Thermodynamic description of crystals in second-order phase transitions near *N*-phase points

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(Submitted May 27, 1975)
Zh. Eksp. Teor. Fiz. **69**, 1428–1439 (October 1975)

Within the framework of the phenomenological theory of second-order phase transitions a thermodynamic investigation is made of the behavior of matter near points at which N phases are contiguous, in the case when N exceeds the number of phases allowed by the Gibbs phase rule. It is shown that for three-component order parameters in the case of two thermodynamic parameters (e.g., pressure and temperature) $N \leq 5$. A quantitative description of the phase transitions in the solid solution $KTa_xNb_{1-x}O_3$ is given.

PACS numbers: 05.70.Jk, 64.70.Kb

In first-order phase transitions the Gibbs rule forbids the coexistance of more than three phases at one point in the plane of the thermodynamic parameters. This prohibition is a consequence of the fact that for first-order phase transitions the thermodynamic potentials of the phases are assumed to be independent, and the requirement that these potentials be equal at the transition point gives rise to independent equations for the thermodynamic parameters. However, for second-order phase transitions it follows from the Landau theory that the number of phases that are stable near certain points in the phase diagram can exceed the number of phases allowed by the Gibbs rule. This conclusion is connected with the fact that for second-order phase transitions the thermodynamic potentials of the different phases, being extrema of the same nonequilibrium thermodynamic potential $\Phi(\eta)$ (η is the order parameter), are related to each other, since they are expressed in terms of the same phenomenological coefficients of $\Phi(\eta)$[1]. In the following we shall call the points at which the phases undergo a continuous transition into each other N-phase points, meaning by N the maximum number of phases that can exist in an arbitrarily small region about such a point.

In Landau's article[2] examples are given in which such points arise at the intersection of two lines of second-order phase transitions with different order parameters, or are isolated second-order transition points lying on lines of first-order phase transitions. However, an N-phase point can also lie on a line of second-order transitions with one order parameter[3,4]. The present article is devoted to an investigation of the structure of phase diagrams in the vicinity of an N-phase point lying on a line of second-order transitions with one order parameter.

We shall assume that the potential $\Phi(\eta)$ is an entire rational function of the components of the order parameter η. Then the low-symmetry phases to which a continuous transition from the symmetric phase is possible only at an N-phase point in the plane of the two thermodynamic parameters can be divided into two types. The first type of phase is characterized by the fact that the diameter of the region of existence of such phases near an N-phase point is of order τ^n ($n \geq 2$, τ is the distance from the N-phase point). The boundaries of the existence of such phases have a common tangent at the N-phase point itself. A direct continuous transition from the symmetric phase to a phase of the first type is possible only when there is a strictly coordinated variation of the thermodynamic parameters—only along a single line in the phase diagram (tangency to the "beak")[3]. For the second type of phase the smallest diameter of the region of existence of the phase about the N-phase point in the plane of the thermodynamic parameters is of order τ. The lines bounding the region of existence of such phases intersect at a finite angle at the N-phase point. A transition from the symmetric phase to a phase of the second type is possible under less stringent restrictions on the varying thermodynamic parameters: a transition to such a phase in the phase plane is possible along any line passing through the N-phase point and lying within a certain finite angle[4].

For second-order phase transitions the possible types of phase diagram are determined by the dimensionality and transformation properties of the order parameter[1]. Which type of phase diagram is realized in each specific case depends on the quantitative relationships between the coefficients of the thermodynamic potential $\Phi(\eta)$. Phase diagrams containing phases of the second type arise only when the order parameter has not less than three components (we are considering the case when the components of the order parameter transform according to an irreducible representation of the symmetry group G of the symmetric phase).

