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FEATURES OF PHASE TRANSITIONS ASSOCIATED WITH TWO- AND THREE-COMPONENT ORDER PARAMETERS

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The restrictions imposed by symmetry considerations on the possibility of second-order phase transitions induced by two- and three-component order parameters are analyzed. An example is given of a physically irreducible representation which satisfies the Lifshitz condition and for which two third-order invariants can be set up. It is shown that, for a two-component order parameter, a second-order transition point at which four phases are contiguous cannot exist in the p, T plane. For a three-component order parameter, isolated second-order transition points at which five phases are contiguous can exist.

1. INTRODUCTION

Many of the known structural phase transitions in crystals can be described by an order parameter, the components of which transform according to a multi-dimensional irreducible representation of the symmetry group of the symmetric phase. Thus, e.g., the antiferroelectric transitions in ammonium dihydrogen phosphate[1] and gadolinium molybdate[2] are associated with a two-dimensional irreducible representation. The order parameter in barium titanate and in a number of other cubic ferroelectrics transforms according to a three-dimensional irreducible representation. Examples are also known of more complicated transitions, associated with an order parameter transforming according to a six-dimensional irreducible representation.[3] All ferromagnetic and antiferromagnetic phase transitions are also associated with multi-dimensional order parameters. In structural phase transitions, a change of the probability density ρ of the distribution of charge (in magnetic transitions—of current) occurs[4], leading also to a change of crystal symmetry.

Most phase transitions in crystals occur as first-order transitions that are almost second-order. The fact that they are first-order transitions can be connected with different physical reasons. Among these reasons, those associated purely with symmetry are in a special position: for certain changes of symmetry of the crystal, a phase transition occurs that is certainly first-order. Even in his first papers on the theory of second-order phase transitions, Landau[4,5] considered the fundamental constraints, following from symmetry theory, on the possibility of a second-order phase transition between different phases of a substance. Although, as is now well known, the range of applicability of Landau's theory is confined to the region of temperatures not too close to the transition point, so that the fluctuations of the order parameter are sufficiently small, all the restrictions enumerated below, for the derivation of which only a knowledge of the change of symmetry of the crystal in the transition was needed, will also remain in any more exact theory.

First of all, in order that a transition can occur as a second-order transition, the symmetry group of one of the phases (the asymmetric phase) must be a subgroup of the symmetry G of the other phase.[4] This, in particular, has made it possible to introduce the concept of an "order parameter", which characterizes the extent of deviation of the symmetry from G. A second restriction states that a second-order transition can occur along a line in the p,T plane only if the components of the order parameter transform according to an irreducible representation of the group G. If this representation is one-dimensional, then the order of the symmetry group changes by a factor of 2 in the transition, and symmetry theory imposes no further restrictions on the possibility of a second-order transition. In the more interesting case of a multi-dimensional representation, there are two more restrictions on the irreducible representation according to which the components of the order parameter transform. One, the Lifshitz condition[5,6], allows second-order transitions only with representations of G for which the vector **k** characterizing the star of the representation lies on the boundary or at the center (**k** = 0) of the Brillouin zone. The second condition, the Landau condition[4,6], forbids a second-order transition with an order parameter transforming according to a representation whose cube contains the identical representation.

Using these restrictions, we can say that the change $\Delta\rho$ of the probability density in the transition can be represented in the form of a linear combination of functions $\varphi_{n\alpha}$ transforming according to the n-th irreducible representation of G, satisfying the Lifshitz condition[1]:

$$\Delta\rho(r)=\sum_{\alpha}c_{n\alpha}\varphi_{n\alpha}(r). \tag{1}$$

Here α labels the row of the irreducible representation. As usual[6], we shall assume below that the coefficients $c_{n\alpha}$, and not the functions $\varphi_{n\alpha}$, transform into each other under the symmetry operations of the group G.

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[1] All the restrictions obtained below were obtained from the same considerations as was the Landau condition, which, therefore, will be considered in the text and is not reflected in (1).

