Superconducting classes in heavy-fermion systems

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A mathematical method for constructing the superconducting classes for nontrivial superconductors is described, and all the phases that can be produced directly in a transition from the normal state are enumerated for the cubic, hexagonal and tetragonal symmetries. It is shown that in the triplet case the type of zeros in the energy gap always corresponds to points on the Fermi surface, whereas whole lines of zeros are possible in singlet pairing. For phases having zeros on lines or at points, the low-temperature heat capacity is proportional to T^2 and T^3, respectively. Superconducting phases that stem from non-one-dimensional representations can have a magnetic moment that generates currents on the surface of a single-domain sample even in the absence of an external magnetic field. A specific example of a domain wall is considered and it is shown that large magnetic currents flow in it.

1. INTRODUCTION

The development of the BCS microscopic theory of superconductivity raised immediately the question of feasibility of a nontrivial superconductivity corresponding (in isotropic Fermi-liquid terms) to Cooper pairing with nonzero angular momentum (Ref. 1).[1)] In Ref. 2 it was shown for the first time that a state with spontaneous breaking of rotational symmetry is possible in such a system. The system in which nontrivial pairing was achieved turned out to be ^{3}He, for which this fact was theoretically predicted[3] as a consequence of the role of Van der Waals attraction forces. The main properties of ^{3}He superfluidity are reported in recent reviews.[4,5] We mention only that in ^{3}He was observed the so-called A-phase (the Anderson-Brinkman-Morel state), the occurrence of which is difficult to explain without invoking an additional interaction mechanism via spin fluctuations of "paramagnons,"[6] Special attention was therefore paid in searches for nontrivial superconductivity (see Ref. 7) to compounds with so-called heavy fermions that have paramagnetic behavior (the Curie law) in a wide temperature range. Without listing for now these specific compounds, we indicate only that their properties are somehow connected with strongly localized $4f$ shells of Ce or $5f$ of U. This is evident from the anomalously large values of the density of states, as deduced from data on the electronic heat capacity and on the Pauli susceptibility at low temperatures. The narrowness of the effective band is conveniently characterized by an effective mass m^* that reaches in these materials values $m^* \sim (10^2–10^{-3})m_e$.

The paramagnetic mechanism favors for ^{3}He, in a simple model, triplet pairing into an A phase. Owing to the nontrivial breaking of the gauge symmetry,[5] the latter has, in particular, the remarkable property that the energy gap in its spectrum vanishes at two points on the Fermi surface. Were there no phase transition in ^{3}He into the isotropic B phase with decreasing temperature, the heat capacity of the A phase would have a T^3 dependence at the lowest temperatures. Calorimetric measurements[8] indeed yielded for UBe_{13} a relation $C_e \sim \gamma(T(T/T_c)^2$ that differs from the BCS-theory activation dependence. This result, however, is as yet not unambiguous. For many heavy-fermion superconductors ($CeCu_2Si_2$, Ref. 9; U_6Fe, Ref. 10; UPt_3, Ref. 11), the results available for the ultrasound-absorption coefficient (UPt_3, Ref. 12) and the reciprocal spin-relaxation time ($CeCu_2Si_2$ Ref. 13; Ube_{13}, Ref. 14) offer evidence in favor of a temperature dependence that would correspond to solid lines of zeros in the energy gap on the Fermi surface. Similar properties would be possessed in ^{3}He by the polar phase, but the latter does not correspond at all to the free-energy minimum and appears in ^{3}He-A only in vertex cores.[15]

The microscopic mechanism of the superconductivity in these compounds, the competition between superconductivity and magnetism, and the mutual role of $5f$ electrons of U and sp electrons of Be (e.g., in UBe_{13}) are all questions that remain far from understood. Yet the answers to many physical questions depend only on the symmetry properties of the superconducting order parameter $\Delta_{\alpha\beta}(\mathbf{k}) = \langle a_{\mathbf{k}\alpha} a_{-\mathbf{k}\beta} \rangle$. One such question is: are we dealing with triplet or singlet pairing? (It would be more correct to speak of parity, as shown below.)

In an earlier paper[16] we have already indicated some of the most symmetric superconducting classes, and have shown that $S = 1$ always corresponded to zeros only at points (not on lines) on the Fermi surface. Our present purpose is a complete analysis of the possible superconducting classes, not only for the cubic group but also for some other symmetries (hexagonal, tetragonal, rhombohedral). Anticipating somewhat, we indicate that the foregoing result remains in force in the general case. In Sec. 2 we describe briefly a method of enumerating all the superconducting classes, with the cubic groups as the example. This classification does not depend at all on the microscopic model. In the sections that follow we show that it is more convenient in practice to employ a certain generalization of the methods of

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phase-transition theory.[17] The region near T_c is experimentally of great interest, and a symmetry-theory analysis will enable us to identify in Secs. 3–5 those superconducting states into which a system can go over directly from the normal phase by a continuous transition (of second order). We find the types of zeros, the magnetic properties, and the degree of degeneracy for each of these states. It is shown in Sec. 6 that in some superconducting phases a magnetic moment is induced by the superconducting transition, and the current-carrying domain walls that separate domains with different magnetic-moment orientations are described.

2. CONSTRUCTION OF SUPERCONDUCTING CLASSES

The order parameter in the superconducting state is the already mentioned quantity $\hat{\Delta}_{\alpha\beta}(\mathbf{k})$, which has the meaning of the Cooper-pair wave function in the condensate. It is precisely its transformation properties under the influence of various symmetry transformations which determine the singularities of the superconducting phase. Since, in accord with the definition of the Bose condensate, there is only one such function, it should be transformed into itself under symmetry transformations that do not alter the superconducting state. The symmetric states of the system can therefore be enumerated by indicating all those possible subgroups, from among the total group, with respect to which the order parameter remains invariant. In the considered crystal-symmetry case, the total group consists of the crystal point group G, of the time-reversal operation R, and the gauge-transformation group $U(1)$. Superconductors are subdivided into superconductivity classes in a manner that is somewhat similar to the construction of magnetic classes (see, e.g., Ref. 18), i.e., by enumerating the subgroups of the expanded group $G\times R\times U(1)$ with account taken, of course, of the fact that the operation R (complex conjugation) does not commute with the transformation from U(1).

The classes of the first type are characterized by the subgroups $H\times R$ from $G\times R$. These are ordinary superconductors or else superconductors whose transition from the normal phase is accompanied by breaking of spatial symmetry (we know of no example of transitions of the latter type).

The second, no longer trivial, type includes classes whose symmetry groups contain combined elements made up of elements of the $G\times R$ group and the $U(1)$ group. The geometric locus of the zeros (if they exist) in the energy gap on the Fermi surface should be determined by the symmetry relations, just as the linkage of the gauge and spatial groups leads in ^{3}He to zeros in the gap for the A phase and for the polar phase. Thus, the main difference from ordinary superconductivity lies in the internal symmetry of the state, and this question can be investigated independently of the microscopic pairing mechanism. It can apparently now be stated that UBe_{13}, UPt_3, and possible $CeCu_2Si_2$ belong to one of the nontrivial superconductivity types.

It has already been noted in Refs. 16 and 19 that although the spin–orbit interactions in the compounds considered are large, their point groups contain inversion. By definition, the order parameter is antisymmetric relative to simultaneous permutation of all the variables: $\hat{\Delta}_{\alpha\beta}(\mathbf{k}) = -\hat{\Delta}_{\beta\alpha}(-\mathbf{k})$. We can therefore immediately distinguish between the parities of the two ansatzes

$$\begin{aligned} &\hat{\Delta}(\mathbf{k})=\psi(\mathbf{k})\,i\hat{\sigma}^y \quad (S=0),\\ &\hat{\Delta}(\mathbf{k})=(\hat{\sigma}\mathbf{d}(\mathbf{k}))\,i\hat{\sigma}^y \quad (S=1), \end{aligned} \tag{1}$$

where $\psi(\mathbf{k})$ is a scalar even function and $\mathbf{d}(\mathbf{k}) = -\mathbf{d}(-\mathbf{k})$ is an odd vector function. Following the already established terminology, we shall call these two possibilities, as before, singlet and triplet states, respectively. In the broad sense in which the nontrivial cases were defined above, the triplet pairing is always of the nontrivial type: the vector $\mathbf{d}(\mathbf{k})$ is invariant not to the subgroup C_i (inversion) but to the group $C_i\exp(\pi i)$. We shall find it more convenient, however, to consider the two cases (1) separately. Then the remaining complete group is $G'\times R\times U(1)$, where G' is the point group of all the rotations. Since the spins, as mentioned, are "frozen" in the lattice, each rotation element A from G' acts in the triplet case as follows: $\hat{A}\,\mathbf{d}\equiv A\,\mathbf{d}(A\,\mathbf{k})$. We shall see later on that the properties of triplet and singlet nontrivial classes are very similar. The differences lie in the types of the zeros and are caused precisely by the different behaviors of the scalar and vector functions on the symmetry-allowed geometric locus of the points under the action of the transformations A from G'.

