Superconducting classes generated by a single irreducible multidimensional representation

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It is shown that the Bose condensates arising as a result of nontrivial pairing in uniaxial crystals whose order parameter forms a basis for a single two-dimensional irreducible representation of the crystal class can occur in seven states with different symmetry or structure in the classes D_{4h} , D_{2d} , D_4 , C_{4v} , D_{6h} , D_6 , D_{3d} , D_{3h} , C_{3v} , and D_3 and in four different states for the classes C_{4h} , S_4 , C_4 , C_{6h} , C_6 , S_6 , and C_3 . The symmetries and the conditions of stability of all of these phases were found. The results presented suggest previously unexamined scenarios of successive phase transitions in UPt₃ and U_{1-x} -Th_xBe₁₃. For cubic symmetry classes and Bose condensates described by a four-component order parameter, all arguments concerning the number of phases and the form of the phase diagram are completely identical to the results and conclusions obtained for hexagonal symmetry classes. The minimum degree of the Landau potential that leads to typical results in the case of Bose condensates in uniaxial crystals is 12. For Bose condensates in cubic crystals, the real and imaginary parts of whose components form independent bases for three-dimensional irreducible representations of cubic crystal classes, with a six-component order parameter either 17 or 9 superconducting phases are possible, depending on the symmetry of the order parameter. It was shown that besides the four oneparameter phases present in the total list of phases initiated by a single irreducible representation of the symmetry group of the problem, there is also a fifth phase that can be obtained within the Landau theory of second-order phase transitions. The main result is a list of the ordered phases that can be reached by successive second-order transitions. It is pointed out that in external fields, a magnetoelectric effect should occur at locations of nonuniform density of the Bose condensate arising as a result of pairing in a state in which the orbital angular momentum of the pairs is not completely frozen. © 1995 American Institute of Physics.

1. INTRODUCTION

During the last ten years, superconductivity, once thought to be among the best understood and most completely studied physical phenomena, has become a vigorous field of physics, full of puzzles and questions. One of the most puzzling and, at the same time, experimentally quite well-studied phenomena is the superconductivity of heavyfermion compounds. Most unexpected was the fact that several different types of superconducting phases have been found among the heavy-fermion compounds. The first member of this series was the compound CeCu₂Si₂ (1979) with the spinel structure,¹ tetragonally distorted by small displacements of the ions; the next member is UBe_{13} (1983) with a special type of cubic structure;^{2,3} and, finally, there is the hexagonal compound UPt₃ (1984) (Ref. 4).¹⁾ The existence of several superconducting phases with different physical characteristics is a direct demonstration of the fact that pairing of charge carriers occurs in a state with nonzero pair angular momentum in these compounds. How is the angular momentum of pairs frozen by the crystal field? Which superconducting states are possible and which succession of phase changes should be observed? The microscopic theory cannot answer these and similar questions.⁷ The first answer to the question of the symmetry and structure of superconducting phases with nontrivial pairing, which can arise as a result of a second-order transition from the normal state for all three

crystals listed above, was given by Volovik and Gor'kov,^{8,9} Ueda and Rice,¹⁰ and Blount.¹¹ The most complete work was Ref. 9, which is based on Landau's theory of second-order transitions,¹² supplemented by the assumption that the spinorbit interaction between the spin and the orbital angular momentum of pairs is strong. The latter assumption is not obvious, even for heavy-fermion compounds, and has been questioned.¹³ However, the results obtained in Ref. 9 can be regarded as symmetry-exact, since the spin-orbit interaction, though weak, is always present. For this reason, it is the results of Ref. 9 that give a precise answer to the question of the choice of structure of the superconducting states which arise directly at the temperature of the second-order transition from the normal state. However, Landau's theory of second-order phase transitions cannot determine which superconducting phases will replace the phases which arose from the normal state.

Our objective in the present paper is to determine the superconducting phases with nontrivial pairing, in the presence of strong spin-orbit interaction between the angular momentum and spin of a pair, that can materialize in a cubic crystal, as well as the sequence in which these phases can appear with successive phase transitions. We underscore the fact that in the present paper we adopt the additional (with respect to Ref. 9) hypothesis that the representations according to which the order parameters transform do not change with successive phase transitions.

The question posed in the present paper is answered on the basis of a phenomenological theory based on the following results, which were obtained in Refs. 14-16.

First, the structures of all low-symmetry phases, which can be described by order parameters referred to a given representation, can be found exactly, if it is assumed that the nonequilibrium potential of the phenomenological theory (Landau potential) is an entire function of the most general form, possibly transcendental,¹⁷ and the degree of the approximating polynomial is limited to a definite value. Moreover, as shown in specific examples,^{16,18,19} an unjustified truncation of the expansion of the approximating polynomial can result in serious errors in the results obtained by the theory. We emphasize that the problem of enumerating all phases belonging to a given representation is solved uniquely and geometrically exactly, on the basis of the given method.¹⁴

Second, there exists a general method for bounding the degree of the polynomial (not less than twelfth in the examples considered) approximating the true Landau potential, so as to take into account all symmetry related features of the phase diagram.^{14,16}

Third, there also exists a geometrically exact and unique method for constructing the phase diagram in the space of the variable coefficients of the approximating Landau polynomial (in deformation space²⁰) according to the form of the subspaces occupied by solutions of the equations of state in the orbit space.²¹

Only the choice of the thermodynamic path, defined as the motion of a point representing a given crystal in the phase diagram in deformation space, contributes a small uncertainty in the questions addressed in this paper for comparing with experiment. This thermodynamic path is largely determined by the microscopic characteristics of a specific crystal.

To make the exposition of the results obtained in this work clearer, the proofs of the assertions listed will be briefly reproduced in the first simple example analyzed in Sec. 2.

Before presenting the main content of this paper, we wish to make an important remark. If the complex superconducting order parameter is, with respect to its transformation properties, a basis function for a one-dimensional representation of the group of the crystal class, then all results obtained by Volovik and Gor'kov will also be true in the approach developed below. For this reason, in the present paper, where only phase transitions into the superconducting states described by a single irreducible representation of the symmetry group Y of the problem are considered, the results of Ref. 9 for the case of the complex one-dimensional irreducible representations Y will not be discussed. However, the method described below must also be used to describe the succession of phases resulting from the existence of two order parameters (for example, this scenario is often suggested for the succession of superconducting phases in U_{1-r} Th_rBe₁₃), and this will substantially alter the results of Refs. 7 and 22, which are based on Refs. 8 and 9.

In accordance with what we have said above, our exposition is organized as follows. In Sec. 2 a relatively detailed discussion is given of the simplest of the two possible variants of a phase transition into the superconducting state with nontrivial pairing in a cubic crystal of class O_h , for which the components of the order parameter form a basis for the two-dimensional irreducible representation E_g of the group O_h . In the last subsection of Sec. 2 the symmetry classification of superconducting phases is presented for nontrivial pairing in all other cubic classes, if the order parameter forms a basis for the two-dimensional representation of the symmetry group of the crystal class G_c . In Sec. 3 the possible superconducting phases in cubic crystals, if the components of the order parameter form a basis for the threedimensional representation G_c , are discussed. A brief exposition of the results for similar calculations for hexagonal systems is given in Sec. 4. The structures of the superconducting phases for crystals of the tetragonal system are discussed in Sec. 5. The last section (Sec. 6) contains a brief discussion of a new magnetoelectric effect, which should be observed at sites where the distribution of the order parameter is nonuniform, for example, within domain walls between different domains of the Bose condensate of a given structure.

As shown in Refs. 8 and 9, the type and number of zeros in the superconducting gap in each phase can be determined according to the symmetry of the phases that is presented in the present paper. This question is not discussed below. It merits a separate study, especially in connection with Refs. 23 and 24.

2. STRUCTURE OF SUPERCONDUCTING PHASES OF A CUBIC CRYSTAL IN A TWO-COMPONENT COMPLEX ORDER PARAMETER

2.1. From the phenomenological standpoint, the order parameter in the case of nontrivial pairing consists of a collection of complex coefficients $\{\eta_p\}$ in the expansion of the fluctuation amplitude of the probability distribution of pairs over basis functions of the irreducible representations of the symmetry group of the problem:⁷⁻¹¹

$$Y(G_c) = G_c R U_1(\alpha), \tag{1}$$

where G_c is the symmetry group of the crystal class, R is the group determined by the time reversal operation R, and $U_1(\alpha)$ is the gauge group of electrodynamics.

As is usually done in Landau's theory, we shall assume below that it is not the basis functions but rather the components of the order parameter that transform under operations from Y. We note that it is convenient to classify the representations of Y, which are constructed on $\{\eta_i, \eta_i^*\}$, according to the representations of G_c , since the imaginary and real parts of $\{\eta, \eta^*\}$ form a basis for the same representation of G_c . It is in the sense of this characteristic that we shall employ below two equivalent terms: the 2m-component order parameter, and the *m*-component complex order parameter. The operation *R* in the space ε_m of the components of the order parameter is complex conjugation, and the operation $U_1(\alpha)$ is rotation by the same angle α in all subspaces $\{\eta'_i, \eta''_i\}$, where $\eta_i = \eta'_i + i\eta''_i$.