The set $\{c_{n\alpha}\}$ is called the order parameter.

The above restrictions were concerned with the selection of those irreducible representations of G with which second-order transitions can be associated. However, in his first paper[4], Landau pointed out that, for complicated transformation properties of the order parameter, a second-order transition to certain phases is impossible even when all the conditions enumerated are fulfilled. The present paper is devoted to a detailed study of the restrictions, following only from symmetry considerations, on the possibility of a second-order phase transition to all phases which can be associated with two- and three-component order parameters. The method developed can also be applied for transitions with order parameters of higher dimensionality.

A general treatment is possible, thanks to the fact that all transitions allowed by the Lifshitz condition[5,6] between the 230 space groups are found to be isomorphous to 48 different types. These types differ in dimensionality and in the form of all the different representation matrices. Since we do not know in advance whether a second-order transition to one or another phase associated with a given order parameter is possible, the asymmetric phases will be enumerated in terms which do not use an expansion of the thermodynamic potential in a series in powers of the components of the order parameter[7]. This enables us to determine, without additional assumptions, the symmetry of the asymmetric phases and the number of independent components of the order parameter in them, and to select a phenomenological model for the description of a particular transition. By the latter, we mean the determination of how many and which terms of the expansion of the thermodynamic potential in powers of the components of the order parameter must be considered in order to describe the transition to this phase within the framework of the Landau theory.

As in a previous paper[7], we introduce an m-dimensional space ϵ, where m is the number of components of the order parameter (the dimensionality of the irreducible representation), and in it a Cartesian system of coordinates, along the axes of which the values of $c_{n\alpha}$ will be plotted. The space group G generates in ϵ a finite point group L, the elements of which correspond to all the different transformation of the $\{c_{n\alpha}\}$. Representations of various groups and different representations of one group can lead to the same group L in ϵ. For example, in three-dimensional space ϵ, only two groups L = O_h and L = O correspond to all the three-dimensional irreducible representations of the group O_h^1 that satisfy the Lifshitz condition. The two-dimensional representations of groups of the classes D_4 and D_{2d} with **k** = 0 and the two-dimensional representations of D_{2h} with **k** = ½($\mathbf{b}_2$ + $\mathbf{b}_3$) lead to L = C_{4v}. Since the $\{c_{n\alpha}\}$ realize a vector representation of the group L, it is easy to enumerate all the possible groups L for a given dimensionality of the space ϵ. Firstly, the L are groups of which the vector representation is irreducible. Secondly, since in the space groups only rotations through angles π, $2\pi/3$, $\pi/2$ and $\pi/3$ are allowed, and the vector **k** lies on the boundary or at the center of the Brillouin zone (the Lifshitz condition), in the space ϵ only rotations through π, $2\pi/3$, $\pi/2$, $\pi/3$, $\pi/4$ and $\pi/6$ are possible.

Restrictions on the possibility of a second-order transition to certain phases definable by an order parameter with which second-order transitions are possible can arise for two reasons. Firstly, the asymmetric phase may be found to be thermodynamically unstable for small values of the order parameter. Mathematically, this requirement reduces to the positive definiteness of the quadratic form whose coefficients are given by the second derivatives of the thermodynamic potential with respect to the components of the order parameter. The second restriction is associated with the properties of the solutions of the nonlinear equations determining the equilibrium values of the components of the order parameter. Certain solutions of these equations, characterizing phases of low symmetry, correspond to real components of the order parameter that start only from certain non-zero values of Σc_α^2. It can be seen from the following how both these restrictions can be studied by starting only from a knowledge of the transformation properties of the order parameter.