As is well-known, the Lifshitz condition restricts the number of possible three-component order parameters to five types[4], of which three can describe second-order transitions on a line in a plane of two thermodynamic variables. Here we shall consider a three-component order parameter admitting the maximum number of low-symmetry phases. The phase diagram in this case turns out to be more complicated than for other three-component order parameters. However, it is precisely this which makes it possible to carry over the method of investigating the phase diagram, and certain conclusions, to the case of N-phase points in diagrams describable by order parameters of high dimensionalities. The maximum number of phases arises in the case of an order parameter for which the matrices of the corresponding irreducible representation in the three-dimensional space of representations E_3 form the point group $L = O_h$. Such order parameters characterize the ferroelectric transitions in $BaTiO_3$, $PbTiO_3$, $KNbO_3$, and also the non-ferroelectric transitions in $SrTiO_3$, $KMnF_3$, $PrAlO_3$, $Pb_3V_2O_8$, $Pb_3P_2O_8$, etc. (cf., e.g.,[5,6]).

1. QUALITATIVE INVESTIGATION OF THE PHASE DIAGRAM NEAR AN N-PHASE POINT

For a three-dimensional order parameter with $L = O_h$ the thermodynamic potential $\Phi(\eta)$ depends only on three functions of the components of the order parameter:

$$J_1=\eta_1^2+\eta_2^2+\eta_3^2,\quad J_2=\eta_1^4+\eta_2^4+\eta_3^4,\quad J_3=\eta_1^2\eta_2^2\eta_3^2,$$

which constitute an entire rational basis of invariants. In accordance with this, the nonlinear equations determining the equilibrium values of the order parameter have the form

$$\partial\Phi/\partial\eta_1=2\eta_1(\Phi_1+2\eta_1^2\Phi_2+\eta_2^2\eta_3^2\Phi_3)=0,$$
$$\partial\Phi/\partial\eta_2=2\eta_2(\Phi_1+2\eta_2^2\Phi_2+\eta_1^2\eta_3^2\Phi_3)=0,$$
$$\partial\Phi/\partial\eta_3=2\eta_3(\Phi_1+2\eta_3^2\Phi_2+\eta_1^2\eta_2^2\Phi_3)=0,$$

where $\Phi = \Phi(J_1, J_2, J_3)$ is the nonequilibrium thermodynamic potential and $\Phi_k = \partial\Phi/\partial J_k$. These equations have six types of solution, describing low-symmetry phases with different symmetry (the trivial solution $\eta_1 = \eta_2 = \eta_3 = 0$ corresponds to the symmetric phase):

$$\eta_1,\ \eta_2,\ \eta_3;\quad \Phi_1=0,\ \Phi_2=0,\ \Phi_3=0, \tag{1}$$
$$\eta_1,\ \eta_2,\ \eta_3=0;\quad \Phi_1=0,\ \Phi_2=0, \tag{2}$$
$$\eta_1=\eta_2,\ \eta_3;\quad 2\Phi_2-\eta_1^2\Phi_3=0,\quad \Phi_1+(2\eta_1^2+\eta_3^2)\Phi_2=0, \tag{3}$$
$$\eta_1=\eta_2,\ \eta_3=0;\quad \Phi_1+2\eta_1^2\Phi_2=0, \tag{4}$$
$$\eta_1=\eta_2=0,\ \eta_3;\quad \Phi_1+2\eta_3^2\Phi_2=0, \tag{5}$$
$$\eta_1=\eta_2=\eta_3;\quad \Phi_1+2\eta_1^2\Phi_2+\eta_1^4\Phi_3=0. \tag{6}$$

Below we shall be interested only in those solutions η_1, η_2, η_3 of the nonlinear equations (1)—(6) that can vanish at the boundary of stability of the symmetric phase. (In the case of two thermodynamic parameters this line is $\Phi_1(X_1, X_2) = 0$ in the (X_1, X_2)-plane.)

The first restriction on the possibility of a second-order phase transition to one or other of the low-symmetry phases follows from the requirement that the number m of independent components of η characterizing the phase (or, in other words, the number of equations determining the magnitude of the independent components of η) not exceed the number k of independently variable external conditions—the thermodynamic parameters $X_1, X_2, \ldots, X_k$. If, e.g., $k = m$, a second-order transition is possible only at a point in the X-space; if $k = m + 1$ it is possible on a line, and so on.