We shall describe here briefly the general method of listing all the expanded groups. The number of superconducting classes is very large, and we confine ourselves to the cubic system as an example. In accordance with the statements made above concerning parity, the group G' is in this case the group O of all the rotation axes of the cube. The group O contains the subgroups $T, D_4, D_3, D_2, C_4, C_3, C_2$ (we use throughout the notation of Ref. 20). The meaning of the required procedure is quite clear—the order parameter for nontrivial superconductors is not invariant to certain transformations from O, but is multiplied by phase factors or is transformed into its complex conjugate. These factors must be compensated for by combining the operations of group O with elements of subgroups from $U(1)$, namely $(1, e^{\pm i\pi/2}, e^{i\pi})$, $(1,\varepsilon,\varepsilon^2)$ and $(1, e^{i\pi})$, which are isomorphic to the rotation subgroups of fourth, third ($\varepsilon = e^{2\pi i/3}$) and second order, respectively, and of time reversal (complex conjugation). The implementation of this procedure is facilitated by the fact that the representations of an arbitrary group contain representation of factor groups made up of all its invariant subgroups.[16] For group O, the invariant subgroups are the tetrahedron group T and the group of rotations D_2 about three mutually perpendicular twofold axes that are perpendicular to the faces of the cube. The factor group O/T has the index 2, is isomorphic to the subgroup $(1, e^{i\pi})$ from $U(1)$, and its representations are one-dimensional. Therefore the combined group $O(T)$ has the elements $(E, 8C_3, 3C_2, 6U_2e^{i\pi}, 6C_4e^{i\pi})$.

The factor-group O/D_2 has the index 6 and is isomorphic to D_3. It corresponds to the two-dimensional representation E of group O. Since the operation R does not commute with operations from $U(1)$, it is possible to construct from their combinations a group isomorphic to O/D_2. The elements of the combined $O(D_2)$ group are

$$(E, 3C_2, 2C_4^xR, 2C_4^y\varepsilon R, 2C_4^z\varepsilon^2R, 4C_3\varepsilon^2, 4C_3^2\varepsilon,$$
$$2U_2^{\perp x}R, 2U_2^{\perp y}\varepsilon R, 2U_2^{\perp z}\varepsilon^2R).$$

From the elements of $U(1)$ and R we can construct a group that has representations with dimensionality higher than two. It is therefore impossible to split the representations of O further without lowering the crystal symmetry. The tetrahedron subgroup admits of the combined group $T(D_3)=(E, 3C_2, 4C_3\varepsilon, 4C_3^2\varepsilon^2)$. This group, however, is a subgroup of $O(D_2)$ and, as will be shown below, cannot stem directly from the cubic normal phase (T-subgroups of lower symmetry (threefold axis) are included in the system D_3).

The next subgroup of O is D_4. There exists a maximal combined group

$$D_4(E)$$
$$=(E, C_2e^{i\pi}, C_4e^{i\pi/2}, C_4^3e^{-i\pi/2}, U_{2x}e^{i\pi}R, U_{2y}R, 2U_2'e^{\pm i\pi/2}R).$$

The invariant subgroups in the group D_4 are C_4 and D_2 (the factor-groups D_4/C_4 and D_4/D_2 have the index 2). Three other combined groups are also possible:

$$D_4(C_4)\times R=(E, C_2, 2C_4, 2e^{i\pi}U_2, 2e^{i\pi}U_2')\times R,$$
$$D_4^{(1)}(D_2)\times R=(E, C_2, 2U_2, 2C_4e^{i\pi}, 2U_2'e^{i\pi})\times R,$$
$$D_4^{(2)}(D_2)\times R=(E, C_2, 2U_2', 2C_4e^{i\pi}, 2U_2e^{i\pi})\times R.$$

For C_4, all the possibilities correspond to subgroups of the just-considered groups from D_4.

The same procedure is used to construct

$$D_3(E)=(E, C_3\varepsilon, C_3^2\varepsilon^2, U_2'R, U_2''\varepsilon^2R, U_2'''\varepsilon R),$$
$$D_3(C_3)\times R=(E, 2C_3, 3U_2e^{i\pi})\times R.$$

In analogy with the case of C_4, the subgroups of these groups exhaust all the possibilities for C_3.

In the subgroup D_2, finally, there are three possibilities:

$$D_2(C_{2x})\times R$$
$$=(E, C_{2x}, C_{2y}e^{i\pi}, C_{2z}e^{i\pi})\times R,\ D_2(C_{2y})\times R,\ D_2(C_{2z})\times R.$$

Their subgroups also exhaust all the possibilities of the subgroup C_2.

We did not mention above the subgroups T, D_4, C_4, D_3, C_3, D_2, and C_2 themselves. For the singlet case they would correspond to the aforementioned usual superconducting classes. The triplet case, as already mentioned, would correspond to linkage of the gauge group for the inversion transformation $C_ie^{i\pi}$.

The combined groups listed above for D_4, D_3, and D_2 indicate also all the possibilities for the tetragonal, rhombohedral, rhombic, and monoclinic systems (for those classes that have an inversion center). The hexagonal system will be considered by us later. We have likewise not written out the basis functions. Some are contained in Ref. 16, where the most symmetric classes were considered, and some are given in the next sections.

A subordination scheme in the Landau theory, for all the possible second-order phase transitions without change of the number of atoms per unit cell, was constructed in Ref. 21. For the superconducting classes this analysis must be carried out anew. Thus, for example, the restrictions that follow from the requirement that the expansion for the energy functional contain no terms of third order in the order parameter are entirely lifted for the complex order parameter of a superconducting phase by gauge invariance. (The terms linear in the gradient—the Lifshitz criterion—do not appear in the systems investigated by us, which have inversion centers.) We consider below only those states to which can be reached directly from the normal metal; this requirement limits the number of classes listed.

The last requirement allows us to confine ourselves to the vicinity of T_c. Of importance to the order parameter $\hat{\Delta}(\mathbf{k})$ near T_c is only one of the representations of the group G. On a specified representation there can be realized not any arbitrary symmetry group (the superconducting class in this case), but only a definite set of classes, from among which we choose only those that can effect an absolute minimum of the Ginzburg-Landau functional in a certain region of the parameters of the latter. Examining all the representations of a given group and finding, in the manner indicated, for each of them the possible symmetry subgroups, we obtain all the symmetry classes that can be realized also at low temperatures, provided, of course, that no additional phase transition takes place when the temperature is lowered, since the symmetry cannot vary continuously.

It was noted in Ref. 22 that, owing to the strong spin-orbit coupling in these systems, the Ginzburg-Landau functional takes the same form for triplet and singlet pairing, inasmuch as all the possibilities are exhausted, at any choice of the order parameter from (1), by enumerating the representations of the rotation group G'. However, as indicated above, the types of zeros on the Fermi surface (as well as the basis functions) are generally speaking different for the two types of pairing.