We now consider an example of the calculation of the structure of the superconducting phases. In this example $G_c = O_h$, and the four-component order parameter forms a

basis for the two-dimensional representation of the group O_h . Let this be the representation E_g ,²⁵ for which we define the unit vectors η_+ and η_-

$$\sqrt{2} \eta_{+} = e_{1} + ie_{2}, \quad \sqrt{2} \eta_{+}^{*} = e_{1}^{*} - ie_{2}^{*},$$

$$\sqrt{2} \eta_{-} = e_{1} - ie_{2}, \quad \sqrt{2} \eta_{-}^{*} = e_{1}^{*} + ie_{2}^{*},$$

$$e_{1} \sim 2k_{z}^{2} - k_{x}^{2} - k_{y}^{2}, \quad e_{2} \sim \sqrt{3}(k_{x}^{2} - k_{y}^{2}),$$

$$(2)$$

so that the expanded order-parameter vector can be written as a vector with the components

$$\{\eta_1 + i\eta_2; \eta_1 - i\eta_2; \eta_1^* + i\eta_2^*; \eta_1^* - i\eta_2^*\}.$$
 (2a)

1

where $\varepsilon = \exp(2\pi i/3)$ and α is a parameter of the continuous²⁵ group $D_1(\infty)$. The diagonal matrices in Eq. (4) are represented as columns. The order parameter inserted on the left in the form of a ket indicates the order of the basis components that determines the specific form of the matrices for subsequent calculations. Examples of the elements of $Y(O_h)$ which correspond to the $U_1(\infty)$ matrices presented in Eq. (4) as generators are indicated in the top row of Eq. (4).

An entire rational basis of invariants (ERBI), consisting of the components of the order parameter, can be easily determined from the form of $L(O_h, E_g)$.¹⁶ In the phenomenological theory the significance of the basis lies in the fact that regardless of the form of the nonequilibrium Landau potential, if the potential is approximated by polynomials, then no matter what the degree of the approximating polynomial, it can always be written as an entire rational function (i.e., a polynomial) using the polynomials in the ERBI. For $L(O_h, E_g)$ the ERBI contains three functions:

$$I_{1} = |\eta_{+}|^{2} + |\eta_{-}|^{2}, \quad I_{2} = |\eta_{+}|^{2} |\eta_{-}|^{2},$$

$$I_{3} = \eta_{+}^{3} \eta_{-}^{*3} + \eta_{+}^{*3} \eta_{-}^{*3}.$$
(5)

Therefore, we can write by definition

$$\Phi(\eta_+,\eta_-,\eta_-^*,\eta_+^*) = F(I_1,I_2,I_3), \tag{6}$$

where F is an approximating polynomial of arbitrarily high degree, possibly an infinite series. In accordance with the results of Refs. 14–16, the Landau potential of minimum degree, describing all structures which a given order parameter can induce, must be of degree 12 in the components of the order parameter. According to Eq. (6), the equations of state that determine the structure of the Bose condensate of the superconducting phases assume the form

The kernel of the homomorphism of this representation (|K) includes only elements of the space group. In accordance with the notation used in Ref. 25, the set of generators of |K can be written in the form

$$|K(O_h, E_g) = \{C_2^z, U_2^x, I\} = |K(O, E)\{I\} \equiv D_{2h}.$$
(3)

The group $L(O_h, E_g) = D_1(\infty)$ (group of all matrices of different form of the corresponding four-dimensional representation of Y)¹⁴⁻¹⁶ is determined by the generators of R, $U(\alpha)$, and G_c :

$$\begin{array}{c} U_{1}(\alpha) \\ \exp i\alpha \\ \exp i\alpha \\ \exp(-i\alpha) \\ \exp(-i\alpha) \end{array} \right|,$$
(4)

$$\frac{\partial \Phi}{\partial \eta_{+}} = \eta_{+}^{*}F_{,1} + \eta_{+}^{*}|\eta_{-}|^{2}F_{,2} + 3\eta_{+}^{2}\eta_{-}^{*3}F_{,3} = 0,$$

$$\frac{\partial \Phi}{\partial \eta} = \eta_{-}^{*}F_{,1} + \eta_{-}^{*}|\eta_{+}|^{2}F_{,2} + 3\eta_{+}^{*3}\eta_{-}^{2}F_{,3} = 0,$$

+ c.c. (7)

To simplify the expressions, the two additional equations of state which are complex conjugates of the equations written out (and designated by + c.c.) are not presented in Eq. (7). The notation $F_{,i}$ represents a derivative of the function F with respect to the *i*th argument. The equations (7) can be regarded as linear equations in $F_{,1}$, $F_{,2}$, and $F_{,3}$.¹⁴ All solutions of these equations that have differing symmetry correspond to a decrease in rank of the 3×4 matrix $M(O_h, E_g)$ consisting of the coefficients of this system of equations (7), which are linear in the F_i .¹⁶ The conditions under which the rank of $M(O_h, E_g)$ decreases, according to Eq. (7), have the form

$$\eta_{+}^{*}(|\eta_{+}|^{2} - |\eta_{-}|^{2})(\eta_{+}^{*3}\eta_{-}^{3} - \eta_{+}^{3}\eta_{-}^{*3}) = 0,$$

$$\eta_{-}^{*}(|\eta_{+}|^{2} - |\eta_{-}|^{2})(\eta_{+}^{*3}\eta_{-}^{3} - \eta_{+}^{3}\eta_{-}^{*3}) = 0,$$

+ c.c. (8)

The system of four equations (8) has seven solutions with different structure and symmetry and, correspondingly, different properties:

1. $\eta_{-}=0$, $I_{1}>0$, $I_{2}=I_{3}=0$, 2. $\xi_{+}=\xi_{-}$, $\cos 3(\Omega_{+}-\Omega_{-})=1$, $4I_{2}=I_{1}^{2}$, $4I_{3}=I_{1}^{3}$, $I_{1}>0$, 3. $\xi_{+}=\xi_{-}$, $\cos 3(\Omega_{+}-\Omega_{-})=-1$,

$$4I_{2} = I_{1}^{2}, \quad 4I_{3} = -I_{1}^{3}, \quad I_{1} > 0,$$

$$4. \quad \xi_{+} = \xi_{-}, \quad 4I_{2} = I_{1}^{2}, \quad I_{3}^{2} < 4I_{2}^{3}, \quad I_{1} > 0,$$

$$5. \quad \cos 3(\Omega_{+} - \Omega_{-}) = 1, \quad I_{3}^{2} = 4I_{2}^{3},$$

$$4I_{2} < I_{1}^{2}, \quad I_{3} > 0, \quad I_{1} > 0,$$

$$6. \quad \cos 3(\Omega_{+} - \Omega_{-}) = -1, \quad I_{3}^{2} = 4I_{2}^{3},$$

$$4I_{2} < I_{1}^{2}, \quad I_{3} < 0, \quad I_{1} > 0.$$
(9)

Here, $\eta_j \equiv |\eta_j| \exp i\Omega_j$, $\eta_+ \equiv \xi_+ \exp i\Omega_+$, and so on. The seventh phase occupies a volume in the three-dimensional space of invariants (5) [in the orbit space Σ_3 of the group $L(O_h, E_g)$] that is bounded by the surfaces 4-6 from Eq. (9) and their lines of intersection 1-3 from Eq. (9). We note that the phases 1-3 were discussed in Refs. 8 and 9, since a second-order transition is possible in them directly from the normal state. To obtain a clear picture of the subsequent calculations, Fig. 1 displays the region of orbit space that is stratified in accordance with the loci of the superconducting phases.

2.2. The structures of the superconducting phases written out in Eq. (9) differ qualitatively with respect to symmetry or structure and, accordingly, with respect to the material tensors constructed from the components of the order parameter. The symmetry of the phases $H_i(O_h, E_g)$ is determined by the product of two groups, $|K(O_h, E_g)$ and $H_i[D_1(\infty)]$, each of which is determined by its own set of generators (following the notation of Ref. 25):

1.
$$H_1(O_h, E_g) = |K(O_h, E_g) \{ U_2(2\pi/3)C_3^{(111)}, U_1(-2\Omega_1)C_4^1R \} \equiv O(D_2),$$

2. $H_2(O_h, E_g) = |K(O_h, E_g) \{ C_4^1, U_1(-2\Omega_+)R \} = D_4 R,$
3. $H_3(O_h, E_g) = |K(O_h, E_g) \{ U_1(\pi)C_4^1, M_1 \} = 0$

$$U_1(\pi - 2\Omega_+)R \} \equiv D_1^{(1)}(D_2)R,$$

4.
$$H_4(O_h, E_g) = |K(O_h, E_g)\{U_1(-\Omega_+ - \Omega_-)R\},$$
 (10)

5.
$$H_5(O_h, E_g) = |K(O_h, E_g) \{ U_1(-2\Omega_+)C_4^1R \},\$$

6.
$$H_6(O_h, E_g) = |K(O_h, E_g) \{ U_1(-2\Omega_+)C_4^1R \},\$$

7.
$$H_7(O_h, E_g) = |K(O_h, E_g)\{E\}$$

As we can see, the spatial symmetry of the Bose condensate is the same in phases 2 and 3, and the total symmetry of phases 5 and 6 is also the same. We shall show that phases 5 and 6 have a qualitatively different structure: They are anti-isostructural.^{16,29} Phases 2 and 3 are also antiisostructural. The fact that phases 2 and 3 are qualitatively distinguishable and lie in different regions of the phase diagram in the space of coefficients of the Landau potential can be easily seen from the results obtained by Volovik and Gor'kov,⁹ who showed that in the first three phases in (9) and (10), a second-order phase transition can occur directly from the high-symmetry normal phase. In addition, a transition into phases 2 and 3 is possible only under incompatible con-