The solution (1) describes the phase with the lowest possible symmetry for the order parameter under consideration. In this phase the three components of the parameter are nonzero and independent. It is obvious that in the general case the system of equations (1) does not have solutions that vanish on the line of loss of stability of the symmetric phase in the (X_1, X_2)-plane, i.e., a second-order transition from the symmetric phase to such a phase is impossible.

The phases corresponding to the solutions (2) and (3) are described by space groups having twice as many symmetry elements as the symmetry group of the phase (1). Equations (2) and (3) can have vanishing solutions only at the point $\Phi_1(X_1, X_2) = 0$, $\Phi_2(X_1, X_2) = 0$. Equations (4)—(6), describing the most symmetric of the phases, characterizable by one independent component of the vector η, admit solutions vanishing on the line $\Phi_1(X_1, X_2) = 0$ in the (X_1, X_2)-plane.

However, the conditions obtained above are only necessary. Now we must investigate the stability conditions near the line $\Phi_1(X_1, X_2) = 0$ for each of the phases, i.e., determine the region in which the matrix composed of the second derivatives $\partial^2\Phi/\partial\eta_i\partial\eta_k$ is positive-definite for $\eta \to 0$. Violation of the stability conditions leads to a second restriction on the possibility of a second-order transition to some low-symmetry phase. A particular case of this restriction is the well-known Landau condition[1].

For the phase (2) the stability conditions have the form

$$\Phi_{11}>0;\quad \Phi_{11}\Phi_{22}-\Phi_{12}^2>0,\quad \Phi_3>0$$

and do not lead to any additional restrictions on the possibility of a second-order transition. For the phase (3) near the line $\Phi_1(X_1, X_2) = 0$ for small η_1 and η_3, the stability conditions

$$\Phi_{11}>0,\quad (\eta_1^2-\eta_3^2)\Phi_3>0,\quad (\eta_3^2-\eta_1^2)\Phi_3>0$$

are contradictory. This contradiction disappears only in the region where $\eta_1^2 - \eta_3^2 \sim \eta^4$. In this region it is necessary to take into account terms of higher order in η in the stability conditions. Hence it follows that the region of existence of a phase (3) describable by solutions that vanish on the line $\Phi_1 = 0$ becomes narrower in proportion to η^4 as the point $\Phi_1 = 0$, $\Phi_2 = 0$ is approached, and lies along the boundary of the existence of solutions corresponding to the phase (6), for which $\eta_1 = \eta_2 = \eta_3$. Consequently, the potential of the phase (3) cannot differ from the potential of the phase (6) by more than a quantity of order $J_1^3 \sim \eta^6$. This result is important for the following analysis.

For the phase (4) the stability conditions are contradictory for finite Φ_2:

$$\Phi_{11}>0,\quad \Phi_2>0(\Phi_1<0),\quad -2\Phi_2+\eta_1^2\Phi_3>0.$$

Consequently, only at the point $\Phi_1 = 0$, $\Phi_2 = 0$ can this phase arise in a second-order transition from the symmetric phase; as this point is approached, the width of the region of existence of the phase (4) decreases like η^2. We note that in the case of finite values of Φ_3 the phase (4) exists only for $\Phi_3 > 0$. The stability conditions for the phase (5)

$$2\Phi_2+\Phi_{11}>0,\quad \Phi_2<0$$

contain no contradictions. For the phase (6) we have:

$$2\Phi_2+\Phi_{11}>0,\quad 4\Phi_2^2+4\Phi_2\Phi_{11}-2\eta^2\Phi_3\Phi_{11}>0,\quad 2\Phi_2+3\Phi_{11}>0,$$

which are also not contradictory.

The third restriction on the possibility of a second-order transition is connected with the overlap of the regions of stability of some of the low-symmetry phases near the line $\Phi_1(X_1, X_2) = 0$. If the regions of lability of the phases overlap, a transition occurs to the thermodynamically stable phase with a thermodynamic potential lower than the potentials of the other phases. We shall study first the stability conditions for the phases (3), (4) and (6), for which, as follows from an analysis of the stability conditions, the regions of lability overlap. The equations of state determining J_1 in the phases (4) and (6) respectively have the form

$$\Phi_1(J_1, {}^1\!/_2J_1^2, 0, X_1, X_2)+J_1\Phi_2(J_1, {}^1\!/_2J_1^2, 0, X_1, X_2)=0, \tag{4'}$$

$$\Phi_1(J_1, {}^1\!/_3J_1^2, {}^1\!/_{27}J_1^3, X_1, X_2)+{}^2\!/_3J_1\Phi_2(J_1, {}^1\!/_3J_1^2, {}^1\!/_{27}J_1^3, X_1, X_2)$$
$$+{}^1\!/_9J_1^2\Phi_3(J_1, {}^1\!/_3J_1^2, {}^1\!/_{27}J_1^3, X_1, X_2)=0. \tag{6'}$$

Since, in (4) and (6), the dependences of the functions Φ_i on their arguments are the same, it is clear that in the region of simultaneous existence of the solutions describing the phases (4) and (6) the difference $J_1(4) - J_1(6)$ is of the same order as $J_1(4)$ and $J_1(6)$ themselves. From a comparison of the stability conditions for phases (4) and (6) for small values of Φ_2:

$$2\Phi_2(4)-{}^1/_2J_1(4)\Phi_3(4)<0,\quad 2\Phi_2(6)-{}^1/_3J_1(6)\Phi_3(6)>0,$$

it can be seen that the regions of lability of these phases overlap in such a way that the width of the overlap region is of the order of J_1. Consequently, the potentials $\Phi(4)$ and $\Phi(6)$ at the boundaries of the regions of lability of phases (4) and (6) differ by an amount of the order of J_1^2. Since, as shown above, the region of lability of the phase (3) can lie only near the boundary of the region of lability of the phase (6), where the potentials of (3) and (6) differ by an amount of order J_1^3, the phase (3) is always metastable for small values of J_1. The stable phase in the region of lability of (3) is the phase (4), whose potential is lower than that of the phase (6) by an amount of the order of J_1^2.

We now analyze how the boundaries of the phases (4) and (5) are positioned with respect to each other. On the phase-(5) side the lability of phase (4) is bounded by the condition $\Phi_2(4) \geq 0$, while the lability of phase (5) is determined by the condition $\Phi_2(5) \leq 0$. We shall consider the solutions of Eqs. (4) and (5) that vanish on the boundary of the region $\Phi_1(0) > 0$.

On the boundary of lability of the phase (5),

$$\Phi_1(J_1, J_1^2, X_1, X_2)=0,\quad \Phi_2(J_1, J_1^2, X_1, X_2)=0. \tag{7}$$

Along the stability boundary, $d\Phi_1(J_1, J_1^2, X_1, X_2) = 0$, $d\Phi_2(J_1, J_1^2, X_1, X_2) = 0$. Hence the slope of the tangent to the boundary of stability of the phase (5) in the (X_1, X_2)-plane will be, for small J_1,

$$\left.\frac{dX_2}{dX_1}\right|_5=\left[\frac{\partial\Phi_1}{\partial X_1}(\Phi_{12}+2J_1\Phi_{22})-\frac{\partial\Phi_2}{\partial X_1}(\Phi_{11}+2J_1\Phi_{12})\right]$$
$$\times\left[\frac{\partial\Phi_2}{\partial X_2}(\Phi_{11}+2J_1\Phi_{12})-\frac{\partial\Phi_1}{\partial X_2}(\Phi_{12}+2J_1\Phi_{22})\right]^{-1}. \tag{8}$$

For the phase (4) on the stability boundary,

$$\Phi_1\left(\tilde{J}_1,\frac{1}{2}\tilde{J}_1^2,X_1,X_2\right)\equiv\tilde{\Phi}_1=0,\quad \Phi_2\left(\tilde{J}_1,\frac{1}{2}\tilde{J}_1^2,X_1,X_2\right)\equiv\tilde{\Phi}_2=0, \tag{9}$$

whence, in analogy with (8), we obtain

$$\left.\frac{dX_2}{dX_1}\right|_4=\left[\frac{\partial\tilde{\Phi}_1}{\partial X_1}(\tilde{\Phi}_{12}+\tilde{J}_1\tilde{\Phi}_{22})-\frac{\partial\tilde{\Phi}_2}{\partial X_1}(\tilde{\Phi}_{11}+\tilde{J}_1\tilde{\Phi}_{12})\right]$$
$$\times\left[\frac{\partial\tilde{\Phi}_2}{\partial X_2}(\tilde{\Phi}_{11}+\tilde{J}_1\tilde{\Phi}_{12})-\frac{\partial\tilde{\Phi}_1}{\partial X_2}(\tilde{\Phi}_{12}+\tilde{J}_1\tilde{\Phi}_{22})\right]^{-1}. \tag{10}$$

From a comparison of (7) and (9) it can be seen that J_1 in phase (5) and $\tilde{J}_1$ in phase (4), like Φ, Φ_i and Φ_{ik} for these phases, differ from each other by an amount of order J_1^2. Consequently, forming the difference

$$\left.\frac{dX_2}{dX_1}\right|_5-\left.\frac{dX_2}{dX_1}\right|_4=J_1\left(\frac{\partial\Phi_1}{\partial X_1}\frac{\partial\Phi_2}{\partial X_2}-\frac{\partial\Phi_1}{\partial X_2}\frac{\partial\Phi_2}{\partial X_1}\right)(\Phi_{11}\Phi_{22}-\Phi_{12}^2)$$
$$\times\left(\frac{\partial\Phi_1}{\partial X_2}\Phi_{12}-\frac{\partial\Phi_2}{\partial X_2}\Phi_{11}\right)^{-2}+o(J_1^2), \tag{11}$$

we find that the tangents to the boundaries of stability of the phases (4) and (5) coincide on the boundary with the high-symmetry phase. The difference in the slopes of the tangents increases like J_1 as one moves away from the line $\Phi_1(X_1, X_2) = 0$.

Considering the different cases

$$\left.\frac{dX_2}{dX_1}\right|_{\eta_1=\eta_2=\eta_3=0}\gtrless 0,$$

it can be shown that if $\Phi_{11}\Phi_{22} - \Phi_{12}^2 > 0$, then, between the regions in which phases (4) and (5) are stable, there is a region of width of the order of J_1^2. In the opposite case ($\Phi_{11}\Phi_{22} - \Phi_{12}^2 < 0$) the regions of existence of the phases (4) and (5) overlap, also with a width of the order of J_1^2.

The fourth restriction on the possibility of a second-order transition to a given low-symmetry phase is connected with the requirements that the solutions of the nonlinear equations determining the value of the order parameter in this phase be real near the line $\Phi_1(X_1, X_2) = 0$. Thus, real solutions of the system of equations (2) exist only for $\Phi_{11} > 0$, $\Phi_{11}\Phi_{22} - \Phi_{12}^2 > 0$. Inasmuch as the values of J_1 in the phases (2), (4) and (5) differ only by J_1^2, the conditions for the solutions of the system (2) to be real for small J_1 coincide exactly with the condition for the existence of a region in the (X_1, X_2)-plane in which only phase (2) is stable. This region of the phase diagram is investigated in more detail below.

We shall state the results briefly:

1. For the order parameter being studied ($L = O_h$), in a plane of two thermodynamic variables five phases (0, 2, 4, 5, and 6) can be contiguous at one point $\Phi_1(X_1, X_2) = 0$, $\Phi_2(X_1, X_2) = 0$.

2. The sequence of low-symmetry phases near the five-phase point is the following: $0 \longleftrightarrow 5 \longleftrightarrow 2 \longleftrightarrow 4 \longleftrightarrow 4 \longleftrightarrow 6 \longleftrightarrow 0$.

3. To describe the phase (4) it is necessary to consider a model potential of degree not lower than η^6, and for the phase (2)—not lower than η^8.

4. The diameter of the region of existence of the phase (2) near the five-phase point is of order η^4, and for phase (4) is of order η^2.

5. The width of the region of metastability in the transition between the phases (4) and (6) is of order η^2, and in the direct transition between phases (5) and (4) is of order η^4.

These conclusions are also valid in a number of cases when the nonequilibrium potential $\Phi(\eta, X_1, X_2)$ has a singularity in X_1 and X_2. For example, all the results remain valid for a singularity of the second kind, in Fisher's classification[7]. The assumption of an entire rational dependence of Φ on η may also turn out to be unimportant for certain results of the analysis, e.g., the number of phases and their symmetry. This is connected with the fact that an entire rational basis of invariants always contains a functional basis[8].

2. MODEL DESCRIPTION OF THE PHASE DIAGRAM NEAR A FIVE-PHASE POINT

Two expansion parameters appear in the Landau theory near the point $\Phi_1 = 0$, $\Phi_2 = 0$, and this enables us to investigate the phase diagram in more detail than usual. The analysis carried out in the previous Section showed that for a complete description of the character of the contiguity of the phases near this point it is necessary to consider a model potential containing terms of at least eighth order in the components of η:

$$\Phi=\alpha_1J_1+\alpha_2J_1^2+\alpha_3J_1^3+\alpha_4J_1^4+\beta_1J_2+\beta_2J_2^2+\gamma_1J_3+c_{12}J_1J_2$$
$$+dJ_1^2J_2+fJ_1J_3. \tag{12}$$

The equalities corresponding to $\Phi_1(0, X_1, X_2) = 0$ and $\Phi_2(0, X_1, X_2) = 0$ in the potential (12) are $\alpha_1(X_1, X_2) = 0$ and $\beta_1(X_1, X_2) = 0$.

From the equation of state for the phase (6) we have, to terms of second order in α_1, β_1,

$$\eta_1^2=\eta_2^2=\eta_3^2=-\frac{\alpha_1}{6\alpha_2}+\frac{\alpha_1\beta_1}{18\alpha_2^2}-\frac{27\alpha_3+9c_{12}+\gamma}{2^33^3\alpha_2^3}\alpha_1^2. \tag{13}$$

The potential of the phase (6) in this approximation is

$$\Phi(6)=-\frac{\alpha_1^2}{4\alpha_2}+\beta_1\frac{\alpha_1^2}{12\alpha_2^2}-\frac{27\alpha_3+9c_{12}+\gamma}{2^3 3^3\alpha_2^3}\alpha_1^3. \qquad (14)$$

The stability conditions for phase (6) reduce to the two inequalities

$$\alpha_2>0, \quad \beta_1>\frac{\alpha_1}{2\alpha_2}\left(c_{12}-\frac{\gamma}{6}\right). \qquad (15)$$

For the phase (5) we have

$$\eta_1=\eta_2=0, \quad \eta_3^2=-\frac{\alpha_1}{2\alpha_2}+\frac{\alpha_1\beta_1}{2\alpha_2^2}-\frac{3\alpha_3+c_{12}}{8\alpha_2^3}\alpha_1^2, \qquad (16)$$

$$\Phi(5)=-\frac{\alpha_1^2}{4\alpha_2}+\beta_1\frac{\alpha_1^2}{4\alpha_2^2}-\frac{\alpha_3+c_{12}}{8\alpha_2^3}\alpha_1^3. \qquad (17)$$

Unlike in the previous case of the phase (6), we shall write out the stability conditions to second order in the small parameters. The necessity for this is connected with the fact that, as has been shown, the region of existence of the phase (2), and, consequently, its boundary with the phase (5), can be described only by starting from this approximation. We have

$$\alpha_2>0, \quad \beta_1<\frac{c_{12}\alpha_1}{2\alpha_2}-\frac{c_{12}\alpha_1\beta_1}{2\alpha_2^2}+\left[\frac{3(\alpha_3+c_{12})c_{12}}{2\alpha_2}-(d+2\beta_2)\right]\frac{\alpha_1^2}{4\alpha_2^2}. \qquad (18)$$

For the phase (4),

$$\eta_3=0, \quad \eta_1^2=\eta_2^2=-\frac{\alpha_1}{2\alpha_2}+\frac{\alpha_1\beta_1}{8\alpha_2^2}-\frac{3(2\alpha_3+c_{12})}{32\alpha_2^3}\alpha_1^2; \qquad (19)$$

$$\Phi(4)=-\frac{\alpha_1^2}{4\alpha_2}+\beta_1\frac{\alpha_1^2}{8\alpha_2^2}-\frac{2\alpha_3+c_{12}}{16\alpha_2^3}\alpha_1^3; \qquad (20)$$

$$\alpha_2>0, \quad \left(c_{12}-\frac{\gamma}{4}\right)\frac{\alpha_1}{2\alpha_2}>\beta_1>\frac{c_{12}\alpha_1}{2\alpha_2}$$
$$-\frac{c_{12}\alpha_1\beta_1}{4\alpha_2^2}+\left[\frac{3(2\alpha_3+c_{12})c_{12}}{4\alpha_2}-(\beta_2+d)\right]\frac{\alpha_1^2}{4\alpha_2^2}. \qquad (21)$$

From the inequality (21) in the first approximation it follows that the phase (4) exists only for positive γ. However, if we assume even so that, for chance reasons, γ is negative but sufficiently small ($\gamma \sim \alpha_1 \sim \beta_1$), the inequality (21) can be fulfilled and the phase (4) can be contiguous with the high-symmetry phase. In this case the region of existence of the phase (4) will be transformed from a "corner" to a "beak."

For the phase (2), which can also be contiguous with the high-symmetry phase at the point $\alpha_1(X_1, X_2) = 0$, $\beta_1(X_1, X_2) = 0$, the equations of state can be brought to the form

$$\eta_1^2+\eta_2^2=J_1=\frac{c_{12}\beta_1-2\beta_2\alpha_1}{4\alpha_2\beta_2-c_{12}^2}+\frac{c_{12}d-6\alpha_3\beta_2}{4\alpha_2\beta_2-c_{12}^2}\left(\frac{c_{12}\beta_1-2\beta_2\alpha_1}{4\alpha_2\beta_2-c_{12}^2}\right)^2,$$
$$\eta_1^4+\eta_2^4=J_2=\frac{c_{12}\alpha_1-2\alpha_2\beta_1}{4\alpha_2\beta_2-c_{12}^2}+\frac{3\alpha_3c_{12}-2\alpha_2d}{4\alpha_2\beta_2-c_{12}^2}\left(\frac{c_{12}\beta_1-2\beta_2\alpha_1}{4\alpha_2\beta_2-c_{12}^2}\right)^2. \qquad (22)$$

In order that the system of equations (22) have a real solution for η_1^2 and η_2^2, it is necessary that one further condition (the fourth restriction from Sec. 1) be fulfilled. However, as was shown by Levanyuk and Sannikov[3] for the analogous case of a two-dimensional order parameter, the corresponding condition is always fulfilled in a certain region of width of order α_1^2. In our case this region is located along the line $\beta_1 = c_{12}\alpha_1/2\alpha_2$. As follows from the general treatment, the stability conditions for the phase (2):

$$\alpha_2>0, \quad 4\alpha_2\beta_2-c_{12}^2>0, \quad \gamma>0, \qquad (23)$$

do not impose any restrictions on the possible boundaries with the other low-symmetry phases. The boundary of the region of existence of real solutions of Eqs. (22) coincides exactly with the boundaries of the phases (5) and (4) for $4\alpha_2\beta_2 - c_{12}^2 > 0$. Therefore, a transition from phase (2) to phase (5) or (4) should occur as a second-order transition. The possible types of phase diagram near the point $\alpha_1(X_1, X_2) = 0$, $\beta_1(X_1, X_2) = 0$ are given in Fig. 1.

The model thermodynamic potential (12) contains ten phenomenological parameters, and to establish it completely a large number of varied experiments is required. However, certain exact relations between measureable quantities can be established on the basis of the analysis performed, even without establishing the thermodynamic potential.

Suppose that the phase boundaries have been established experimentally for a certain substance, and the phase diagram has the form depicted in Fig. 1b or 1c. In this case, without establishing the thermodynamic potential, it is possible to calculate exactly for the phases (4) and (6) the lability boundaries defining the region of the maximum possible temperature hysteresis in the corresponding transitions. We shall consider this problem in the approximation linear in the deviations of the thermodynamic parameters from the point $\alpha_1 = 0$, $\beta_1 = 0$. We shall transform from the coordinates α_1 and β_1 in the phase diagram to the pressure and temperature coordinates, p and T:

$$\alpha_1=A_1\Delta T+A_2\Delta p, \quad \beta_1=B_1\Delta T+B_2\Delta p. \qquad (24)$$

We shall introduce the notation $k_i = \Delta T_i/\Delta p_i$ for the slopes of the transition lines between the phases, where i is the label of a line in accordance with Fig. 1b or 1c. Then, on the experimental phase diagram, the lines 2 and 3 are described by the equations

$$\beta_1=\frac{c_{12}\alpha_1}{2\alpha_2}\to k_2\frac{2\alpha_2B_1}{c_{12}A_1}+\frac{2\alpha_2B_2}{c_{12}A_1}=k_2-k_1,$$
$$\beta_1=\left(c_{12}-\frac{2\gamma}{9}\right)\frac{\alpha_1}{2\alpha_2}\to k_3\frac{2\alpha_2B_1}{c_{12}A_1}+\frac{2\alpha_2B_2}{c_{12}A_1}=k_3-k_1-\frac{9\gamma}{2c_{12}}(k_3-k_1). \qquad (25)$$

This gives a system of two equations for the three combinations of phenomenological parameters:

$$M=2\alpha_2B_1/c_{12}A_1, \quad N=2\alpha_2B_2/c_{12}A_1, \quad R=\gamma/c_{12}.$$

The equation of the line $\beta_1 = (c_{12} - \gamma/6)\alpha_1/2\alpha_2$ determining the left-hand boundary of stability of the phase (6) has in the Tp-plane the form

$$k_4M+N=(k_4-k_1)(1-{}^1/_6R). \qquad (26)$$

Here $k_4 = \Delta T_4/\Delta p_4$ is the slope of this line in the Tp-plane. The equation $\beta_1 = (c_{12} - \gamma/4)\alpha_1/\alpha_2$ of the right-hand boundary of the phase (4) takes the form

$$k_5M+N=(k_5-k_1)(1-{}^1/_4R). \qquad (27)$$

Substituting M and N from (25) into (26) and (27), we obtain two independent equations of the form

$$Rf(k_1, k_2, k_3, k_4, k_5)=0. \qquad (28)$$

Inasmuch as $R \equiv \gamma/c_{12} \neq 0$, we obtain relations determining k_4 and k_5 in terms of k_1, k_2 and k_3:

$$k_4=\frac{k_1k_2+3k_1k_3-4k_2k_3}{4k_1-3k_2-k_3}, \quad k_5=\frac{k_1k_2-9k_1k_3+8k_2k_3}{-8k_1+9k_2-k_3}. \qquad (29)$$

3. THERMODYNAMIC DESCRIPTION OF THE PHASE TRANSITIONS IN KTN

We shall carry out concrete calculations using the example of the solid solution KTN ($KTa_xNb_{1-x}O_3$). