0) is given by $(a/\sqrt{2},ia/\sqrt{2})e^{i\phi}$, so that F_0 and F_2 depend only on $|a|^2=|u|^2+|v|^2$. Finally, then

$$F=F_0(|u_0|^2+|v_0|^2)+|u-iv|^2|u+iv|^2$$
$$\times F_2(|u_0|^2+|v_0|^2)+\text{higher-order terms} .$$

Thus (u_0,v_0) is an extremum; in fact, it is either a maximum or minimum, since $(u-iv)$ appears only in its absolute value.

Recapitulating, we see that there are three possible types of minima for a second-order transition:

Type	Order parameter
1	$u=1,\ v=0$
2	$u=0,\ v=1$
3	$u=\frac{1}{\sqrt{2}},\ v=\frac{1}{\sqrt{2}}$

All these types are required by symmetry to be extrema and no other points are required to be. Other minima can occur, but cannot be reached by a second-order transition from the normal state.

APPENDIX B

All the three-dimensional representations of the cubic group have very similar structures. When the order parameter is real there is only one fourth-order invariant other than the square of the second-order invariant. In the complex case, the situation changes. If we call the components of the order parameter u_1,u_2,u_3, the second-order products form the following representations:

$$C_1:\ u_1^2+u_2^2+u_3^2 ,$$
$$C_2:\ (\omega u_1^2+\bar{\omega}u_2^2+u_3^2,\bar{\omega}u_1^2+\omega u_2^2+u_3^2) , \tag{B1}$$
$$C_3:\ (u_2u_3,u_3u_1,u_1u_2) .$$

The absolute squares of these are the invariants

$$I_1:\ |u_1^2+u_2^2+u_3^2|^2=\sum_i|u_i|^4+\sum_{i\neq j}u_i^2u_j^{*2} ,$$
$$I_2':\ 2\sum_i|u_i^4|-\sum_{i\neq j}u_i^2u_j^{*2} , \tag{B2}$$
$$I_3':\ \sum_{i\neq j}|u_i|^2|u_j|^2 .$$

These can be rearranged into the set

$$I_1:\ \left|\sum_i u_i^2\right|^2 ,$$
$$I_2:\ \sum_i|u_i|^4 , \tag{B3}$$
$$I_3:\ \left[\sum_i|u_i|^2\right]^2 .$$

The anisotropic part can then be written

$$F=AI_1+BI_2 . \tag{B4}$$

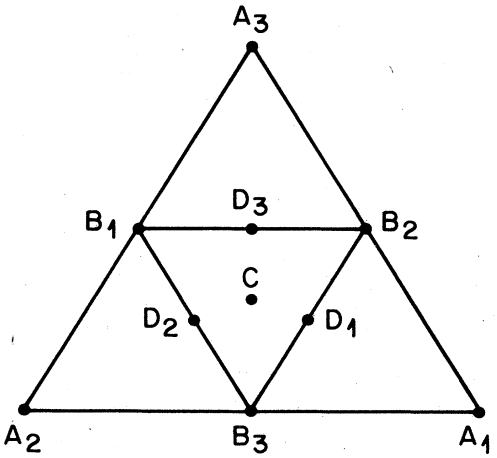

FIG. 1. The large triangle represents the region $\{\sum_i x_i=1, x_i\geq 0\}$. The corner A_i is the point $\{x_i=1, x_j=x_k=0\}$. At B_i, $x_i=0$, $x_j=x_k=\frac{1}{2}$. At C, $x_i=\frac{1}{3}$. At D_i, $x_i=\frac{1}{2}$, $x_j=x_k=\frac{1}{4}$.

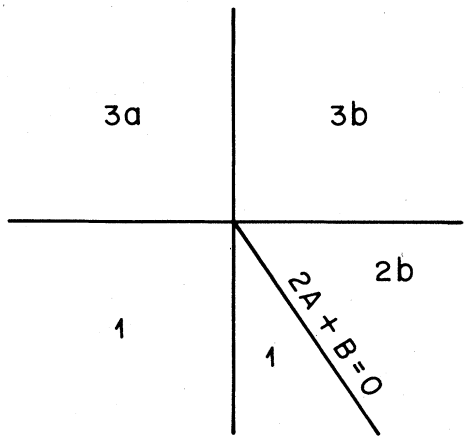

FIG. 2. Phase diagram in A-B space for the cubic group.

We now call $|u_i^2| \equiv x_i$,

$$F = A\left|\sum_i x_i e^{i\phi_i}\right|^2 + B\sum_i (x_1^2)\ . \tag{B5}$$

We want to minimize this subject to the condition $\sum_i |u_i^2| = \sum_i x_i = 1$.

It is clear that if A is negative, we want all ϕ's equal, which brings us to the unitary case with I_1 constant and the issue determined by B. If A is positive, however, we can arrange the ϕ's to minimize the first term. There are two cases:

(1) The x_i obey the triangle inequality. Then the phases can be chosen to make I_1 vanish.

(2) Otherwise, if, say, $x_3 > x_1 + x_2$, we choose $\phi_3 = 0$ and $\phi_1 = \phi_2 = \pi$.

This situation is shown graphically in Fig. 1. The large triangle represents the region $\sum_i x_i = 1 x_i,\ \geq 0$. x_i is the distance of x from the ith side. The inner triangle is the region where the triangle inequality is satisfied. In the small triangle with corner A_i, $I_1 = (2x_i - 1)^2$ when the ϕ's are chosen to minimize I_1. The value of I_2 is easily seen to be $x^2 + \frac{1}{3}$, where x is the distance from the point x to the center of the triangle.

If $A > 0$, $I_1 = 0$ in the center triangle, and the only points in it where I_2 can be minimized are the center C or corners B. The only such points in the outer triangles are the corners A_i, B_i, or the midpoints D_i but the latter are ruled out as minima by the limits set in the previous sentence.

If $A < 0$, $I_1 = 1$ everywhere and the minimum of I_2 can only be in the center C or at a corner A_i.

The possible minima and the value of F are then

(1) Corner	$F = A + B$,
(2) Edge center	(a) $A + \frac{B}{2}$ for $A < 0$,
	(b) $\frac{B}{2}$ for $A > 0$,
(3) Center	(a) $A + \frac{B}{3}$ for $A < 0$,
	(b) $\frac{B}{3}$ for $A > 0$.

Figure 2 shows the phase diagram in A-B space. 2(b) and 3(b) are the nonunitary regions. In 3(b), the u_i's have distinct phases 1, $e^{\pm 2\pi i/3}$. In 2(b) the u's are $(1,i,0)$. Note that 2(a) is never an absolute minimum.

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