FIG. 1. Loci representing different phases in the orbit space Σ_3 for the group $D_1(\infty)$ (a) and the group $D_3(\infty)$ (b).

ditions imposed on the coefficients of the Landau potential. For phases 5 and 6 (of course, just as for phases 2 and 3), this follows from the fact that they lie in different subspaces of the orbit space (Fig. 1). The fact that the physical properties of these phases are different can be seen, for example, from the form of the physical tensors, which are proportional to the square of the components of the order parameter. If the true scalar—the density of the Bose-condensate pairs

$$\rho = |\eta_{+}|^{2} + |\eta_{-}|^{2} = I_{1} = |e_{1}|^{2} + |e_{2}|^{2}$$
(11)

is ignored, the other components of the physical tensors, which are bilinear in the components of the order parameter, are a component proportional to the "antiferromagnetic" vector of the Bose condensate⁹

$$Z = |\eta_{+}|^{2} - |\eta_{-}|^{2} = \pm \sqrt{I_{1}^{2} - 4I_{2}} = 2i(e_{2}e_{1}^{*} - e_{1}e_{2}^{*}) \quad (12)$$

and the two components of the symmetric irreducible tensor of rank 2

$$A = \eta_{+} \eta_{-}^{*} + \eta_{-} \eta_{+}^{*} = 2(|e_{1}|^{2} - |e_{2}|^{2}),$$

$$iB = \eta_{+} \eta_{-}^{*} - \eta_{-} \eta_{+}^{*} = 2i(e_{1}e_{2}^{*} - e_{2}e_{1}^{*}).$$
(13)

As we can see from Eq. (9), the antiferromagnetic moment characterizes the Bose condensate in phases I, 5, 6, and 7, in complete agreement with the symmetry of the phases (10). The components A and B of the rank-2 tensor are manifested, for example, in the interaction of the Bose condensate with the elastic subsystem of the crystal. To describe the interaction of the Bose condensate with the elastic subsystem of the crystal, taking into account the fact that these interactions are small, it is sufficient to supplement the potential (6) with two terms. The first is the nonequilibrium energy of elastic deformations

$$\Delta \Phi_e = (1/2)(C_{11} - C_{12})(E_1^2 - E_2^2) + (1/2)(C_{11} + 2C_{12})$$
$$\times (\Delta V)^2 + C_{44}(U_{xy}^2 + U_{yz}^2 + U_{xz}^2), \qquad (14)$$

where C_{ik} are the elastic moduli in Voigt's notation,²⁶ U_{ik} are the components of the deformation tensor, and $\sqrt{6}E_1 \equiv (2U_{zz} - U_{xx} - U_{yy}), \quad \sqrt{2}E_2 \equiv U_{xx} - U_{yy}, \text{ and}$ $\sqrt{3}\Delta V \equiv U_{xx} + U_{yy} + U_{zz}.$

The second term in $\Delta \Phi$ is the part of the nonequilibrium potential that determines the interaction of the order parameter characterizing the Bose condensate and the elastic subsystem:

$$\Delta \Phi_{es} = E_1 [\alpha_1 A + \alpha_2 (A^2 - B^2)] + E_2 [\alpha_1 B - 2\alpha_2 A B].$$
(15)

The components of the total Landau potential (14) and (15) are written in a form that is convenient for describing the Bose-condensate domain of phases 2, 3, 5, and 6, where $\sin(\Omega_+ - \Omega_-) = 0$. The spontaneous deformation responsible for the difference of the parameters of the unit cell along the x and y axes in phases 2, 3, 5, and 6, whose tetragonal spatial symmetry is determined by the Bose condensate, equals zero:

$$E_2 \sim U_{xx} - U_{yy} = 0,$$

since B=0. The spontaneous deformation of the cell along the z axis is either greater or less than the spontaneous deformation of the cell along the x axis, depending on the sign of $\cos(\Omega_+ - \Omega_-) = \pm 1$ and the sign of the interaction between the elastic subsystem and the Bose condensate:

$$E_{1} = (C_{11} - C_{12})^{-1} \xi_{+} \xi_{-} \cos(\Omega_{+} - \Omega_{-}) \\ \times [\alpha_{1} + \alpha_{2} \xi_{+} \xi_{-} \cos(\Omega_{+} - \Omega_{-})].$$
(16)

Therefore, the phases 5 and 6 are, by definition,¹⁶ antiisostructural. Indeed, if for example $\alpha_1 - \alpha_2 \xi_+ \xi_- > 0$, then (c - a) is positive in phases 2 and 5 and negative in phases 3 and 6.

2.3. The region of the coefficient space of the Landau potential where some phase is stable are determined by the positive-definiteness of the 4×4 matrix of second derivatives $\partial^2 \Phi / \partial \eta_i \partial \eta_k$ and the relative magnitude of the minima of Φ

that correspond to that phase. As we have already mentioned, the minimal Landau potential possessing all symmetry properties must be of twelfth degree in the components of the order parameter. In the general case such a potential corresponds to a modal catastrophe,^{27,28} corresponding to four modal parameters and 14 deformation parameters.²⁸ If, however, only the simplest structure-sensitive potential that possesses all symmetry properties of the phase diagram is of interest, then it is sufficient to study a primitive potential^{21,29,30} of the form

$$F = a_1 I_1 + b_1 I_2 + c_1 I_3 + a_2 I_1^2 + b_2 I_2^2 + c_2 I_3^2.$$
(17)

Of all conceivable potentials of degree 12, the potential (17) leads to the simplest phase diagram in the three-dimensional space of deformations $A_3(a_1,b_1,c_1)$. The simplicity lies in the fact that if a second-order phase transition between any two phases is not symmetry-forbidden, then according to Eq. (17) the lines of stability which bound these phases will always coincide. Therefore, the theory based on Eq. (17) will lead to a phase diagram with the maximum number of second-order transition boundaries between the phases (9). On the other hand, the potential (17) can be formally replaced by an arbitrary potential of degree 12 by making a nonlinear substitution of the maximum number of deformation parameters for (a_1, b_1, c_1) and the seven maximum possible independent coefficients of an arbitrary potential of degree 12 for (a_2, b_2, c_2) . In accordance with Landau's basic idea, such a nonlinear substitution is completely analogous to a nonlinear multiparameter substitution of 21 invariants of the form $(I_1, I_1^2, I_2, I_1I_3, I_2I_3, I_2^2, \dots, I_1^3I_3)$ for $\{I_1, I_2, I_3\}$. Such a substitution corresponds in orbit space to a continuous nonlinear deformation of the surfaces and, correspondingly, the lines displayed in Fig. 1. Therefore, on the one hand, having obtained a phase diagram in the space a_1, b_1 , and c_1 of the potential (17), a three-dimensional section of the twelve-dimensional phase diagram of the most general form can be represented by an imaginary deformation of the phase boundaries. On the other hand, a number of general assertions, based on the following two general relations from Ref. 14, have been proved²¹ for a potential of the form (17):

A.
$$d\Phi = (d\Phi/dx_r)dx_r = (d\Phi/dI_p)(dI_p/dx_r)dx_r$$

= $(d\Phi/dI_p)dI_p$. (18)

Here $\{x_r\} = \{\eta_r, \eta_r^*\}$, and summation over repeated indices is implied. Therefore, in the orbit space Σ_3 the vector **dI** with components $\{dI_p\}$ tangent to the stratum occupied by the phase is perpendicular to $\partial \Phi / \partial I_p$. For Eq. (17) this means that

$$a_{1} = + \Sigma \lambda_{i} n_{i} - 2a_{2}I_{1}, \quad b_{1} = + \Sigma \lambda_{i} n_{i} - 2b_{2}I_{2};$$

$$C_{1} = + \Sigma \lambda_{i} n_{i} - 2C_{2}I_{3}, \quad (19)$$

where λ_i are arbitrary coefficients of the unit vectors n_i from the subspace of the normals to **dI**.

B.
$$d^2 \Phi = F_{,pr} dI_p dI_r + F_{,p} d^2 I_p$$

= $(F_{,pr} dI_r) dI_p + \lambda_i n_i d^2 I_p$. (20)







FIG. 2. Phase diagram in the space (a_1,b_1,c_1) , corresponding to the potential (17) and the set of invariants (5) (a) and (36) (b). c) Cross section of the diagram in b) in the (a_1,b_1) plane in the half space $c_1>0$.

The solutions (18) which correspond to positive-definiteness of $d^2\Phi$ exist in the region defined parametrically by Eq. (19) as a function of the surface that is a map of the stratum of the phase A_3 in Fig. 1 onto the normals to this surface, which are parameterized by the image points of the stratum.^{21,29,30} A real solution of the equations of state exists right up to the branch surface of this solution—the envelope of the family of normals.²¹ With these rules we obtain Fig. 2 from Fig. 1—the form of the phase diagram in the space (a_1,b_1,c_1) . Figure 2 displays only the phase stability boundaries. In the figures the phase numbers are circled and correspond to the notations for a—Eqs. (9) and (10) and b and c—Eq. (38). In all figures the lines *OL* are the lines of four-phase points of second-order transitions, which are a specific characteristic of the phase diagrams induced by multicomponent order parameters, and the lines PR are the lines of the critical points at which a second-order transition is succeeded by a firstorder transition; the lines OT are the lines of three-phase points which become Gibbs points of equilibrium of three phases in the more complete theory; the lines KM and KNare the lines of critical tangency of the stability boundaries of phases 5 and 6 from Eqs. (9) and (10). In b, N is the normal to the phase and in a the boundary with the normal phase in the plane $a_1=0$ is not drawn. It is evident from Fig. 2 that the anti-isostructural phases 5 and 6 do indeed lie in different regions of the phase diagram. Moreover, when the nonlinear interactions which distort (Fig. 2) the phase diagram are sufficiently weak, the transition between phases 2 and 3, and between phases 5 and 6, always proceeds through an intermediate phase. 2.4. After such a detailed discussion of the structure of the phases corresponding to $Y(O_h)$ and $L(O_h, E_g)$, we now briefly discuss other possible variants of the structure of Bose condensates in which the symmetry of the order parameter is determined by the two-dimensional irreducible representations of cubic groups. For $Y(O_h)$ there is another possibility: the components of the order parameter form a basis for E_u . The kernel of the homomorphism

$$|K(O_h, E_u) = |K(O, E) \{ U_1(\pi) I \}$$

but by definition $L(O_h, E_u) = L(O_h, E_g)$. Therefore, the ERBI, the number of phases, and the form of the phase diagram, which are determined only by the group $L(O_h, E_u) = D_1(\infty)$, for the case of the components of the order parameter which form a basis for E_u , are identical to the number of phases, the form of the phase diagram, and the number and form of the polynomials in ERBI for the example of E_g already analyzed above. The symmetry of each of the seven ordered phases can be written in the form (10) with $|K(O_h, E_g)$ replaced by $|K(O_h, E_u)$.

Similar replacements must be made when studying phases of a Bose condensate which are induced by the twodimensional representation of class O. The only additional point is that |K(O,E)| consists of four and not eight elements:

$$|K(O,E) = \{C_2^z, U_2^x\} \equiv D_2.$$

Calculations are also not required to investigate phases induced by the two-dimensional representation T_d , since $L(T_d, E) = L(O_h, E_g)$. In the group $L(T_d, E)$ (4), however, the second matrix corresponds to the element S_4^1 of the space group. Correspondingly, to determine the structure of the Bose condensates (10), the operations C_4^1 , $U_1(\pi)C_4^1$, C_4^1R , and so on must be replaced everywhere by S_4^1 , $U_1(\pi)S_4^1$, and S_4^1R .

For the groups T_h and T, which have two and one twodimensional physically irreducible representations, respectively, the groups L are identical for all three representations:

$$L(T_h, E_g) = L(T_h, E_u) = L(T, E) \equiv D_2(\infty) \subset D_1(\infty)$$

The group $D_2(\infty)$ is determined by the set of generators L_1 without the one parameter represented by the second matrix in Eq. (4) and corresponding to the C_4^1 operation in O_h . It follows from this that the ERBI for $D_2(\infty)$ contains four polynomials. Besides the three polynomials (5), $D_2(\infty)$ appears in ERBI in the form of the polynomial

$$I_4 = i(\eta_+^3 \eta_-^{*3} - \eta_+^{*3} \eta_-^3) = 2\xi_+^3 \xi_-^3 \sin 3\varphi.$$
 (21)

As a result, three phases of the Bose condensate, which have different symmetry and structure and are determined by the two-dimensional representation E_g in the crystal class T_h , are possible. All of these phases lie on the cone $I_3^2 + I_4^2 = 4I_2^3$ in the four-dimensional orbit space Σ_4 :

1.
$$\xi_{-}=0$$
, $I_{1}>0$, $I_{2}=I_{3}=I_{4}=0$,
 $H_{1}(T_{h}E_{g}) = |K(T_{h}, E_{g})\{U_{1}(2\pi/3)C_{3}^{(111)}\},$
2. $\xi_{+}=\xi_{-}$, $I_{1}^{2}=4I_{2}$, $I_{1}>0$,
 $I_{3}^{2}+I_{4}^{2}=4I_{2}^{3},$
 $H_{2}(T_{h}, E_{g}) = |K(T_{h}, E_{g})\{U_{1}(\Omega_{+}+\Omega_{-})R\},$
3. $I_{3}^{2}+I_{4}^{2}=4I_{2}^{3}, H_{3}=|K(T_{h}, E_{g}).$ (22)

Here

 $|K(T_h, E_u) = \{U_2^x, C_2^z, I\} \equiv D_{2h}.$ For $E_u(T_h)$

$$|K(T_h, E_u) = \{U_2^x, C_2^z, U_1(\pi)I\}$$

and for the class T

$$|K(T,E) = \{C_2^z, U_2^x\}.$$

Otherwise, the relations (22) remain in force for the condensate phases determined by $E_u(T_h)$ and E(T).

3. STRUCTURE AND SYMMETRY OF BOSE CONDENSATES IN SUPERCONDUCTING PHASES OF CUBIC CRYSTALS WITH A THREE-COMPONENT COMPLEX ORDER PARAMETER

3.1. The symmetry of the order parameter of a Bose condensate, whose components form a basis for threedimensional irreducible representations of the crystal classes O_h , O, and T_d , is described by the same group $L = E_1(\infty)$.¹⁶ The elements of the point group $E_1(\infty)$ are 6×6 matrices describing the transformation of a vector with components $\{\eta_1, \eta_2, \eta_3, \eta_1^*, \eta_2^*, \eta_3^*\}$ in the six-dimensional space ε_6 . All matrices $E_1(\infty)$, just like the matrices $D_1(\infty)$, have either block-diagonal or block-antidiagonal structure. The maximum dimensions of the blocks are 3×3 , and the top block is always the complex conjugate of the bottom block. We shall exploit this to simplify the notation. We write the generators of $E_1(\infty)$, which are diagonal matrices, just as in the case of $D_1(\infty)$, in the form of columns, each element of which is a diagonal element of a matrix $l_i \in E_1(\infty)$. The block-diagonal or antidiagonal matrices will be written in the form of 3×3 matrices, lying in the top half of a 6×6 matrix. We shall distinguish the block-diagonal matrices from the blockantidiagonal matrices by a symbol placed to the right or left at the bottom of the matrix: \Box for diagonal or \bot for antidiagonal matrices. Thus, any element $l_i \in E_1(\infty)$ can be represented as a product of the following six matrices [generators of $E_1(\infty)$]:



The first column in Eq. (23) determines the order of the basis functions which is chosen to write the matrix l_i . It is written in the form of a "half-ket." The same elements of the enumerated crystal classes $U_2^{(100)}$, $C_2^{(001)}$, and $C_3^{1(111)}$ correspond to matrices 2-4 in all four three-dimensional representations of $O_h(F_{1g}, F_{2g}, F_{1u}, F_{2u})$ as well as in the two threedimensional representations of $O(F_1, F_2)$ and two threedimensional representations of $T_d(F_1, F_2)$. Matrix 5 corresponds to time reversal R. Matrix 6 corresponds in $L(O_h, F_{2g}), L(O_h, F_{2u})$, and $L(O, F_2)$ to an element of the crystal class $C_2^{(110)}$ and in $L(O_h, F_{1g}), L(O_h, F_{1u})$, and $L(O, F_1)$ to the element $U_1(\pi)C_2^{(110)}$. To determine the structure of the ordered phases of the Bose condensate, it must also be kept in mind that the kernel of the homomorphism |K of the representation of the group $Y(O_h)$ with respect to $E_1(\infty)$ for $L(O_h, F_{2g})$ and $L(O_h, F_{1g})$ consists of two elements: the identity element (E) and space inversion $\{E,I\}$, and for $L(O_h,F_{2u})$ and $L(O_h,F_{1u})$ the kernel $|K = \{E, U_1(\pi)I\}$. For Y(O) the representations of $L(O, F_1)$ and $L(O, F_2)$ are exact: $|K(O, F_i) = \{E\}$.

For the crystal class T_d , the groups $L(T_d, F_1)$ and $L(T_d, F_2)$ are also exact representations of $Y(T_d)$. In the case of $L(T_d, F_1)$ the element $\sigma^{(110)} \in Y(T_d)$ corresponds to the sixth matrix of Eq. (26), and for $L(T_d, F_2)$ we have $U_1(\pi)\sigma^{(110)} \in Y(T_d)$.

For the crystal classes T_h and T the group $L = E_2(\infty)$, which describes the transformation properties of Bose condensates with nontrivial pairing, is determined only by the first five matrices from the set (23). They also correspond to the same elements, which are enumerated above for the classes O_h , O, and T_d . The kernel of the homomorphism $|K(T_h, F_g) = \{E, I\}$, and $|K(T_h, F_u) = \{E, U_1(\pi)I\}$. For Y(T), $E_2(\infty)$ is an exact representation.

According to Eq. (23) we find, in accordance with Ref. 16, that the entire rational basis of invariants that corresponds to Eq. (23) consists of eight functions, among which one is of sixteenth degree in the components of the order parameter. Therefore, the Landau potential that describes the problem of the symmetry and structure of the ordered phases of Bose condensates with nontrivial pairing has the following form in the case of an order parameter with three complex components:

$$\Phi(\eta_1, \eta_2, \eta_3, \eta_1^*, \eta_2^*, \eta_3^*) = F(I_1, I_2, \dots, I_8).$$
(24)

Here

$$\begin{split} &I_1 = \xi_1^2 + \xi_2^2 + \xi_3^2, \quad I_2 = \xi_1^2 \xi_2^2 + \xi_2^2 \xi_3^2 + \xi_3^2 \xi_1^2, \quad I_3 = \xi_1^2 \xi_2^2 \xi_3^2, \\ &I_4 = 2 \{ \xi_1^2 \xi_2^2 \cos 2(\Omega_1 - \Omega_2) + \xi_2^2 \xi_3^2 \cos 2(\Omega_2 - \Omega_3) \\ &+ \xi_3^2 \xi_1^2 \cos 2(\Omega_3 - \Omega_1) \}, \end{split}$$

$$I_{5} = 2\xi_{1}^{2}\xi_{2}^{2}\xi_{3}^{2}\{\xi_{3}^{2}\cos 2(\Omega_{1} - \Omega_{2}) + \xi_{1}^{2}\cos 2(\Omega_{2} - \Omega_{3}) + \xi_{2}^{2}\cos 2(\Omega_{3} - \Omega_{1})\},\$$

$$I_6 = i_1^2, \quad I_7 = i_1 i_2, \quad I_8 = i_2^2,$$

where

$$\begin{split} i_1 &= 2\{\xi_1^2\xi_3^2\sin 2(\Omega_1 - \Omega_3) + \xi_2^2\xi_1^2\sin 2(\Omega_2 - \Omega_1) \\ &+ \xi_3^2\xi_2^2\sin 2(\Omega_3 - \Omega_2)\}, \\ i_2 &= 2\xi_1^2\xi_2^2\xi_3^2\{\xi_1^2\sin 2(\Omega_2 - \Omega_3) + \xi_2^2\sin 2(\Omega_3 - \Omega_1)\} \end{split}$$

$$+\xi_3^2 \sin 2(\Omega_1 - \Omega_2)$$
.

All of these polynomials of the components $\{\eta_1, \eta_2, \eta_3, \eta_1^*, \eta_2^*, \eta_3^*\}$ are linearly independent. It is also obvious that two syzygys can be established between the invariants (24). They are quite complicated, and we do not need them in the present investigation.

In Eq. (24), just as in Eq. (9), $\eta_j = \xi_j \exp i\Omega_j$. We note that one invariant is quadratic in the components of the order parameter, two are quartic (they also occur in Ref. 9), one is of sixth degree, two are of eighth degree, and there are two each of twelfth and sixteenth degrees. Therefore, if the expansion of the Landau potential in the components of the order parameter were used and the potential were required to describe all possible states with a given order parameter, it would be necessary to work with a potential with a minimum degree of 32. For this reason, the methods developed in Refs. 14-16 must be used to solve the equations of state, and the mathematical apparatus proposed in Ref. 14 is completely adequate for the problem.

Repeating calculations similar to those in Sec. 2.2, we find that in the case $L = E_1(\infty)$, seventeen ordered phases of different symmetry are possible.

3.2. To obtain the form of the solutions of the equations of state, all 48 6×6 matrices of different form, which depend on one continuous parameter α (the rotation angle in the subspace $\{\eta'_i, \eta''_i\}$, which corresponds to the gauge transformations of electrodynamics), were written out following the geometric method of Refs. 14-16. Next, the different values of $\alpha = \alpha_n$, for which the matrix $l_i(\alpha_n)$ has a form such that the action of the matrix on the space ε_6 of the components of the order parameter leaves a subspace invariant, were determined for each of the 48 matrices parameterized by α , $l_i(\alpha)$, and $E(\infty)$. Then, all different invariant subspaces of the space ε_6 of the components of the order parameter and all of their possible intersections, which, according to Refs. 14-16, also correspond to their own phases (higher symmetry) were determined. Then, the subspaces in the orbit space Σ_{∞} that correspond to these subspaces in ε_6 were calculated. As is well known¹⁴⁻¹⁶ and illustrated above for the example of a twocomponent order parameter, to each subspace of orbits identified in this manner, there corresponds a unique phase described by the order parameter under study. The stability region of this phase in the space A_{∞} of the phenomenological parameters of the structurally stable Landau potential can be obtained, as mentioned above, using a well-defined procedure to project out of the orbit space according to the rules of differential geometry. The results of these calculations are presented below.

If the same simplifications are used to write down the symmetry groups and invariant subspaces as in Eq. (23), the possible structures of the Bose condensates can be written in the form given below. We note that only one domain—the representative of the phase—is written everywhere, but the gradient invariance is preserved in the expression of the symmetry of the domain.

obtained by taking into account the kernel of the homomorphism from the group $H_i(O)$. Obvious replacements of the symmetry operations in H_i are required to obtain similar answers for other crystal classes.

The phase symmetry group was written for the group $O(F_2)$. The groups $H_i(O_h, F_{2u})$ and $H_i(O_h, F_{2g})$ can be

1.
$$\begin{vmatrix} 0 \\ 0 \\ \xi_3 \exp i\Omega_3 \end{vmatrix}$$
 $I_1 > 0, \quad I_2 = I_3 = I_4 = I_5 = I_6 = I_7 = I_8 = 0, \\H_1(O, F_2) = \{C_2^{001}\}\{U_1(\pi)U_2^{100}\}\{U_2^{110}\}\{U_1(-2\Omega_1)R\}.$ (25)

The phase corresponding to this solution of the equations of state is denoted by the number 4 in Ref. 9. Its symmetry group H_1 is written here as a product of groups represented by the generators. In what follows, we shall write the symmetry group of the Bose condensate as a product of symmetry groups of its normal series.¹⁴⁻¹⁶ We write the abelian subgroups themselves only by indicating the generators.²⁾ In the eight-dimensional orbit space this phase, as noted above, occupies a one-dimensional subspace $I_1>0$ and $I_p=0$ for p=2,...,8.

2.
$$\begin{vmatrix} \xi_{1} \exp i\Omega_{1} \\ \xi_{1} \exp i\Omega_{1} \\ \xi_{1} \exp i\Omega_{1} \end{vmatrix} = \begin{cases} 3I_{2} = I_{1}^{2}, & 27I_{3} = I_{1}^{3}, & 3I_{4} = 2I_{1}^{2}, \\ 27I_{5} = 2I_{1}^{4}, & I_{6} = I_{7} = I_{8} = 0, \\ H_{2}(O, F_{2}) = \{C_{3}^{1(11)}\}\{C_{2}^{110}\}\{U_{1}(-2\Omega_{1})R\}. \end{cases}$$
(26)

In Ref. 9 this phase is indicated by the number 2,²⁾ and as one can see, it also occupies a one-dimensional subspace in the orbit space Σ_8 .

3.
$$\begin{cases} \xi_1 \exp i\Omega_1 \\ \xi_1 \exp i(\Omega_1 - \pi/3) \\ \xi_1 \exp i(\Omega_1 + \pi/3) \end{cases}$$

$$3I_2 = I_1^2, \quad 27I_3 = I_1^3, \quad 3I_4 = -2I_1^2, \quad 27I_5 = -I_1^4, \\ 27I_6 = I_1^4, \quad 3^5I_7 = -I_1^6, \quad 3^7I_8 = I_1^8, \\ H_3(O, F_2) = \{U_1(4\pi/3)C_3^{(111)}\}\{U_1(-2\Omega_1 + 4\pi/3)C_2^{(110)}R\}.$$
 (27)

In Ref. 9 this structure is designated by the number $1.^{2}$

In Ref. 9 this structure is given the number $3.^{2}$

One other structure of the superconducting phase, previously not discussed, though this structure, just as the preceding four structures, lies in a one-dimensional subspace in the orbit space and is described by the order parameter under consideration, is possible. We note that the phase 5 can also be obtained as a stable phase within the theory of Ref. 9 taking into account the sixth power of the components of the order parameter. This phase can adjoin the normal phase at a second-order transition point. The situation is completely analogous to the one described in detail for the orthorhombic phase $BaTiO_3$:^{15,16}

In the transverse case, the regions of existence of phases 1 and 5 in the phase diagram are separated by regions of existence of other phases of lower symmetry. The transition between phases 1-5 is always only a first-order transition, at least because their symmetries are not related by the group-subgroup relation.¹²

The projection of the regions of existence of the first five phases on the three-dimensional subspace $\Sigma_3(I_1, I_2, I_4) \subset \Sigma_8$ of the orbit space is displayed in Fig. 3.

The two-parameter phases, following next in size, can no longer be obtained as stable phases within the theory of Ref. 9, which takes into account powers no higher than the sixth in the components of the order parameter in the Landau potential.