2. TRANSITIONS ASSOCIATED WITH A TWO-COMPONENT ORDER PARAMETER

In a two-dimensional space ϵ, there are only two types of point groups of which the vector representation is irreducible: $L_1 = C_{nv}$ and $L_2 = C_n$ with n = 3, 4, 6, 8, 12. For $L_1 = C_{nv}$, the entire rational basis of invariants constructed from the components of the vector $\{c_1, c_2\}$ consists of two functions (this is connected with the fact that L_1 is a group generated by reflections[8]):

$$I_1 = c_1^2 + c_2^2 \equiv r^2, \quad I_2 = r^n \cos n\varphi \quad (\mathrm{tg}\,\varphi = c_1/c_2),$$

i.e., any invariant under C_{nv}, being an entire rational function of c_1 and c_2, can be represented as an entire rational function of I_1 and I_2. Consequently, the thermodynamic potential Φ depends on c_1 and c_2 only through their combinations I_1 and I_2:

$$\Phi \equiv \Phi[I_1(c_i),\ I_2(c_i)].$$

We note that, in the given case, the assumption of a rational dependence $\Phi(c_i)$ is unimportant, since the entire rational basis in the case C_{nv} coincides with the entire irrational basis. The assumption that $\Phi(c_i)$ is an entire function is natural, since otherwise Φ would have singularities as the c_i approach certain values (the singularity in Φ associated with fluctuations of c_i in the neighborhood of the transition point is unimportant for the following).

Therefore, the equations determining the equilibrium values of r and φ have the form

$$\begin{gathered} r(2\Phi_1 + nr^{n-2}\Phi_2 \cos n\varphi) = 0, \\ -nr^n\Phi_2 \sin n\varphi = 0. \end{gathered} \tag{2}$$

Here and below, we use the notation:

$$\Phi_k \equiv \frac{\partial\Phi}{\partial I_k}, \quad \Phi_{mk} \equiv \frac{\partial^2\Phi}{\partial I_m\,\partial I_k}.$$

The solution of the system (2) for r = 0 corresponds to the symmetric phase, which is stable only when $\Phi_1(p, T, r = 0) \equiv a(p, T) > 0$. In order that a second-order transition to some other phase be possible, when a(p, T) goes to zero stable solutions of the system (2) corresponding to the new phase and to arbitrarily small r should arise. Among the solutions of the system (2) that describe asymmetric phases, there are solutions of two types. Corresponding to the first type of solution there is an extremum of the thermodynamic potential Φ, lying in the symmetry planes in the space ϵ: $\sin \varphi = 0$, and the quantity r is determined from the equation

$$\Phi_1 \pm nr^{n-2}\Phi_2 = 0. \tag{3}$$

In the asymmetric phases described by these solutions, the magnitude r of the order parameter changes with change of the temperature (or pressure), while the angle φ remains constant. Corresponding to the second type of solution there is an extremum of Φ that does not lie in a symmetry plane in the space ϵ. In this case, the equilibrium values of r and φ are determined from a system of two nonlinear equations:

$$\Phi_1 = 0, \quad \Phi_2 = 0. \tag{4}$$

In the phase corresponding to this solution, both r and φ vary with temperature. Phases of the second type have been discovered experimentally, e.g., in crystallographic transitions (the phase C_S^4 in boracites[9] and the phase C_1 in the hydrogen selenites[10]).

The group H_1 (= C_S) corresponds to asymmetric phases of the first type in the space ϵ, and contains two symmetry elements: the identical element E and reflection in a plane, σ^V. If L_1 is C_{3V}, all the reflections σ^V belong to the same class, and phases for which $\cos 3\varphi = +1$ or $\cos 3\varphi = -1$ possess the same symmetry. For $L_1 = C_{nV}$ with $n \geq 4$, the symmetry group G_1 can differ depending on the sign of $\cos n\varphi$ (in other words, depending on which of the two possible classes of the group L_1 the reflection σ^V belongs to).

Let G_{11} correspond to $\cos n\varphi = +1$, and G_{12} to $\cos n\varphi = -1$. For $L_1 = C_{nV}$ with $n \geq 4$ also, the symmetries G_{11} and G_{12} may coincide in certain cases, e.g., for transitions with a two-dimensional order parameter (with $\mathbf{k} = 0$) from the space groups of the classes

$$D_{nd} \quad (n = 2, 3) \quad \text{or} \quad D_{nh} \quad (n = 4, 6).$$

However, even in this case, there are different phases, which can border on each other only along a first-order phase transition line. In fact, the stability conditions for phases of the first type have the form

$$\begin{gathered}\mp\Phi_2 \geqslant 0, \quad 4r^2\Phi_{11} \pm (n-2)nr^{n-2}\Phi_{12} \\ \pm 4nr^4\Phi_{21} + n^2r^{2n-2}\Phi_{22} > 0.\end{gathered} \tag{5}$$

Here the upper sign corresponds to the phase G_{11}, and the lower to G_{12}. Comparing the first condition of (5) with Eq. (3), we see that, on the boundary between these phases, the magnitude of the order parameter changes discontinuously. Each of these phases can be contiguous with the symmetric phase in the p,T plane, along a second-order transition line:

$$\lim_{r\to 0} \Phi_1[p, T, r(p, T)] = a(p, T) = 0,$$

since the stability conditions (5) are in no way connected with the stability of the symmetric phase, and when $r \to 0$ are consistent for $n \geq 4$. For n = 3, the stability conditions (5) are consistent for a second-order transition only at a point in the p, T plane at which $a(p, T) = 0$ and $\lim_{r\to 0} \Phi_2(p, T, r) = 0$. This is in complete agreement with the well known result of Landau for representations admitting cubic invariants[4].

A second-order transition from the symmetric phase to a phase of the second type is impossible. The system of equations (4) determining the equilibrium values of r and φ in this phase has no real solutions for a small magnitude r of the order parameter. In order to show this, we expand the thermodynamic potential Φ in the invariants I_1 and I_2:

$$\Phi = a_1I_1 + a_2I_1^2 + b_1I_2 + b_2I_2^2 + cI_1I_2. \tag{6}$$

In the thermodynamic potential (6) we have kept all terms of fourth order in r and terms of the minimum degree in r necessary for the fulfillment of the stability conditions for a phase of the second type:

$$\begin{gathered}4\Phi_{11} + 4nr^{n-2}\Phi_{21}\cos n\varphi + n^2r^{2(n-2)}\Phi_{22}\cos^2 n\varphi > 0, \\ \Phi_{22}\Phi_{11} - \Phi_{12}^2 > 0.\end{gathered} \tag{7}$$

For (6), Eqs. (4) assume the form

$$\begin{gathered}\Phi_1 = a_1 + 2a_2I_1 + cI_2 = 0, \\ \Phi_2 = b_1 + 2b_2I_2 + cI_1 = 0.\end{gathered} \tag{8}$$

Solutions of the system (8) with r tending to zero are possible only for $a_1(p, T) \to 0$ and $b_1(p, T) \to 0$. But $I_2 \equiv I_1^{\frac{n}{2}} \cos n\varphi$ and, in order that the system (8) have a solution with $|\cos n\varphi| \leq 1$, it is necessary to impose one further condition on the coefficients: e.g., $c(p, T) \to 0$. The conclusion reached will not be changed when other terms in the thermodynamic potential (6) are taken into account.

Our conclusion about the impossibility of a second-order phase transition to phases of the second type differs from the result of Levanyuk and Sannikov[11,12], inasmuch as they, in studying the specific case of possible transitions with $L = C_{4V}$, neglected the invariants of sixth order in the order parameter. When these invariants are taken into account, the conclusion about the contiguity of four phases at one point in the p, T plane for a two-component order parameter becomes incorrect.

A transition from each phase of the first type to a phase of the second type is possible along a second-order phase-transition line. This is shown most simply by starting from the fact that the space group G_2 of a phase of the second type is a subgroup of index 2 of the space groups G_{11} and G_{12}. Consequently, a transition between them is described by a one-component order parameter, and in this case there are no symmetry restrictions on the possibility of a second-order transition.