3. SUPERCONDUCTIVITY IN THE CUBIC GROUP

The symmetry O_h is possessed by UBe_{13}. Separating in the O_h group the rotation subgroup $O_h=O\times C_i$, we have for O five representations: two one-dimensional A_1 and A_2, one two-dimensional E, and two three-dimensional F_1 and F_2 (see, e.g., Ref. 20).

a) One-dimensional representations. A_1 is the only representation of the O group. At $S=0$ it describes the state A_{1g}, which has the symmetry of the complete cubic group $O_h\times R$ and corresponds to ordinary superconductivity. Parity is violated for $S=1$, therefore the state is of the nontrivial type and coincides with the odd representation A_{1u} of the O_h group (total group $O\times R\times C_1e^{i\pi}$). Whereas in the former case ($S=0$) the wave function $\psi(\mathbf{k})$ can be chosen to be a real function of $f(\mathbf{k})$ and invariant to all cube-symmetry transformations, for $S=1$ the basis function is of the form

$$\mathbf{d}(\mathbf{k})\propto(\tilde{\mathbf{x}}k_x+\tilde{\mathbf{y}}k_y+\tilde{\mathbf{z}}k_z)f(\mathbf{k}),\tag{2}$$

where $\tilde{\mathbf{x}}$, $\tilde{\mathbf{y}}$, $\tilde{\mathbf{z}}$ are the unit vectors of the principal cubic axes. The properties of this phase are similar to the B phase of ^3He, with the natural exception that the state (2) is not degenerate on account of crystal symmetry. The question of the zeros of the gap in the excitation spectrum of the triplet phase is equivalent to the possibility of vanishing of the scalar $\mathbf{d}^2(\mathbf{k})$

$= k^2 f^2(\mathbf{k})$ on the Fermi surface. There are no symmetry-based grounds for the apperans of zeros for either $S = 0$ or $S = 1$, and the heat capacity decreases exponentially at low temperatures. The state (2) is not magnetic, since time reversal was not violated.

The representation A_2 is not unique and corresponds, as can be easily verified from the table of characters, to the nontrivial class $O(T)\times R$. The basis functions are

$$\psi(\mathbf{k}) \propto (k_x^2-k_y^2)(k_y^2-k_z^2)(k_z^2-k_x^2)f(\mathbf{k}), \quad (3)$$

$$\mathbf{d}(\mathbf{k}) \propto \{\tilde{\mathbf{x}}k_x(k_z^2-k_y^2)+\tilde{\mathbf{y}}k_y(k_x^2-k_z^2)+\tilde{\mathbf{z}}k_z(k_y^2-k_x^2)\}f(\mathbf{k}) \quad (4)$$

for $S = 0$ and $S = 1$, respectively. Wave-function zeros exist in (3) on the lines of intersection of the Fermi surface (FS) with all the diagonal planes of the cube, whereas in the triplet state the zeros appear on the intersection of the FS with threefold and fourfold axes (the last fact was not noted in Ref. 16).

We show now that the appearance of these zeros is connected with nontrivial elements of the $O(T)\times R$ group. For $S=0$ we have $C_2\psi = \psi$, $C_i\psi = \psi$ and $U_2e^{i\pi}\psi = \psi$. We take an arbitrary point $\mathbf{k}_0 = (a, a, k_z)$ (i.e., $k_x = k_y = a$) on a diagonal plane of the cube and use the equations

$$\psi(\mathbf{k}_0) = -\psi(U_2\mathbf{k}_0) = -C_iC_2^z\psi(a, a, -k_z) = -\psi(a, a, k_z) = -\psi(\mathbf{k}_0) = 0. \quad (5)$$

Thus, in the singlet phase the zeros appear in the gap on a whole line and the heat capacity at low temperature varies like T^2.

In the triplet phase $O(T)\times R$ the form of the basis function (4) indicates that a similar analysis need be carried out only for points lying on threefold and fourfold axes. Let $\mathbf{k}_0$ lie on a threefold axis. Since rotation of C_3 around this axis is an invariant operation, it follows that $\mathbf{d}(\mathbf{k}_0)$ is parallel to $\mathbf{k}_0$. On the other hand, we should have $\hat{U}_2e^{i\pi}\mathbf{d}(\mathbf{k}_0) = \mathbf{d}(\mathbf{k}_0)$ (the rotation axis U_2 perpendicular to the chosen threefold axis). We have then

$$\mathbf{d}(\mathbf{k}_0) = \hat{U}_2e^{i\pi}\mathbf{d}(\mathbf{k}_0) = -U_2\mathbf{d}(U_2\mathbf{k}_0) = \mathbf{d}(-\mathbf{k}_0) = -\mathbf{d}(\mathbf{k}_0) = 0 \quad (5')$$

when account is taken of the fact that the representation is odd. Let now the point $\mathbf{k}_0$ lie on a fourfold axis. Again $\mathbf{d}(\mathbf{k}_0)\|\mathbf{k}_0$ (C_2 transformation). Applying the transformation $C_4e^{i\pi}$, we have

$$\mathbf{d}(\mathbf{k}_0) = \hat{C}_4e^{i\pi}\mathbf{d}(\mathbf{k}_0) = -\mathbf{d}(\mathbf{k}_0) = 0.$$

The gap thus vanishes in such a triplet superconducting state at 14 points on the FS, so that at $T \ll T_c$ we have for the heat capacity $C_e \propto T^3$.

The properties of superconducting phases on one-dimensional representations are gathered in Table I. Since the representations are one-dimensional, there is no discrete degeneracy (a domain structure is impossible) and the phases are not magnetic (the time reversal R is not violated).

b. Two-dimensional representation. The order parameter for $S = 0$ and $S = 1$ can be written in like form as a sum over the basis functions:

$$\hat{\Delta}(\mathbf{k}) = \eta_1\hat{\Phi}^{(1)}(\mathbf{k}) + \eta_2\hat{\Phi}^{(2)}(\mathbf{k}), \quad (6)$$

where the basis functions for $S = 0$ can be represented in the form

$$\Phi^{(1)}(\mathbf{k}) \propto k_x^2+\varepsilon k_y^2+\varepsilon^2 k_z^2, \quad \Phi^{(2)}(\mathbf{k}) \propto k_x^2+\varepsilon^2 k_y^2+\varepsilon k_z^2, \quad (7)$$

and for $S = 1$,

$$\boldsymbol{\Phi}^{(1)}(\mathbf{k}) \propto \tilde{\mathbf{x}}k_x+\varepsilon\tilde{\mathbf{y}}k_y+\varepsilon^2\tilde{\mathbf{z}}k_z, \quad \boldsymbol{\Phi}^{(2)}(\mathbf{k}) \propto \tilde{\mathbf{x}}k_x+\varepsilon^2\tilde{\mathbf{y}}k_y+\varepsilon\tilde{\mathbf{z}}k_z \quad (8)$$

[here $\varepsilon = \exp(2\pi i/3)$], and the remaining $\mathbf{k}$-dependences corresponding to cubic symmetry have been left out. As usual, it is convenient to refer the transformation properties of the order parameter under symmetry transformations to two complex components (η_1, η_2).

The Ginzburg-Landau functional takes the form

$$F = -\alpha(|\eta_1|^2+|\eta_2|^2)+\beta_1(|\eta_1|^4+|\eta_2|^4) + 2\beta_2|\eta_1|^2|\eta_2|^2+\gamma(\eta_1^3\eta_2^{*3}+\eta_1^{*3}\eta_2^3). \quad (9)$$

We have added here a sixth-order term which will be needed later. If we neglect this term initially, the minimum of the functional corresponds at $\beta_2 > \beta_1$ to a state with $|\eta_1|^2 = \alpha/2\beta_1$, $\eta_2 = 0$, and at $\beta_2 < \beta_1$ to a state with $|\eta_1|^2 = |\eta_2|^2 = \alpha/2(\beta_1+\beta_2)$. In the latter case there is additional degeneracy

TABLE I. Superconductivity classes for one-dimensional representations of the cubic group.