We now list these lower-symmetry phases, indicating their symmetry. The first five low-symmetry phases depend on two parameters, and for these we can also give their position in orbit space:

6.
$$\begin{vmatrix} \xi_{1} \exp i\Omega_{1} \\ \xi_{1} \exp i\Omega_{2} \\ 0 \end{vmatrix} \qquad 4I_{2}=I_{1}^{2}, \quad I_{4}^{2}+I_{6}=4I_{2}^{2}, \quad I_{3}=I_{5}=I_{7}=I_{8}=0, \\ H_{6}(O,F_{2})=\{U_{1}(-\Omega_{1}-\Omega_{2})U_{2}^{(110)}R\}\{U_{1}(\pi)C_{2}^{001}\}; \\ 7. \begin{vmatrix} \xi_{1} \exp i\Omega_{1} \\ \xi_{2} \exp i\Omega_{1} \end{vmatrix} \qquad I_{4}=2I_{2}, \quad I_{3}=I_{5}=I_{6}=I_{7}=I_{8}=0, \\ H_{7}(O,F_{2})=\{U_{1}(\pi)C_{2}^{(001)}\{U_{1}(-2\Omega_{1})R\}; \end{vmatrix}$$

0

8.
$$\begin{vmatrix} \xi_{1} \exp i\Omega_{1} \\ \xi_{2} \exp i(\Omega_{1} + \pi/2) \\ 0 \end{vmatrix} \qquad I_{4} = -2I_{2}, \quad I_{3} = I_{5} = I_{6} = I_{7} = I_{8} = 0, \\ H_{8}(O,F_{2}) = \{U_{1}(\pi)C_{2}^{(001)}\}\{U_{1}(-2\Omega_{1})U_{2}^{(100)}R\}; \\ 9. \begin{vmatrix} \xi_{1} \exp i\Omega_{1} \\ \xi_{1} \exp i\Omega_{1} \\ \xi_{3} \exp i\Omega_{1} \end{vmatrix} \qquad 2I_{2} = I_{4}, \quad I_{5} = -2I_{3}, \quad I_{6} = I_{7} = I_{8} = 0, \\ 4I_{2}^{3} - 3I_{1}^{2}I_{2}^{2} - 10I_{1}I_{2}I_{3} + I_{3}(I_{3} + 12I_{1}^{2}) = 0, \\ H_{9}(O,F_{2}) = \{U_{2}^{(110)}\}\{U_{1}(-2\Omega_{1})R\}; \\ 10. \begin{vmatrix} \xi_{1} \exp i\Omega_{1} \\ \xi_{3} \exp i(\Omega_{1} + \pi/2) \end{vmatrix} \qquad I_{6} = I_{7} = I_{8} = 0, \quad 4I_{3}^{2}(2I_{2} - I_{4}) = (2I_{1}I_{3})^{2} - I_{5}^{2}, \\ 16I_{3}^{2}(2I_{2} + I_{4}) = (2I_{1}I_{3} - I_{5})^{2}, \\ H_{10}(O,F_{2}) = \{U_{2}^{(110)}\}\{U_{1}(-2\Omega_{1} + \pi)C_{2}^{(001)}R\}.$$
(30)

For the six four-parameter solutions of the equations of state, we present below only the relations between the components of the order parameter and the symmetry of the corresponding phases:

11. $\xi_3 = 0$, $H_{11}(O, F_2) = \{U_1(\pi)C_2^{(001)}\};$ 12. $\xi_1 = \xi_2$, $\Omega_1 = \Omega_2$, $H_{12}(O, F_2) = \{U_2^{(110)}\};$ 13. $\Omega_1 = \Omega_2 = \Omega_3$, $H_{13}(O, F_2) = \{U_1(-2\Omega_1)R\},$ 14. $\Omega_1 = \Omega_2 = \Omega_3 - \pi/2,$ $H_{14}(O, F_2) = \{U_1(-2\Omega_1 + \pi)C_2^{(001)}R\};$ 15. $\xi_1 = \xi_2, \quad 2\Omega_3 = \Omega_1 + \Omega_2,$ $H_{15}(O, F_2) = \{U_1(-\Omega_1 - \Omega_2)U_2^{(110)}R\};$

16.
$$\xi_1 = \xi_2$$
, $2\Omega_3 = \Omega_1 + \Omega_2 + \pi$,
 $H_{16}(O, F_2) = \{ U_1(-\Omega_1 - \Omega_2 + \pi) U_2^{(110)} R \}.$ (31)



FIG. 3. Three-dimensional section $\Sigma_3(I_1, I_2, I_4)$ of the phase diagram in the eight-dimensional orbit space Σ_8 (24). Only regions occupied by five phases, in which a second-order transition is possible directly from the normal state, are indicated. All of these phases occupy one-dimensional subspaces in Σ_8 . The surfaces whose intersection determines the region of existence of these phases (25)–(29) in Σ_3 are also indicated.

For the lowest-symmetry ordered superconducting phase, for which there are no relations between the components of the order parameter, $H(O,F_2) = \{E\}$.

For the order parameters describing superconducting phases whose components form a basis for $F_{1g}(O_h)$, $F_{2g}(O_h)$, $F_{1u}(O_h)$, $F_{2u}(O_h)$, $F_1(O)$, $F_1(T_d)$, and $F_2(T_d)$, the symmetry groups of the ordered phases can be easily determined by multiplying H_i from Eqs. (25)–(31) by the corresponding kernel of the homomorphism with the substitution of operations described in Sec. 3.1. To determine which of these phases can have ferro- or antiferromagnetic structure, it is sufficient to look at their symmetry. The presence of the operation R or $U(\alpha)R$ indicates that no magnetic structure is possible.³¹ If the operation R is present in combination with the crystallographic elements, then an antiferromagnetic density of ordered moments is possible.

3.3. For the case of nontrivial pairing, in which the superconducting state is described by a three-component order parameter, and the crystal class is T_h or T in accordance with the fact that the symmetry of the order parameter is described by $E_2(\infty)$, only nine phases with different symmetry and (according to Ref. 30) fundamentally different structure are possible. These phases are characterized by the following relations between the components of the order parameter and the symmetry of the phases $H_i(T,H)$:

1. $\xi_1 = \xi_2 = 0$, $H_1(T,F) = \{U_1(\pi)U_2^{(100)}\}\{C_2^{(001)}\}\{U_1(-2\Omega_1)R\};$ 2. $\xi_1 = \xi_2 = \xi_3$, $\Omega_1 = \Omega_2 = \Omega_3$, $H_1(T,F) = \{C_3^{111}\}\{U_2(-2\Omega_1)R\};$ 3. $\xi_1 = \xi_2 = \xi_3$, $\Omega_2 = \Omega_1 - \pi/3 = \Omega_3 - 2\pi/3$, $H_2(T,F) = \{U_1(4\pi/3)C_3^{111}\};$

$$\begin{split} \xi_1 &= \xi_2; \quad \xi_3 = 0, \quad \Omega_2 &= \Omega_1 + \pi/2, \\ H_4(T,F) &= \{ U_1(\pi) C_2^{(001)} \} \{ U_1(-2\Omega_1) U_2^{(100)} R \}; \end{split}$$

5.
$$\xi_3 = 0$$
, $\Omega_2 = \Omega_1 + \pi/2$,
 $H_5 = \{U_1(\pi)C_2^{(001)}\}\{U_1(-2\Omega_1)U_2^{(100)}R\};$
6. $\xi_1 = 0$, $H_1(T, E) = \{U_1(\pi)C_2^{(001)}\};$

7.
$$\Omega_1 = \Omega_2 = \Omega_3$$
, $H_7(T,F) = \{U_1(-2\Omega_1)R\}$

8.
$$\Omega_1 = \Omega_2 = \Omega_3 - \pi/2,$$

 $H_8(T,F) = \{U_1(-2\Omega_1 + \pi)C_2^{(001)}R\};$
9. $H_9(T,F) = \{E\}.$ (32)

To determine the symmetry of the phases $H_i(T_h, E_g)$ and $H_i(T_h, E_u)$, the corresponding groups $H_i(T, F)$ must be multiplied by the corresponding kernel of the homomorphism $|K(T_h, E_g) = \{I\}, |K(T_h, E_u) = \{U_1(\pi)I\}$. The correspondence between the symmetries of phases 1–4 from (32) and phases 1–3, and 5 from $E_1(\infty)$ is obvious.

In agreement with the general results of Ref. 16, because of the crystal fields which destroy the C_4 symmetry in the group O and give rise to additional nonlinear interactions between the components of the order parameter, phases 4 and 8 from (28) and (30) combine in symmetry to form phase 4 from (32), and are no longer fundamentally different, though they can correspond to different isostructural phases.³⁰

Phases 6 and 7 from (30) and phase 11 from (31) combine into the phase 6 from (32). In exactly the same way, phases 9 and 13 from (30) and (31) acquire the symmetry of phase 7 from (32), and phases 10 and 14 from (30) and (31) transform into phase 8 from (32). The remaining phases 12 and 15–17 from (31) give isostructural minima³⁰ in the lowest-symmetry phase 9 from (32).

4. STRUCTURE OF BOSE CONDENSATES IN THE SUPERCONDUCTING PHASES OF HEXAGONAL CRYSTALS

In the hexagonal symmetry classes the maximum dimension of the multidimensional irreducible representations is 2. In the case of nontrivial pairing, the order parameters of interest to us are therefore of dimension 4. From the standpoint of the abstract symmetry, the hexagonal classes contain two types of four-dimensional order parameters, which describe Bose condensates in the case of nontrivial pairing. For all two-dimensional representations of the classes D_{6h} , D_6 , D_{3d} , C_{6v} , D_{3h} , C_{3v} , and D_3 , the symmetry of the order parameters is characterized $D_1(\infty)$ (4). The corresponding homomorphism kernels are

$$\begin{split} |K(D_{6h}, E_g^{(1)}) &= \{C_2^z\}\{I\}; \\ |K(D_{6h}, E_u^{(1)}) &= \{C_2^z\}\{U_1(\pi)I\}; \\ |K(D_{6h}, E_g^{(2)}) &= \{I_1(\pi)C_2^z\}\{I\}; \\ |K(D_{6h}, E_u^2) &= \{U_1(\pi)C_2^z\}\{U_1(\pi)I\}; \\ |K(D_6, E_1) &= \{C_2^z\}; \\ |K(D_6, E_2) &= \{U_1(\pi)C_2^z\}; \\ |K(D_{3d}, E_g) &= \{I\}; \\ |K(D_{3d}, E_g) &= \{I\}; \\ |K(C_{6v}, E_1) &= \{C_2^z\}; \\ |K(C_{6v}, E_2) &= \{U_1(\pi)C_2^z\}; \\ |K(C_{6v}, E_2) &= \{U_1(\pi)C_2^z\}; \\ |K(D_{3h}, E_1) &= \{\sigma_h\}; \end{split}$$

$$|K(D_{3h}, E_2) = \{U_1(\pi)\sigma_h\}.$$
(33)

Matrices 1, 3, and 4 in all of the hexagonal classes listed above correspond to the same operations: C_3^{1z} , R, and $U_1(\alpha)$. The operation σ^v corresponds to the generator of $D_1(\infty)$, determined by the second matrix, in the groups D_{6h} , C_{6v} , D_{3d} , and C_{3v} , and the operation U_2 plays this role in the groups D_6 , D_{3h} , and D_3 (see Ref. 12).