The second type of group, $L = C_n$ (n = 3, 4, 6, 8, 12), in a two-dimensional space ϵ arises for physically irreducible two-dimensional representations. Since the C_n are subgroups of groups generated by reflections of index 2, the entire rational basis of invariants in this case consists of three functions: $I_1 = r^2$, $I_2 = r^n \cos n\varphi$ and $I_3 = r^n \sin n\varphi$, and only one ordered phase is possible, for which r and φ are determined from the system of equations

$$\begin{gathered}r[\Phi_1 + nr^{n-2}(\Phi_2 \cos n\varphi + \Phi_3 \sin n\varphi)] = 0, \\ nr^n(-\Phi_2 \sin n\varphi + \Phi_3 \cos n\varphi) = 0.\end{gathered} \tag{9}$$

Such a type of transition is observed in, e.g., ammonium dihydrogen phosphate[1], gadolinium molybdate[2], etc.

In an ordered phase in which r departs from zero, the system (9) gives one condition on p and T:

lim $\Phi_1(p, T, r) = 0$; the value of the resulting angle φ_0 with respect to an arbitrarily chosen x-axis is determined from the equation

$$\Phi_2 \sin\varphi_0|_{r=0} - \Phi_3 \cos\varphi_0|_{r=0} = 0.$$

If, in the second derivatives of the thermodynamic potential with respect to r and φ for these transitions, we retain the terms of lowest order in r, then

$$\Phi_{rr} \approx 4r^2\Phi_{11}|_{r=0} + (n-2)r^{n-2}(\Phi_2 \cos n\varphi|_{r=0} + \Phi_3 \sin n\varphi|_{r=0}) \ldots > 0,$$
$$\Phi_{\varphi\varphi} \approx -r^n n^2(\Phi_2 \cos n\varphi|_{r=0} + \Phi_3 \sin n\varphi|_{r=0}) \ldots > 0,$$
$$\Phi_{\varphi r} \approx 2r^{n-1}n(-\Phi_{21} \sin n\varphi|_{r=0} + \Phi_{31} \cos n\varphi|_{r=0}).$$

Hence it can be seen that, for $n \geq 4$, the stability conditions can be fulfilled irrespective of Φ_1 for small r. Consequently, in this case a transition to an asymmetric phase can occur along a second-order phase-transition line. For n = 3, in the general case for sufficiently small r, the two conditions $\Phi_{\varphi\varphi} > 0$ and $\Phi_{rr} > 0$ can be simultaneously fulfilled only when $\Phi_2 = 0$ and $\Phi_3 = 0$. These, together with the condition $\Phi_1 = 0$, will be three conditions on the two variables p and T, and, consequently, this transition can occur only with the appearance of a finite r at the transition point.

Actually, this is an example of a representation whose cube contains two invariants:

$$I_2 = c_1^3 - 3c_1^2c_2, \qquad I_3 = c_2^3 - 3c_2^2c_1.$$

Since the question of the existence of such a representation has already been discussed[6,13], we point out that C_3 is realized in ϵ, e.g., for transitions from the groups of the class T that are associated with a two-dimensional representation characterized by $\mathbf{k} = 0$. Many alums undergoing structural transitions have the symmetry group T^4 of the symmetric phase. However, there are insufficient experimental data to indicate whether any of these transitions are associated with $\mathbf{k} = 0$ and a two-component order parameter. A transition from the group T^4 to D_2^4 could be such a transition. We note that this example does not contradict Shur's theorem[13], which states that in the case of a transition associated with an order parameter transforming according to an irreducible representation of G, there can be no more than one third-order invariant. The representation considered is only physically irreducible, and for physically irreducible representations no more than two third-order invariants can exist.

3. PHASE DIAGRAMS FOR TRANSITIONS WITH A THREE-COMPONENT ORDER PARAMETER

There are five groups L corresponding to all the crystallographically possible transitions with a three-component order parameter in the three-dimensional space ϵ, allowed by the Lifshitz condition. These are the cubic point groups of which the vector representation is irreducible: O_h, T_h, O, T_d and T. If L = O_h, six ordered phases with a three-dimensional order parameter are possible. The largest subgroups of the point group O_h that conserve at least one component of the vector $\mathbf{r} = \mathbf{i}x + \mathbf{j}y + \mathbf{k}z$ are associated with corresponding subspaces in the space ϵ. Here x, y and z are functions transforming respectively according to the first, second and third rows of the vector representation of O_h.

Phase transitions with a three-component order parameter

Phase label	L				
	O_h	T_h	O	T_d	T
	I_1, I_2, I_3	I_1, I_2, I_3, I_4	I_1, I_2, I_3, I_4'	I_1, I_2, I_3'	I_1, I_2, I_3', I_4
1	$C_0(-)$	C_0	$C_0(-)$	$C_0(-)$	$C_0(-)$
2	$C_s(-)$	C_s	—	—	—
3	C_s	—	—	$C_s(-)$	—
4	C_{2v}	—	C_2	—	—
5	$C_{4v}(+)$	$C_{2v}(+)$	$C_4(+)$	C_{2v}	C_2
6	$C_{3v}(+)$	$C_3(+)$	$C_3(+)$	C_{3v}	C_3

We shall label these phases and the changes of probability density corresponding to them:

1) $\Delta\rho_1 = c_1x + c_2y + c_3z$, 2) $\Delta\rho_2 = c_1x + c_2y$,
3) $\Delta\rho_3 = c_1(x+y) + c_2z$, 4) $\Delta\rho_4 = c(x+y)$,
5) $\Delta\rho_5 = cx$, 6) $\Delta\rho_6 = c(x+y+z)$.

By analogy with the case of a two-dimensional order parameter, we shall call the phases 4—6 phases of the first type, since, on variation of the external conditions (p and T), within the boundaries of these phases only the magnitude of the order parameter changes, and not its angular coordinates in the space ϵ. The phases 1—3 will be called phases of the second type. The results of the complete analysis of the possible changes of the probability density for all five types of three-dimensional irreducible representation are given in the Table. The results of the Table differ from those of Levanyuk and Sannikov[12], both in the number of phases and in the nature of the transition to these phases; below, therefore, we give explanations of the origin of the restrictions noted in the Table. In the first row of the Table we indicate the groups L and the corresponding functions occurring in the entire rational basis of invariants of the vector representation of each group:

$$I_1 \equiv c_1^2 + c_2^2 + c_3^2, \qquad I_2 \equiv c_1^4 + c_2^4 + c_3^4,$$
$$I_3 \equiv c_1^2c_2^2c_3^2, \qquad I_3' \equiv c_1c_2c_3,$$
$$I_4 \equiv c_1^4(c_2^2 - c_3^2) + c_2^4(c_3^2 - c_1^2) + c_3^4(c_1^2 - c_2^2),$$
$$I_4' \equiv I_3'I_4.$$

The labels of the phases, in accordance with the notation introduced above, are given in the first column of the Table. The dashes in the Table indicate the absence of the corresponding phases for the given group L.

As is shown by an analysis analogous to that performed above for transitions with a two-component order parameter, allowance for higher terms in the expansion of Φ in powers of the order parameter imposes no further restrictions on the possibility of a second-order phase transition from the symmetric phase to the phases 5 and 6. For the groups L = O_h, O and T_h, for which there are no third-order invariants in the entire rational basis of their vector representation, such transitions are possible along a second-order transition line in the p, T plane. In the Table this is indicated by the sign (+). For L = T_d or T, because of the presence of third-order invariants in the entire rational basis, a transition to the phases 5 and 6 is possible only at a point. For the phase 4, which is possible only in O_h and O, a second-order transition is also possible only at a point in the p, T plane. This is connected with the violation of the stability of the phase 4 for small values of the order parameter. Indeed, in this phase, for a small magnitude of the order parameter, it follows from the two stability conditions that $\Phi_2 + \Phi_{11} > 0$ and $\Phi_2 > 0$, the equality $\Phi_1 = -2c_1^2\Phi_2$ being satisfied, and this contradicts the third stability condition: $\Phi_1 + c_1^4\Phi_3 > 0$ for small c. A second-order transition to this phase from the symmetric phase is possible at the point of intersection of the lines $\Phi_1(p, T, c = 0) = 0$ and $\Phi_2(p, T, c = 0) = 0$; in the vicinity of this point, Φ_1 becomes of order c^4, which removes the contradictions in the stability conditions.

A transition to the phases 1—3 from the symmetric phase along a second-order transition line in the p, T plane is completely impossible. We shall consider the transition to the phase 3 for L = O_h. In this case, the equations determining the equilibrium values of the order parameter have the form

$$\Phi_1 + 2c_1^2\Phi_2 + c_2^4\Phi_3 = 0, \quad \Phi_1 + 2c_2^2\Phi_2 + c_1^2c_2^2\Phi_3 = 0. \tag{10}$$

A solution of these equations with $c_1 \neq c_2$ that describes a second-order transition is possible when the two conditions: $\Phi_1(p, T, r = 0) = 0$ and $\Phi_2(p, T, r = 0) = 0$ are fulfilled. Consequently, such a transition is possible only at an isolated point in the p, T plane. In this case, the stability conditions do not impose any additional restrictions. A phase of the type 3 can exist also when L = T_d. However, a second-order transition to this phase is totally impossible. In fact, apart from the conditions for the existence of a phase with $c_1 \neq c_2$ for small r,

$$\Phi_1(p, T, r = 0) = 0, \quad \Phi_2(p, T, r = 0) = 0,$$

which also arise for L = T_d, in this case an additional requirement $\Phi_{11}(p, T, r = 0) = 0$, follows from the stability conditions for the phase 3. Impossibility of a second-order transition to the corresponding phase from the symmetric phase is indicated in the Table by the sign (–).

For L = O_h, the transition to the phase 2 is forbidden as a second-order transition. This can be shown by repeating verbatim the arguments given above for a phase of the second type, a two-dimensional order parameter and L = C_{nv}, since the equations for the equilibrium values of the order parameter in this case have the form

$$\Phi_1 + 2c_2^2\Phi_2 = 0, \quad \Phi_1 + 2c_3^2\Phi_2 = 0 \tag{11}$$

and the interesting solution of (11), with $c_1^2 \neq c_2^2$, is determined by the fact that it makes Φ_1 and Φ_2 go to zero separately. A phase of type 2 is still possible for L = T_h. In this case, a second-order transition is possible at a point in the p, T plane, since the equations of state

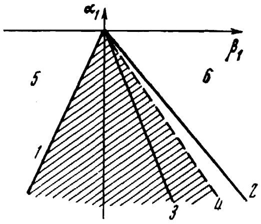
$$\Phi_1 + 2c_1^2\Phi_2 + c_2^2(2c_1^2 - c_2^2)\Phi_4 = 0,$$
$$\Phi_1 + 2c_2^2\Phi_2 + c_1^2(c_1^2 - 2c_2^2)\Phi_4 = 0$$

permit us to carry through arguments analogous to those concerning the phase 3 for L = O_h, and the stability conditions impose no additional restrictions.

For all groups L, apart from L = T_h, a transition from the symmetric phase to the phase 1 cannot occur as a second-order transition, since, for these groups L, the equations of state describing the phase of type 1 lead to not less than three independent conditions on p and T. In the case L = T_h, the presence of two sixth-order invariants in the entire rational basis of invariants leads to the result that, from the equations of state

$$\Phi_1 + 2c_1^2\Phi_2 + c_2^2c_3^2\Phi_3 + [2c_1^2(c_2^2 - c_3^2) + c_3^4 - c_2^4]\Phi_4 = 0,$$
$$\Phi_1 + 2c_2^2\Phi_2 + c_1^2c_3^2\Phi_3 + [2c_2^2(c_3^2 - c_1^2) + c_1^4 - c_3^4]\Phi_4 = 0,$$
$$\Phi_1 + 2c_3^2\Phi_2 + c_2^2c_1^2\Phi_3 + [2c_3^2(c_1^2 - c_2^2) - c_1^4 + c_2^4]\Phi_4 = 0$$

for small c_1, c_2 and c_3, only two conditions on p and T follow, and the stability conditions give no other restrictions.



Possible phase diagram of transitions when L = O_h, in the neighborhood of the point $\alpha_1(p, T) = 0$, $\beta_1(p, T) = 0$ ($\alpha_2 > 0$, $c_{12} > 0$, $\alpha_1 > 0$).

One of the possible phase diagrams, which illustrates the possibility that several phases touch at a second-order transition point, is given in the Figure. We shall assume that, in the vicinity of this point, the phase 3 is unstable ($\Phi_{11}\Phi_{22} - \Phi_{12}^2 < 0$). Then the phases 4, 5 and 6 are those phases which are observed in barium titanate and potassium niobate. The phase 4 always lies between the phases 5 and 6, as is observed experimentally. The transitions between the phases 5 and 4 and 4 and 6 are always first-order. To analyze this case, it suffices to expand the thermodynamic potential near the second-order transition point up to sixth powers in the order parameter:

$$\Phi = \alpha_1 I_1 + \alpha_2 I_1^2 + \alpha_3 I_1^3 + \beta_1 I_2 + \gamma_1 I_3 + \delta_{12} I_1 I_2.$$

In the figure, the lines 1 and 2 delineate the region of stability of the phase 4:

$$\delta_{12}\alpha_1 / 2\alpha_2 < \beta_1 < \delta_{12}\alpha_1 / 2\alpha_2 - \gamma_1\alpha_1 / 8\alpha_2.$$

The line 1 is not only the line along which the potentials of phases 4 and 5 are equal, but is also the stability boundary of phase 5; therefore, although the transition between phases 4 and 5 is always first-order, there is no region of joint (metastable) existence of the phases 4 and 5. To the right of line 3, the phase 6 is stable

$$-\beta_1 > \delta_{12}\alpha_1 / 2\alpha_2 - \gamma_1\alpha_1 / 12\alpha_2.$$

The transition between phases 4 and 6 occurs when their potentials are equal:

$$\beta_1 = \delta_{12}\alpha_1 / 2\alpha_2 - \gamma_1\alpha_1 / 9\alpha_2.$$

The region of existence of phase 4 is shaded.

If the stability condition for phase 3 ($\Phi_{11}\Phi_{22} - \Phi_{12}^2 > 0$) is fulfilled, five phases can be contiguous at the second-order transition point, and to analyze this case it is necessary to perform an expansion of the thermodynamic potential to the eighth power in the order parameter.

A transition between asymmetric phases is possible as a second-order transition only when the subgroup H_1 (of the group L) characterizing one of the asymmetric phases in the space ϵ is also the subgroup H_2 characterizing another asymmetric phase. When this condition is fulfilled, all the restirctions for transitions associated with two-dimensional order parameters are applicable to phase transitions between the phases under consideration. Thus, e.g., a transition from the phase 6 to the phase 3 for L = T_d can occur as a second-order transition only at a point in the p, T plane, because of the presence of third-order invariants in the entire rational basis of invariants of the point group C_{3v}. A second-order transition from the phase 5 to the phase 1 for L = T_h is also possible only at an isolated point, since it is described by a two-dimensional reducible representation of the group C_{2v}, and so on. With a four-dimensional order parameter, there are, in all, 24 possible types of group L, for a six-dimensional order parameter there are six types of group, and so on. The treatment of such transitions is more cumbersome, and can be performed in each particular case separately, by the method described.

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210