Representation		Class	Heat capacity $C_e(T)$
A_1	$S=0$, A_{1g}	$O\times R$	$\exp(-\Delta/T)$
	$S=1$, A_{1u}		$\exp(-\Delta/T)$
A_2	$S=0$, A_{2g}	$O(T)\times R$	T^2
	$S=1$, A_{2u}		T^3

For the type of the basis functions see expressions (2), (3), and (4) in the text. The superconducting phases with symmetry $O\times R$ have no zeros in the gap of the Fermi-excitation spectrum. The heat capacity decreases therefore in the usual exponential manner with decreasing temperature. The triplet phase from the class $O(T)\times R$ must contain zeros at the points where the FS intersects the three- and fourfold axes, whereas the zeros of the singlet phase with the same symmetry $O(T)\times R$ lie on the lines of intersection of the FS with the diagonal planes of the cube. As a result, the heat capacities of the triplet and singlet phases behave differently at low temperatures, like T^3 and T^2, respectively.

with respect to the phase difference $\varphi_1 - \varphi_2$ between the components $\eta_1 = |\eta_1| \exp i\varphi_1$, $\eta_2 = |\eta_2| \exp i\varphi_2$. The additional symmetry of functional that contains only fourth-order terms is lifted by the sixth-order terms which take the form

$$\frac{\gamma}{4}\left(\frac{\alpha}{\beta_1+\beta_2}\right)^3 \cos 3(\varphi_1-\varphi_2). \tag{10}$$

As a result it follows from (10) that $\varphi_1 - \varphi_2 = (\pi + 2\pi n)/3$, at $\gamma > 0$ and $\varphi_1 - \varphi_2 = 2\pi n/3$ at $\gamma < 0$.

The two-dimensional representation offers therefore three possibilities. At $\beta_2 > \beta_1$, as can be seen from (6)–(8), the state corresponds to the superconducting class $O(D_2)$, in which the symmetry calls for the vanishing of the gap in the intersections of all the threefold axes with the Fermi surface, for both singlet and triplet pairing.[16] In fact, applying a combined-symmetry element, say to $\psi(\mathbf{k}_0)$ ($\mathbf{k}_0$ on a threefold axis), we obtain

$$\psi(\mathbf{k}_0) = C_3 e^{2\pi i/3}\psi(\mathbf{k}_0) = \varepsilon\psi(C_3\mathbf{k}_0) \equiv \varepsilon\psi(\mathbf{k}_0) = 0. \tag{11}$$

By analogous reasoning we verify that in the case of triplet pairing $\mathbf{d}^2(\mathbf{k}_0)$ vanishes at the point $\mathbf{k}_0$. The types of the zeros in the gap likewise coincides for this class in both cases of (1). The heat capacity always varies asymptotically like T^3.

The eight points where the FS intersects the threefold axes constitute the so-called boojums on the Fermi surface, viz., topologically stable point vortices in $\mathbf{k}$ space, and when these are bypassed the phase of the function $\psi(\mathbf{k})$ or $\mathbf{d}^2(\mathbf{k})$ changes by $2\pi N$.[23] In this case N on the values ± 1. The boojum arrangement is shown in Fig. 1, where the points and crosses mark boojums with $N = 1$ and $N = -1$, respectively. It is easily seen that both superconducting states are doubly degenerate, so that domain walls are possible. We defer the discussion of the domain wall and of the magnetic nature of the superconducting state (which is ferromagnetic) to Sec. 6.

To establish the symmetry of the states produced at $\beta_2 < \beta_1$ and $\gamma > 0$, we write one of the solutions:

$$\psi(\mathbf{k}) \propto 2k_x^2 - k_z^2 - k_y^2 \quad (S=0), \tag{12}$$

$$\mathbf{d}(\mathbf{k}) \propto 2\tilde{\mathbf{x}}k_x - \tilde{\mathbf{z}}k_z - \tilde{\mathbf{y}}k_y \quad (S=1). \tag{13}$$

Obviously the symmetry is $D_4 \times R$, i.e., in the singlet state we have a transition to a trivial type of superconductivity (with tetragonal symmetry of the real order parameter). The transition to the triplet state is essentially of the same type, if we disregard the linking of gauge-invariance element $\exp(i\pi)$ with the inversion $C_i \exp(i\pi)$. In (12), $\psi(\mathbf{k})$ has lines of zeros.

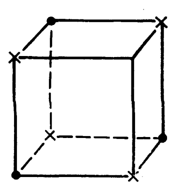

FIG. 1. Arrangement of zeros in class $O(D_2)$. The points and crosses show boojums with $N = 1$ and $N = -1$, respectively.

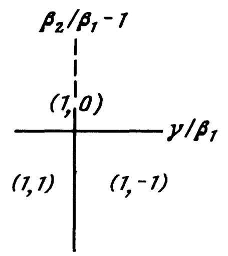

FIG. 2. Phase diagram of superconducting states near T_c for two-dimensional representation of the cubic group.

There are no combined symmetry elements in the $D_4 \times R$ group, and the zeros in (12) have a random character (a property of the functions of the representation E itself). In the nonlinear problem, i.e., with decrease of temperature, these zeros are smeared out because of the mixing of several representations of like symmetry. From the viewpoint of symmetry theory, the heat capacity should decrease exponentially at the very lowest temperatures. Within the framework of a theory of the BCS type, the admixture of solutions corresponding to other eigenvalues in the integral equation for the gap is small to the extent that the dimensionless interaction constant is small.

Finally, the states corresponding to $\beta_2 < \beta_1$, $\gamma > 0$, have basis functions of the type

$$\psi(\mathbf{k}) \propto k_x^2 - k_y^2 \quad (S=0), \tag{14}$$

$$\mathbf{d}(\mathbf{k}) \propto \tilde{\mathbf{x}}k_x - \tilde{\mathbf{y}}k_y \quad (S=1). \tag{15}$$

The symmetry of these solutions corresponds to the combined group $D_4^{(1)}(D_2) \times R$. The or the zeros in this group stem from nontrivial combined $C_4 \exp(i\pi)$ and $U_2 \exp(i\pi)$ symmetry elements. In the singlet state the zeros lie on the lines where the FS intersects the diagonal planes of the cube (heat capacity $\propto T^2$), and in the triplet states the zeros correspond to the points of intersection of the FS with one of the fourfold axes. The results for the two-dimensional representation E are gathered in Table II. Figure 2 shows the phase diagram for the functional (9).

c. Three-dimensional representations. The rotation group O has two irreducible three-dimensional representations: the vector representation F_1 and a representation F_2 that corresponds to transformations of a symmetric tensor of the form (xy, yz, xz). In the expansion of the order parameter

$$\hat{\Delta}(\mathbf{k}) = \sum_{i=1}^{3} \eta_i \hat{\Phi}^{(i)}(\mathbf{k}) \tag{16}$$

the three basis functions $\Phi^{(i)}(\mathbf{k})$ can be chosen such that the Ginzburg-Landau functional takes the form

$$F = -\alpha(\eta\eta^*) + \beta_1(\eta\eta^*)^2 + \beta_2|\eta^2|^2 + \beta_3(|\eta_x|^4 + |\eta_y|^4 + |\eta_z|^4), \tag{17}$$

which is the same for the representations F_1 and F_2 (and, of course, for $S = 0$ and 1). The three coefficients η_i are regarded hereafter as a complex three-dimensional vector. This choice for F_1 can be:

TABLE II. Superconductivity classes from two-dimensional representations E of the cubic group.

(η_1, η_2)	Class	$C_e(T)$	Degeneracy	Magn. properties
$(1,0)$ $\begin{cases} S=0, E_g \\ S=1, E_u \end{cases}$	$O(D_2)$	T^3 T^3	2 2	A A
$(1,-1)$ $\begin{cases} S=0, E_g \\ S=1, E_u \end{cases}$	$D_4^{(1)}(D_2)\times R$	T^2 T^3	3 3	– –
$(1,1)$ $\begin{cases} S=0, E_g \\ S=1, E_u \end{cases}$	$D_4\times R$	$\exp(-\Delta/T)$ $\exp(-\Delta/T)$	3 3	– –

For the types of basis function see expressions (7), (8), and (12)–(15) in the text; A—"antiferromagnetism." The triplet and singlet phases from the class $O(D_2)$ have zeros at the points where the FS intersects the threefold axes, the phase $D_4^{(1)}(D_2)\times R$ $(S=1)$ has zeros at the intersectionof the FF with the fourfold axis, and the phase $D_4^{(1)}(D_2)\times R$ $(s=1)$ on the lines of intersection of the FS with two mutually perpendicular vertical symmetry planes.

$$F_{1g}(S=0):\quad k_yk_z(k_y^2-k_z^2),\ k_zk_x(k_z^2-k_x^2),\ k_yk_x(k_x^2-k_y^2), \tag{18}$$

$$F_{1u}(S=1):\quad \tilde{\mathbf{y}}k_z-\tilde{\mathbf{z}}k_y,\ \tilde{\mathbf{z}}k_x-\tilde{\mathbf{x}}k_z,\ \tilde{\mathbf{x}}k_y-\tilde{\mathbf{y}}k_x, \tag{19}$$

and for F_2,

$$F_{2g}(S=0):\quad k_yk_z,\ k_zk_x,\ k_xk_y, \tag{20}$$

$$F_{2u}(S=1):\quad \tilde{\mathbf{y}}k_z+\tilde{\mathbf{z}}k_y,\ \tilde{\mathbf{z}}k_x+\tilde{\mathbf{x}}k_z,\ \tilde{\mathbf{x}}k_y+\tilde{\mathbf{y}}k_x \tag{21}$$

(the subscript g or u indicates that the representation is constructed on an even or odd representation of the O_h group, depending on the choice of S in (1).

The cubic anisotropy is represented in (17) only by the term with β_3. Omitting this term for a while, we see that the first term is invariant in the SO(6) group, and the second introduces a linkage between the real and imaginary components of the three-dimensional complex vector

$$\boldsymbol{\eta}=\boldsymbol{\eta}'+i\boldsymbol{\eta}'', \tag{22}$$

leaving the SO(3) symmetry. Elementary calculations show that in the isotropic case the minimum of (17) at $\beta_2<0$ corresponds to the choice of one real vector ($\boldsymbol{\eta}=\boldsymbol{\eta}'$), whereas at $\beta_2>0$ the vector is substantially complex, $|\boldsymbol{\eta}'|=|\boldsymbol{\eta}''|$, $\boldsymbol{\eta}'\perp\boldsymbol{\eta}''$, (i.e., $\boldsymbol{\eta}^2=0$) and the state is characterized by a triad of vectors $\boldsymbol{\eta}'\perp\boldsymbol{\eta}''$ and $\mathbf{l}$, where $\mathbf{l}=\boldsymbol{\eta}'\times\boldsymbol{\eta}''$. The continuous degeneracy is lifted by the cubic anisotropy.

The case of a real vector ($\beta_2<0$) is simpler. The expected symmetric solutions for $\boldsymbol{\eta}$ correspond to fourfold, threefold, and twofold anisotropy axes $\boldsymbol{\eta}=(1,0,0)$, $(1,1,1)$, and $(1,1,0)$, respectively. The third solution does not correspond to a minimum of the functional (17) at arbitrary β_3 and is therefore discarded. The symmetry group of the remaining solutions can be easily determined from the form of the basis functions. These groups are, of course, different for the representations F_1 and F_2. The solution $(1,1,1)$ corresponds to $D_3(C_3)\times R$ in F_1 and to $D_2\times R$ in F_2. The solution $(1,0,0)$, similarly, corresponds to $D_4(C_4)\times R$ for F_1 and to $D_4^{(2)}(D_2)\times R$ for F_2.

If a complex vector is chosen ($\beta_2>0$) the symmetry is lowered primarily via the choice of the direction of the vector $\mathbf{l}$, whose physical meaning is the direction of the magnetic moment (see below). The remaining degeneracy is connected with the choice of $\boldsymbol{\eta}'$ and $\boldsymbol{\eta}''$. The crystal anisotropy can, in particular, lift the condition that the vectors be equal. This

TABLE III a. Superconductivity classes from three-dimensional representation F_1 of the cubic group.

(η_x, η_y, η_z)	Class	$C_e(T)$	Degeneracy	Magn. properties
$(1, \varepsilon, \varepsilon^2)$ $\begin{cases} S=0, F_{1g} \\ S=1, F_{1u} \end{cases}$	$D_3(E)$	T^3 T^3	8 8	F F
$(1,1,1)$ $\begin{cases} S=0, F_{1g} \\ S=1, F_{1u} \end{cases}$	$D_3(C_3)\times R$	T^2 T^3	4 4	– –
$(1,i,0)$ $\begin{cases} S=0, F_{1g} \\ S=1, F_{1u} \end{cases}$	$D_4(E)$	T^2 T^3	6 6	F F
$(1,0,0)$ $\begin{cases} S=0, F_{1g} \\ S=1, F_{1u} \end{cases}$	$D_4(C_4)\times R$	T^2 T^3	3 3	– –

See expressions (18) and (19) of the text for the type of basis functions; F stands for "ferromagnetism." The phases $D_3(E)$ $(S=0,1)$ and $(D_3(C_3)\times R$ $(S=1)$ have zeros at the points of intersection of the FS with spontaneous-anisotropy axis (threefold axis). The phases $D_4(C_4)\times R$ $(S=1)$, $D_4(E)$ $(S=1,0)$ have zeros at the points of intersection of the FS with a fourfold axis, and the last of them $D_4(E)$ $S=0)$ has in addition a line of zeros on the intersection of the FS with the horizontal symmetry plane. The singlet phases $D_3(C_3)\times R$ and $D_4(C_4)\times R$ have lines of zeros on the intersection of the FS with the diagonal planes of the cube and with the vertical symmetry planes, respectively.

TABLE IIIb. Superconductivity classes from three-dimensional representations F_2 of cubic group.

(η_x, η_y, η_z)		Class	$C_e(T)$	Degeneracy	Magn. properties
$(1, \varepsilon, \varepsilon^2)$	$S=0,\ F_{2g}$	$D_3(E)$	T^3	8	F
	$S=1,\ F_{2u}$		T^3	8	F
$(1, 1, 1)$	$S=0,\ F_{2g}$	$D_3\times R$	$\exp(-\Delta/T)$	4	–
	$S=1,\ F_{2u}$		$\exp(-\Delta/T)$	4	–
$(1, i, 0)$	$S=0,\ F_{2g}$	$D_4(E)$	T^2	6	F
	$S=1,\ F_{2u}$		T^3	6	F
$(1, 0, 0)$	$S=0,\ F_{2g}$	$D_4^{(2)}(D_2)\times R$	T^2	3	–
	$S=1,\ F_{2u}$		T^3	3	–

See Eqs. (20) and (21) of the text for the type of basis functions. The zeros phases are at the points of intersection of the FS with a threefold axis in both $D_3(E)$ phases and at the points of intersection of the FS with a fourfold axis in the phases $D_4^{(2)}(D_2)\times R$ $(S=1)$, $D_4(E)$ $(S=0,1)$. In addition, the phase $D_4(E)$ $(S=0)$ has a line of zeros on the intersection of the FS with the horizontal symmetry plane. The singlet $D_4^{(2)}(D^2)\times R$ phase has zeros on the lines of intersection of the FS with two mutually perpendicular vertical symmetry planes.

takes place, for example, if the vector **l** is directed along a twofold axis.[2)] This choice can again be rejected, since it does not minimize the functional (17) in any range of values of the parameter β_3.

A vector **l** directed along a threefold axis corresponds to the solutions $(1,\varepsilon,\varepsilon^2)$. The superconductivity class is in this case $D_3(E)$ for both representations F_1 and F_2.

A direction of **l** along a fourfold axis corresponds to the solution $(1,i,0)$. The superconductivity class for both representations F_1 and F_2 is $D_4(E)$.

Figure 3 shows the regions of existence of the different phases for three-dimensional representations (we did not determine the boundary where the degeneracy just discussed is lifted). The properties of all four solutions and of the phases corresponding to them are listed in Tables IIIa and IIIb. All the complex solutions should be magnetic, since time reversal is violated in them. The magnetism (spontaneous moment) is caused by the boojums that stem from the nontrivial combined symmetry $C_3e^{2\pi i/3}$ or $C_4e^{i\pi/2}$. We see that the disposition of the boojums in these superconducting classes is "ferromagnetic." The magnetism due to boojums will be discussed in Sec. 6. Table III illustrates also the low-temperature behavior of the heat capacity. We note again that in the triplet case the energy gap can have zeros only at points on the FS. In evaluating the procedural aspect of our subject, we see that the use of basis functions is advantageous because it frequently yields the symmetry of the state. The disposition of the zeros in the nonlinear problem, however, is governed just by symmetry and generally speaking does not coincide with that of the basis-function zeros.

4. SUPERCONDUCTING PHASES IN CRYSTALS OF THE $D_{6h}\times R$ GROUP

The superconductivity classes in hexagonal crystals (such as UPt_3) are obtained similarly. Since $D_{6h}=D_6\times C_i$, we shall need hereafter representations of only the rotation

TABLE IV. Superconductivity classes from one-dimensional representations of group D_6.

Representation		Type of basis functions	Class	$C_e(T)$
A_1	$S=0,\ A_{1g}$	Symm. function	$D_6\times R$	$\exp(-\Delta/T)$
	$S=1,\ A_{1u}$	$a\tilde{z}k_z+b(\tilde{x}k_x+\tilde{y}k_y)$		$\exp(-\Delta/T)$
A_2	$S=0,\ A_{2g}$	$(k_x^3-3k_xk_y^2)(k_y^3-3k_yk_x^2)$	$D_6(C_6)\times R$	T^2
	$S=1,\ A_{2u}$	$\tilde{z}k_z(k_x^3-3k_xk_y^2)(k_y^3-3k_yk_x^2)$		T^3
B_1	$S=0,\ B_{1g}$	$k_z(k_x^3-3k_xk_y^2)$	$D_6(D_3)\times R$	T^2
	$S=1,\ B_{1u}$	$\tilde{z}(k_x^3-3k_xk_y^2)$		T^3
B_2	$S=0,\ B_{2g}$	$k_z(k_y^3-3k_yk_x^2)$	$D_6(D_3')\times R$	T^2
	$S=1,\ B_{2u}$	$\tilde{z}(k_y^3-3k_yk_x^2)$		T^3

Elements of combined groups $D_6(C_6)=(E,C_2,2C_3,2C_6,3U_2e^{i\pi},\ 3U_2'e^{i\pi})$; $D_6(D_3)=(E,2C_3,3U_2,C_2e^{i\pi},2C_6e^{i\pi},3U_2'e^{i\pi})$; $D_6(D_3')\mapsto D_6(D_3)(U_2\to U_2')$. The triplet phases from classes $D_6(C_6)\times R$, $D_6(D_3)\times R$, $D_6(D_3')\times R$ have zeros at the points of intersection of the FS with the sixfold axis. The relative positions of the zero lines in the singlet phases are on the intersections of the FS with all vertical symmetry planes in the $D_6(C_6)\times R$ phase, on the intersection of the FS with the horizontal plane and with three vertical ones in the $D_6(D_3)\times R$ phase, and on the intersections with the horizontal and with three other vertical planes in the $D_6(D_3')\times R$ phase.

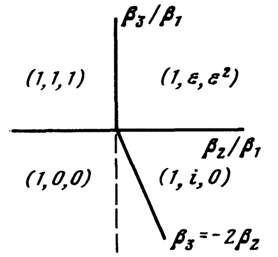

FIG. 3. Regions of existence of various solutions for three-dimensional representations of the cubic group.

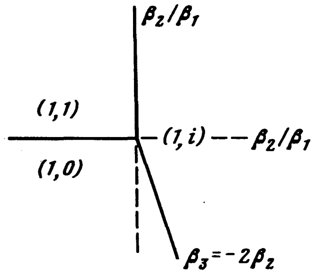

FIG. 4. Regions of existence of solutions for the two-dimensional representation E_1 of the hexagonal group.

group D_6 which contains four one-dimensional and two two-dimensional representations.

a. One-dimensional representations. The superconducting phases in these representations are not degenerate (there are no domain walls) and have no spontaneous ferro- or antiferromagnetism. The order parameter is always a complex scalar, and the corresponding Ginzburg-Landau functional is of standard form. The superconducting classes (nontrivial subgroups of the $D_6\times R\times U(1)$ group) can be constructed either directly from the characteristics of the representations, as explained in Sec. 2, or from the form of the basis functions of these representations. All these data (including the location of the zeros, which generally speaking does not coincide with that of the zeros of the simplest basis functions) are gathered in Table IV.

b. The two-dimensional representation E_2. The order parameter contains, in analogy with (6) two complex components (η_1,η_2). The basis functions can be chosen in the form

$$S=0:\quad (k_x+ik_y)^2,\quad (k_x-ik_y)^2, \tag{23}$$

$$S=1:\quad (\tilde{\mathbf{x}}+i\tilde{\mathbf{y}})(k_x+ik_y),\quad (\tilde{\mathbf{x}}-i\tilde{\mathbf{y}})(k_x-ik_y). \tag{24}$$

The functional invariant to the total group $D_6\times R\times U(1)$ is, as usual, the same for the triplet and singlet pairings in the case of strong spin-orbit coupling and coincides with the already investigated expression (9) for the two-dimensional representation of the cubic group. For (η_1,η_2) we have again the following solutions: (1,0) at $\beta_2>\beta_1$; $(1,-1)$ at $\beta_2<\beta_1$, $\gamma>0$ and (1.1) at $\beta_2<\beta_1$, $\gamma<0$. The corresponding function symmetries, gap zeros, heat capacity, and magnetic properties are indicated in Table V.

c. Two-dimensional representation E_1. In contrast to the representation E_2, the two-component order parameter (η_1,η_2) is transformed in the E_1 representation as a two-dimensional vector located in a plane perpendicular to the axis:

$$\psi(\mathbf{k})\propto\eta_x k_z k_x+\eta_y k_z k_y\quad (S=0), \tag{25}$$

$$\mathbf{d}(\mathbf{k})\propto\eta_x\tilde{\mathbf{z}}k_x+\eta_y\tilde{\mathbf{z}}k_y\quad (S=1). \tag{26}$$

The Ginzburg-Landau functional, naturally, takes the same form as for the vector order parameter in the cubic group (17):

$$F=-\alpha(\eta\eta^*)+\beta_1(\eta\eta^*)^2+\beta_2|\eta^2|^2+\beta_3(|\eta_x|^4+|\eta_y|^4). \tag{27}$$

The solutions are obtained in the same way. There are three of them: (1,0), (1,1), and $(1,i)$. (The statements made above concerning the hidden symmetry of the functional (17) are valid also for (27) in the last case of the solution with $\eta'\perp\eta''$). For each of the phases there is on the (β_2,β_3) plane a region where this phase has a lower energy that the others (see Fig. 4). The properties of the singlet and triplet phases are gathered in Table VI.

TABLE V. Superconductivity classes from representations E_2 of group D_6.

(η_1,η_2)	Class	$C_e(T)$	Degeneracy	Magn. properties
(1, 0) $S=0$, E_{2g}	$D_6(C_2)$	T^3	2	F
(1, 0) $S=1$, E_{2u}		T^3	2	F
(1, −1) $S=0$, E_{2g}	$D_2(C_2)\times R$	T^2	3	–
(1, −1) $S=1$, E_{2u}		T^3	3	–
(1, 1) $S=0$, E_{2g}	$D_2\times R$	$\exp(-\Delta/T)$	3	–
(1, 1) $S=1$, E_{2u}		$\exp(-\Delta/T)$	3	–

See Eqs. (23) and (24) for the basis functions. The elements of the combined groups are $D_6(C_2)=(E,C_2,\varepsilon^2C_3,\varepsilon C_3^2,\varepsilon C_6,\varepsilon^2C_6^5,U_2R,U_2'\varepsilon R,\ldots)$; $D_2(C_2)=(E,C_2,U_2e^{i\pi},U_2'e^{i\pi})$. Both phases from Class $D_6(C_2)$ and the triplet phase from $D_2(C_2)\times R$ have zeros at the point of intersection of the FS with a sixfold axis. The singlet phase from $D_2(C_2)\times R$ has a line of zeros on the intersection of the FS with two mutually perpendicular vertical symmetry planes.

TABLE VI. Superconductivity classes from two-dimensional representations E_1 of group D_6.

(η_1, η_2)	Class	$C_e(T)$	Degeneracy	Magn. properties
$(1, i)$ $\begin{cases} S=0, E_{1g} \\ S=1, E_{1u} \end{cases}$	$D_6(E)$	T^2 T^3	2 2	F F
$(1, 0)$ $\begin{cases} S=0, E_{1g} \\ S=1, E_{1u} \end{cases}$	$D_2(C_2)\times R$	T^2 T^3	3 3	– –
$(1, 1)$ $\begin{cases} S=0, E_{1g} \\ S=1, E_{1u} \end{cases}$	$C_2(E)\times R$	T^2 $\exp(-\Delta/T)$	3 3	– –

The triplet phases $D_4(C_4)\times R$, $D_4^{(1)}(D_2)\times R$, $D_4^{(2)}(D_2)\times R$ have zeros at the points of intersection of the FS with a fourfold axis. The singlet phases have zeros on the following lines of intersection of the FS: for $D_4(C_4)\times R$—with all the vertical symmetry planes, for $D_4^{(1)}(D_2)\times R$—with two mutually perpendicular planes, and for $D_4^{(2)}(D_2)\times R$—with the two remaining vertical symmetry planes.

5. SUPERCONDUCTIVITY CLASSES IN TETRAGONAL SYMMETRY

This symmetry is possessed, e.g., by $CeCu_2Si_2$ and U_6Fe. The rotation subgroup D in the group $D_{4h} = D_4\times C_i$ four one-dimensional and one two-dimensional representation. The properties of the nondegenerate nonmagnetic superconducting phases that are possible on the basis of the one-dimensional representations are given in Table VII. In a two-dimensional representation the order parameter transforms again as a planar vector (η_x, η_y). The functional is of the same form (27) and has the same solutions. The expansion in the basis functions coincides with (25) and (26). The properties of the corresponding phases obtained from the two-dimensional representations are shown in Table VIII.

Since no rhombohedral-system compounds with heavy fermion are known so far, we shall not discuss this system in detail (see Sec. 2).

6. SUPERCONDUCTING STATES WITH SPONTANEOUS MAGNETISM

It was shown above that, on going to certain superconducting states belonging to a nontrivial class, invariance to time reversal is violated and consequently one should expect the appearance of magnetic properties in these states. These are the classes $D_3(E)$, $D_4(E)$, $D_6(E)$, $D_6(C_2)$ as well as the class $O(D_2)$, which are realized both in singlet and in triplet pairing. Moreover, a property of these classes is that they contain vectors whose transformation properties are analogous to the magnetic moment. These are vectors that emerge from boojums with negative "charge" $N = -1$ on the Fermi surface and enter the point of the boojum with $N=1$ (crosses and dots in Fig. 1). Time reversal (complex conjugation) reverses the signs of the charges, the points become crosses, and the system goes into another degenerate state.

The structures of these states are similar in many respects to the A phase of ^{3}He, where the Cooper pair is in a state with orbital angular momentum $L = 1$ and with projection $L_z = 1$ on the axis $\mathbf{l}\|\mathbf{z}$, and has consequently an angular momentum $\hbar\mathbf{l}$. It is intuitively clear that, say at $T=0$, when the system is totally in a coherent state, its orbital angular momentum should be $\hbar N\mathbf{l}/2$, where N is the total number of particles in the volume. Yet calculations show that the local angular momentum in ^{3}He-A is small and finite only to the extent that the asymmetry of the particles and hole on the FS is small. The angular momentum is only of the order of $\hbar(T_c/$

TABLE VII. Superconductivity classes from one-dimensional representations of group D_4.

Representation	Type of basis function	Class	$C_e(T)$
A_1 $\begin{cases} S=0, A_{1g} \\ S=1, A_{1u} \end{cases}$	Symmetr. Function $a\tilde{z}k_z+b(\tilde{x}k_x+\tilde{y}k_y)$	$D_4\times R$	$\exp(-\Delta/T)$ $\exp(-\Delta/T)$
A_2 $\begin{cases} S=0, A_{2g} \\ S=1, A_{2u} \end{cases}$	$k_xk_y(k_x^2-k_y^2)$ $(\tilde{x}k_y+\tilde{y}k_x)(k_x^2-k_y^2)$	$D_4(C_4)\times R$	T^2 T^3
B_1 $\begin{cases} S=0, B_{1g} \\ S=1, B_{1u} \end{cases}$	$k_x^2-k_y^2$ $\tilde{x}k_x-\tilde{y}k_y$	$D_4^{(1)}(D_2)\times R$	T^2 T^3
B_2 $\begin{cases} S=0, B_{2g} \\ S=1, B_{2u} \end{cases}$	k_xk_y $\tilde{x}k_y+\tilde{y}k_x$	$D_4^{(2)}(D_2)\times R$	T^2 T^3

The triplet phases $D_4(C_4)\times R$, $D_4^{(1)}(D_2)\times R$, $D_4^{(2)}(D_2)\times R$ have zeros at the points of intersection of the FS with a fourfold axis. The singlet phases have zeros on the following lines of intersection of the FS: for $D_4(C_4)\times R$—with all the vertical symmetry planes, for $D_4^{(1)}(D_2)\times R$—with two mutually perpendicular planes, and for $D_4^{(2)}(D_2)\times R$—with the two remaining vertical symmetry planes.

TABLE VIII. Superconductivity classes from two-dimensional representations of group D_4.

(η_1, η_2)		Class	$C_e(T)$	Degeneracy	Magn. properties
$(1, i)$	$S=0$, E_g	$D_4(E)$	T^2	2	F
	$S=1$, E_u		T^3	2	F
$(1, 0)$	$S=0$, E_g	$D_2(C_2)\times R$	T^2	2	–
	$S=1$, E_u		T^3	2	–
$(1, 1)$	$S=0$, E_g	$D_2(C_2')\times R$	T^2	2	–
	$S=1$, E_u		T^3	2	–

See Eqs. (25) and (26) of the text for the type of basis functions. The phases from the class $D_4(E)$ have zeros at the points of intersection of the FS with a fourfold axis, while the singlet phase has furthermore a line of zeros on the intersection of the FS with the horizontal symmetry plane. The triplet phases $D_2(C_2)\times R$ and $D_2(C_2')\times R$ have zeros at the points of intersection of the FS with the corresponding twofold axis, and the singlet phases from these classes have zeros on the lines of intersection of the FS with the horizontal plane and one of the vertical symmetry planes.

$T_F)^2$ per atom of the liquid. According to an explanation proposed for this paradox in Refs. 23 and 24, the angular momentum should be defined not in an infinite system, but with account taken of the geometry of the vessel holding the liquid. The internal angular momentum of the pair produces a superfluid flow along the boundary of the A-phase with the vessel, and this flow imparts to the fluid a total angular momentum that is no longer small and is of the order of $\hbar$ per ^{3}He atom (to our knowledge, there is no proof that this angular momentum is identically equal to $\hbar/2$ per ^{3}He atom, since at first glance the flows in the texture could depend on the boundary conditions.

The question of the value of the angular momentum in a superconductor is even more important from the viewpoint of its physical manifestions, since the carriers are charged and a finite angular momentum would mean existence of an orbital (and spin) magnetic moment. At the same time, the local moment in the interior of the superconductor must be exactly zero because of the Meissner effect. Owing to the crystal-lattice field, the states of a Cooper pair cannot be classified at all in accordance with the value of the orbital angular momentum (as well of the spin, in view of the spin-orbit coupling). Nonetheless, the indicated close analogy between the aforementioned nontrivial superconductivity classes and ^{3}He-A suggests that here, too, circulating superconducting currents can flow over the surface of a single-domain superconductor even in the absence of an external magnetic field. The analysis of the structure of such a surface current is quite complicated, since the entire question is closely connected with the problem of choosing the boundary conditions. As for the latter, there are as yet none in general form. Obviously, the boundary conditions are very sensitive to the quality of the surface.

To answer the fundamental question of the existence of surface magnetic current, we shall circumvent the complications with the boundary conditions by studying the current distribution on the interface between two degenerate superconducting states (domains) with different orientations of the angular momentum (more accurately, of the boojums). In contrast to the usual domain wall in a magnet, the boundary between two superconducting domains that appear only during a transition into the superconducting state is described (near T_c) in terms of the very same Ginzburg-Landau functional as for the superconductivity itself, without invoking additional terms for the anisotropy. By way of a very simple example, we choose the class $D_4(E)$ (for either the singlet or triplet case) from the two-dimensional representation of the group D_4. Other examples are more difficult to calculate, but should lead to the same conclusions.

To find the structure of the wall separating domains with different order-parameter orientations, we must add to the corresponding Ginzburg-Landau functional of the last section, which describes a two-dimensional representation in the D_4 group, the gradient terms

$$F=-\alpha(\eta\eta^*)+\beta_1(\eta\eta^*)^2+\beta_2|\eta^2|^2+\beta_3[|\eta_x|^4+|\eta_y|^4]$$
$$+\frac{1}{2m_1'}(|\partial_x\eta_x|^2+|\partial_y\eta_y|^2)+\frac{1}{2m_1''}(|\partial_x\eta_y|^2+|\partial_y\eta_x|^2)$$
$$+\frac{1}{2m_2}(|\partial_z\eta_x|^2+|\partial_z\eta_y|^2)+\frac{1}{4m_3'}[(\partial_x\eta_y)(\partial_y\eta_x^*)$$
$$+(\partial_x\eta_y^*)(\partial_y\eta_x)]+\frac{1}{4m_3''}[(\partial_y\eta_y)(\partial_x\eta_x^*)+(\partial_y\eta_y^*)(\partial_x\eta_x)]. \tag{28}$$

Here ∂_k is the covariant derivative

$$\partial_k\eta=\nabla_k\eta-(2ie/c)A_k\eta. \tag{29}$$

The answer given in Ref. 22 contains $m_1^{-1}\equiv(m_1')^{-1}+(m_1'')^{-1}$, while $m_3'=m_3''$. In the enumeration of all the possible invariants in the real functional (28), m_3' and m_3'' are independent. Their equality (accurate to terms of order T_c^2/T_F^2) is due to the approximate electron-hole symmetry on the FS. We assume also that the penetration depth δ of the magnetic field exceeds substantially the coherence length ξ. The condition $\delta\gg\xi$ is apparently well satisfied in superconductors with heavy fermions. The vector potential can then be left out of the Ginzburg-Landau equations.

We consider the following geometry. The domain wall lies in the yz plane, so that the order parameter η depends only on the x coordinate, and the "magnetic moment" is directed along the z axis as $x\rightarrow\infty$ and is oppositely directed as $x\rightarrow-\infty$. In this geometry the current should flow along the y axis. Varying (28) with respect to $\delta\mathbf{A}$ and taking (29) into account, we get

$$j_y=\frac{ie}{2m_3}[\eta_x\eta_y^{*\prime}-\eta_x^*\eta_y'+\eta_y\eta_x^{*\prime}-\eta_y^*\eta_x']. \tag{30}$$

We consider for simplicity the case of strong anisotropy, $\beta_3 \gg \beta_1, \beta_2$. In the initial approximation η_x and η_y have equal moduli but different phases:

$$\eta_x=(\alpha/2\beta_3)^{1/2}e^{i\varphi_1}, \quad \eta_y=(\alpha/2\beta_3)^{1/2}e^{i\varphi_2}. \tag{31}$$

The small term

$$\beta_2|\eta^2|^2=\frac{\beta_2\alpha^2}{2\beta_3^{\,2}}[1+\cos 2(\varphi_1-\varphi_2)]$$

determines the phase difference outside the domain wall, with $\beta_2>0$ to ensure just the $D_4(E)$ phase far from the wall. Different orientations of the angular momentum on the right and left correspond to the conditions

$$\varphi_1-\varphi_2=\begin{cases}\pi/2, & x\to\infty\\ -\pi/2, & x\to-\infty\end{cases}. \tag{32}$$

The equations for φ_1 and φ_2 follow from variations of (28):

$$\frac{1}{2m_1'}\varphi_1''+\frac{2\beta_2\alpha}{\beta_3}\sin 2(\varphi_1-\varphi_2)=0, \tag{33}$$
$$\frac{1}{2m_1''}\varphi_2''+\frac{2\beta_2\alpha}{\beta_3}\sin 2(\varphi_2-\varphi_1)=0.$$

The condition that the current component perpendicular to the wall be zero yields

$$\varphi_1'/m_1'+\varphi_2'/m_1''=0. \tag{34}$$

With the aid of this condition we can rewrite the system (33) in the form of the standard sine-Gordon equation for the difference $u=\varphi_2-\varphi_1$:

$$\lambda^2u''+\sin 2u=0, \tag{35}$$

where $\lambda^2=\beta_3/4\beta_2\alpha(m_1'+m_1'')$.

A solution of (35) satisfying the boundary conditions (32) is

$$\sin u(x)=\operatorname{th}(\sqrt{2}x/\lambda). \tag{36}$$

Returning to Eq. (30) for the current density j_y and using (31) and (34), we obtain

$$j_y(x)=\frac{\alpha e}{2m_3\beta_3}\frac{m_1''-m_1'}{m_1''+m_1'}\cos u\, u'. \tag{37}$$

Integration of this expression with respect to x with the aid of (36) yields directly the total current in the wall:

$$i=\int_{-\infty}^{+\infty} j_y(x)\,dx=\frac{\alpha e}{m_3\beta_3}\frac{m_1''-m_1'}{m_1''+m_1'}, \tag{38}$$

which differs from zero, since there are no special conditions whatever on the relation between m_1' and m_1''. This current is small only to the extent that T_c-T is small (at $\beta_3\sim\beta_2$), and this proves the validity of the arguments advanced at the beginning of this section.

According to (38), the magnetic moment is $M_n\sim i/2c$. Comparing this with the estimate for the thermodynamic critical field $H_c^2/8\pi\sim\alpha^2/\beta$, we get

$$M_n\sim(\xi/\delta)H_c\sim(1/\varkappa)H_c\sim H_{c1}. \tag{39}$$

The moment produced at the domain wall in the region ξ is screened at a distance δ by the superconducting currents. Unlike for a ferromagnet, for a superconductor there are thus no large magnetic-energy terms that prevent the existence of large single-domain samples. The exact relation in (39) contains a complicated combination of parameters of the Ginzburg-Landau functional. In principle, M_n could exceed the lower critical field H_{c1} at which vortex formation becomes favored. The situation wherein a magnetic-moment field screened in the interior of a superconductor exists on its very surface could turn out by the same token to be unstable to vortex formation in the screening region.

7. CONCLUSION

We have considered above all the possible superconducting states into which a system can go directly from the normal metallic state in the case of nontrivial pairing. These states are determined for the most part by that symmetry-group representation which is responsible for the onset of superconducting instability at T_c in a given specific substance. This representation can be determined, as indicated in Ref. 22, by measuring the anisotropy of the upper critical field H_{c2} near T_c. The properties of the corresponding phases below T_c are described in practically the same way in both the singlet and the triplet cases, except for important differences in the types of the zeros. In triplet pairing zeros appear in the energy gap only at points on the FS, whereas in singlet pairing the geometric loci of the zeros can be whole lines on the FS. This is so far the only method that permits identification of the pairing with some degree of assurance. If, say, the heat capacity depends on temperature like T^2, triplet pairing is excluded, but a T^3 dependence is possible for both types of pairing. The experimental situation is in this respect not yet clear. According to Ref. 8, in UBe_{13} this law corresponds to a T^3 dependence, whereas the data on UPt_3 (Ref. 12) and $CeCu_2Si_2$ (Ref. 13) favor more readily singlet superconductivity, as already mentioned in Sec. 1.

An interesting distinguishing feature of the new superconductors is that they have magnetic properties. The presence of a magnetic moment, meaning hence of a magnetic field near the sample surface even in the absence of an external field, can undoubtedly be investigated by nuclear-magnetic-resonance methods.

[1)] In §20 of Ref. 1 the discussion of pairing with nonzero angular momentum is based on unpublished results obtained in 1958 by A. A. Abrikosov, L. P. Gor'kov, L. D. Landau, and I. M. Khalatnikov.

[2)] This was pointed out to us by N. Konyshev.

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