For the symmetry classes C_{6h} , C_6 , C_{3h} , S_6 , and C_3 , the symmetry of the four-component superconducting order parameter is characterized by the group $L = D_2(\infty)$. We recall that the second matrix of Eq. (4) is missing from the generators of this group. The homomorphism kernels of the corresponding representations have the form

$$|K(C_{6h}, E_{(i)}^{(k)}) = |K(D_{6h}, E_{(i)}^{(k)});$$

$$|K(C_{6}, E^{(i)}) = |K(D_{6}, E^{(i)});$$

$$|K(S_{6}, E_{(i)}) = |K(D_{3d}, E_{i});$$

$$|K(C_{3h}, E_{(i)}) = |K(D_{3h}, E_{(i)}).$$
(34)

The elements of $Y(G_k)$ corresponding to the elements of $D_2(\infty)$ are also obvious from the preceding description.

Since the abstract symmetry (that is, of the group L) of the multicomponent order parameters describing the Bose condensate in hexagonal crystals is identical to the symmetry of the order parameters (4) for Bose condensates in cubic crystals, the entire rational basis of invariants is the same. The Landau potentials have the same form and, accordingly, the number and form of the solutions of the equations of state are the same. Likewise, the stability conditions for the same phase in the space of coefficients of the Landau potential are also the same. For this reason, we shall not present any calculations in this section. The interested reader can easily construct, using Eqs. (5)-(13) and the corresponding elements of $Y(G_k)$ and L as well as the kernels of the representations (33)-(34), a complete table of all elements of the symmetry groups and the characteristic physical properties.

5. STRUCTURE OF BOSE CONDENSATES IN THE SUPERCONDUCTING PHASES OF TETRAGONAL CRYSTALS

In the tetragonal crystal classes, just as in the hexagonal classes, the maximum dimension of multidimensional representations is 2. Therefore, in multidimensional representations of tetragonal classes, the order parameter has four components. The symmetry of the order parameter is determined by $L = D_3(\infty)$ and $L = D_4(\infty)$, which are characterized by 32 and, correspondingly, 16 different matrices which are functions of the parameter α . The group $D_3(\infty)$ is determined by five generators. In the notation adopted for $E_1(\infty)$, the generators of $D_3(\infty)$ have the form



The group $D_3(\infty)$ describes the symmetry of Bose condensates in the crystal classes D_{4h} , D_4 , C_{4v} , and D_{2d} . The group $D_4(\infty) \subset D_3(\infty)$ describes the symmetry of the order parameters in the classes C_{4h} , C_4 , and S_4 . The generators of $D_4(\infty)$ are identical to (35), if the matrices corresponding to l_2 and $l_3 \in D_3(\infty)$ are omitted. In the groups $Y(G_c)$ with $G_c = D_{4h}$, D_4 , and D_{2d} these matrices correspond to the operations $U_2^{(100)}$ and $U_2^{(010)}$. For $G_c = C_{4v}$, $\sigma^{(100)}$ and $\sigma^{(010)}$ of $\in Y(G_c)$ correspond to the operations l_2 and l_3 . The operations $l_1 \in D_{3,4}$ correspond in $Y(G_c)$ with $G_c = D_{4h}$, C_{4v} , D_4 , and C_{4h} to the operation C_4^1 , and with $G_c = D_{2d}$ or S_4 to the operations $U_1(\pi)U_2^{xy} \in Y(G_c)$.

In accordance with (35), for $L = D_3(\infty)$ the entire rational basis of invariants, which are functions of the components of the order parameter, consists of three polynomials. They are given below in cylindrical coordinates in the space of the components of the order parameter:

$$I_1 = \xi_1^2 + \xi_2^2, \quad I_2 = \xi_1^2 \xi_2^2, \quad I_3 = 2\xi_1^2 \xi_2^2 \cos 2\varphi.$$
(36)

For $L = D_4(\infty)$, a polynomial of the Cartesian coordinates of the order parameter of degree 6 is added to the basis (36), and can be written in the form

$$I_4 = 2(\xi_1^2 - \xi_2^2)\xi_1^2\xi_2^2 \sin 2\varphi, \tag{37}$$

where $\varphi = \Omega_1 - \Omega_2$. Correspondingly, for $L = D_3(\infty)$, seven ordered (superconducting) phases are possible. They are characterized for $Y(D_4, E)$ by the following relations between the components of the order parameter and the symmetry of the Bose condensate:

1.
$$\xi_1 = 0$$
, $H_1 = \{U_1(\pi)C_2^x\}\{U_1(2\Omega_2)R\}|K(D_4,E);$

2.
$$\xi_1 = \xi_2$$
, $\varphi = \pm \pi/2$,

$$H_2 = \{U_1(\pi/2)C_4^{1z}\}\{RU_1(-2\Omega_1 + \pi)U_2^x\}|K(D_4,E);$$

3. $\xi_1 = \xi_2$, $\varphi = \pi n$,

$$H_3 = \{U_2^{xy}U_1(\pi)\}\{U_1(2\Omega_1)R\}|K(D_4,E);$$

4.
$$\xi_1 = \xi_2$$
, $H_4 = \{U_1(\Omega_1 + \Omega_2 - \pi)RU_2^{xy}\}|K(D_4, E);$

- 5. $\varphi = \pi n$, $H_5 = \{U_1(2\Omega_1)R\} | K(D_4, E);$
- 6. $\varphi = (\pi/2)(2n+1),$

$$H_6 = \{U_1(2\Omega_1 + \pi)RU_2^x\} | K(D_4, E);$$

7.
$$H_7 = |K(D_4, E).$$
 (38)

Here, the kernel of the homomorphism is $|K(D_4,E)| = \{U_1(\pi)C_2^z\}$. For D_{4h}

$$|K(D_{4h}, E_g) = |K(D_4, E)\{I\},\$$
$$|K(D_{4h}, E_u) = |K(D_4, E)\{U_1(\pi)I\}.$$

We note also that

$$|K(D_4,E)| = |K(C_4,E)| = |K(C_{4v},E)| = |K(D_{2d},E)|$$
$$= |K(S_4,E), \quad |K(C_{4h},E_i)| = |K(D_{4h},E_i).$$

To determine the symmetry of the phases in these cases, which are not described here, the changes in $H_i(G_c)$ described at the beginning of the section must be made in Eqs. (38).

For the group $D_4(\infty)$, only four states of the Bose condensate which have different symmetry are possible. They are characterized by the same relations between the components of the order parameter as phases 1, 2, 3, and 7 from Eqs. (38).

In the present paper we confine our attention only to the brief description, presented above, of the symmetry of these phases, and we shall postpone the discussion of physical properties predicted on the basis of the symmetry until we describe specific phase transitions.

6. MAGNETOELECTRIC EFFECT IN "MAGNETIC" SUPERCONDUCTING SYMMETRY CLASSES OF TETRAGONAL CRYSTALS

In the preceding sections, our discussion of the symmetry of the superconducting classes corresponding to Bose condensates with nontrivial pairing completely ignored the question of nonuniform states. This question was first studied in detail by Anderson and Morel³³ with respect to the structure of ³He phases. The crux of the matter is that the symmetry of some superconducting phases does not forbid the existence of a characteristic magnetic or antiferromagnetic moment in the Bose condensate, irrespective of the chemical composition of the crystal matrix. In particular, it follows from such symmetry of the uniform state that a constant surface current in the thermodynamic equilibrium state should exist in the corresponding superconductors. This question was discussed in detail by Volovik and Gor'kov,⁹ who presented estimates showing that the internal magnetic field of the Bose condensate can be so strong that the uniform state of the Bose condensate with such symmetry will be unstable: A state with vortices will arise. In general, the question of the equilibrium state of a Bose condensate whose symmetry group admits a magnetic moment can be solved only taking into account Maxwell's equations.³⁾ However, the absence of a globally uniform, thermodynamic equilibrium state does not mean that the answer obtained on the basis of the Landau theory, which takes only uniform states into account, becomes completely meaningless. The abovedescribed symmetry of the Bose condensates determines their local properties in physically small, "almost" uniform regions. We note that it is on this level that all calculations of the properties of ordinary superconductors, in which the crystal matrix is characterized by ferro- and antiferromagnetic order, are presented.^{5,34}

We now discuss the symmetry of one interaction, specific to weakly nonuniform magnetically active superconducting states, on the basis of similar qualitative considerations. The point is that in almost all magnetically active superconducting phases, the symmetry admits bilinear interactions between the electric and magnetic fields.^{31,32}

In describing the effect of an electric field, the question of the penetration depth of a constant external electric field (in particular, the field existing in a ferroelectric state of the crystal matrix) into the region of nonuniformity of the Bose condensate is added to the question of the possibility of a weakly nonuniform state formed by a constant surface current in the equilibrium state.⁹ This question was already discussed in Ref. 34 for a crystal matrix with a characteristic magnetic structure and electric polarization in the case when isotropic *s*-superconductivity arises in the crystal. Here we also call attention to the fact that the characteristic symmetry of some equilibrium superconducting states admits bilinear interactions in the external electric *E* and magnetic *B* fields (linear magnetoelectric effect^{31,32}).

Since the character of these interactions has not been discussed anywhere, we present only the magnetoelectric potentials for the tetragonal classes. The tetragonal classes were chosen as an example because of the possible charge separation mechanism in oxide superconductors in a current-carrying circuit, as observed in polycrystalline and quasi-monocrystalline films^{35,36} as well as in YBa₂Cu₃O_{7- δ} ceramic samples.³⁷

Effects associated with a constant surface current in an equilibrium thermodynamic state are difficult to observe directly because it is almost always possible to think of a mechanism that is specific to a given crystal and is associated with the crystal matrix and not with the state of the Bose condensate; such a mechanism leads to similar effects. For example, magnetic ordering of the Bose condensate should result in a higher superconducting transition temperature in an external magnetic field or lead to the phenomenon of re-entrant superconductivity. Both phenomena have been observed,^{5,38} but they have been explained only by compensation effects. Both an increase in the critical current in hightemperature superconductors in an electric field³⁹ and magnetoelectric interactions have been observed directly⁴⁰ in recent experiments. The first effect is explained in Ref. 39 by surface phenomena and the second effect is associated in Ref. 40 with anionic superconductivity. The results presented below point out a possible direction of research, in which many effects obtained in the compounds $YBa_2Cu_3O_{7-\delta}$ can be explained on the basis of a unified picture of a superconducting state with nontrivial pairing.

The calculations, together with the excitation spectrum in magnetically active phases and the temperature dependence of the magnetoelectric coefficients, will not be discussed here. We present only the part of the thermodynamic potential that is bilinear in the electric and magnetic fields.

For crystalline classes that are subgroups of D_{4h} : D_4 , D_{2d} , and C_{4v} , the superconducting phases exhibiting symmetry that admits an ordered arrangement of the angular momenta of the pairs forming the Bose condensate correspond to numbers 6, 2, and 4. As one can see from the phase diagram in Fig. 2, phases 6 and 4 adjoin phase 2 along the boundary of the second-order transition, and for these phases we shall therefore write the potentials that are bilinear in the electric and magnetic fields in the order 6-2-4:

$$D_{4}: \quad F_{(6)} = \alpha_{12}e_{x}B_{y} + \alpha_{21}e_{y}B_{x},$$

$$F_{(2)} = \alpha_{12}(e_{x}B_{y} - e_{y}B_{x}),$$

$$F_{(4)} = \alpha_{12}(e_{x}B_{y} - e_{y}B_{x}) + \alpha_{11}(e_{x}B_{x} - e_{y}B_{y}),$$

$$D_{2d}: \quad F_{(6)} = \alpha_{12}e_{x}B_{y} + \alpha_{21}e_{y}B_{x},$$

$$F_{(2)} = \alpha_{12}(e_{x}B_{y} + e_{y}B_{x}),$$

$$F_{(4)} = \alpha_{12}(e_{x}B_{y} + e_{y}B_{x}) + \alpha_{33}e_{z}B_{z}$$

$$+ \alpha_{11}(e_{x}B_{x} + e_{y}B_{y}),$$

$$C_{4v}: \quad F_{(6)} = \alpha_{11}e_{x}B_{x} + \alpha_{22}e_{y}B_{y} + \alpha_{33}e_{z}B_{z},$$

$$F_{(2)} = \alpha_{11}(e_{x}B_{x} + e_{y}B_{y}) + \alpha_{33}e_{z}B_{z},$$

$$F_{(4)} = \alpha_{11}(e_{x}B_{x} + e_{y}B_{y}) + \alpha_{33}e_{z}B_{z} + \alpha_{12}(e_{x}B_{y})$$

$$- e_{y}B_{y}).$$
(39)

For the subgroups C_{4h} , C_4 , and S_4 , only phase 2 is magnetically active. Accordingly,

$$F(C_4) = \alpha_{11}(e_x B_x + e_y B_y) + \alpha_{33} e_z B_z + \alpha_{12}(e_x B_y - e_y B_x),$$

$$F(S_4) = \alpha_{11}(e_x B_x - e_y B_y) + \alpha_{12}(e_x B_y + e_y B_x).$$
(40)

7. BRIEF DISCUSSION OF THE RESULTS

Theoretically predicted phase diagram topologies can seriously alter ideas about the character of the change in symmetry accompanying successive phase transitions in heavyfermion superconductors. The necessity of such a revision of transition scenarios is discussed in the detailed analysis given in Ref. 41, where it is shown that none of the eight scenarios of successive transitions in UPt₃ considered in the literature satisfies all the experimental data. The most recently published work on this subject⁴² likewise does not explain the phase changes along the H=0 axis in the *H*-*T* phase diagram, taking into account the results obtained by Aeppli *et al.*,⁴³ using the same arguments discussed in Ref. 41.

The succession of superconducting phases in U_{1-r} Th_rBe₁₃ was explained in a series of papers as a change in the one-component superconducting order parameters, each of which forms a basis for a one-dimensional represen-tation of the crystal class O_h .^{7,22} This analysis did not yield a complete description of the experiment. It follows from the experiment that only the intermediate phase, which exists for 0.0175 < x < 0.05, is magnetically active.^{7,44-47} A break in the superconducting transition temperature as a function of the concentration is observed at the limits of this concentration range, and a second transition to a new superconducting phase is observed in the same concentration range.^{7,44-47} Too many assumptions must be made, including that the concentration dependence of the coefficients of the Landau potential is strongly nonlinear, to explain these features of the phase diagram of U_{1-r} Th_rBe₁₃ on the basis of the transition scenario described by two one-component complex order parameters. Even in this case, however, one phase-transition line in the theory is certainly a line of first-order transitions.46

The most detailed and comprehensive analysis of the experimental situation on the basis of a quartic Landau potential was performed by Luk'yanchuk and Mineev.⁴⁶ They showed that no theory based on a Landau potential of low degree can explain all experimental results. Of course, this confirms that it is necessary to solve the problem discussed

in the present paper, just as the question of the phases described by two irreducible representations must be solved in greater detail.

As indicated in Ref. 46, to discuss in detail the theory of transitions in $U_{1-x}Th_xBe_{13}$, all experiments, and in particular the NMR data, must be compared. This falls outside the scope of the present work, though, as we can see, the results presented above open up new possibilities which are neglected in Ref. 46.

In addition, we note that the existing theory is incomplete in the case of the scenario with two order parameters. In particular, it is necessary to take into account the fact that two one-component complex order parameters can describe (in the case of strong spin-orbit interactions) six ordered phases and not three, as discussed in the literature. Moreover, each order parameter chosen for a scenario can describe only magnetically passive phases, while four ordered phases, described simultaneously by two nonmagnetic order parameters, can be magnetically active. The phase diagram calculated for specific alternatives should help to determine which magnetically active phase is most likely to appear in a narrow concentration range. Such a scenario, which includes transitions between phases described by two magnetically passive one-component order parameters, seems to be more likely than all previously discussed scenarios,⁷ and it does not require the assumption that the concentration dependence of the coefficients in the Landau potential be strongly nonlinear.

If one order parameter is a one-component parameter and the other is a two-component parameter, eleven superconducting phases of differing symmetry are possible. The two-dimensional section of the phase diagram in the case of such a transition scenario admits the merging of two secondorder transition lines into one second-order transition line; this is very reminiscent of the phase diagram of $U_{1-x}Th_xBe_{13}$ near x=0.0175. An isolated coincidence of this type is in itself, of course, insufficient for drawing any conclusions about the transition scenario. This fact shows, however, that the list of phases described by a single irreducible representation, presented above, opens up new possibilities for the theory, since all other variants of symmetry lowering are formed by combining the symmetries of the phases listed above and in Ref. 9.

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tion is given in all cases for superconducting classes induced by the representations that are even and odd under spatial inversion.

- ³⁾I am grateful to G. M. Vereshkov, who called my attention to the need for such an approach. Preliminary calculations show that an external magnetic field can eliminate the qualitative differences between some magnetically active phases.
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¹⁾Of course, these substances and solid solutions based on them do not exhaust the list of heavy-fermion compounds with nontrivial carrier pairing in the superconducting state. They also include many low-symmetry crystals:⁵ the almost cubic crystals URu₂Si₂,⁶ NdRu₆B₆, SmRh₄B₄, and so on⁵ and the almost hexagonal crystal Dy_{1.2}Mo₆S₈. However, the three substances enumerated above are typical, and they have been most completely studied experimentally.

²⁾In Ref. 9 the superconducting phases arising in the class O_h and corresponding to the solutions given for the equations of state are specially labeled. We do not reproduce them here, because for different groups they correspond to a different gauge. For example, in Ref. 9 the same designa-

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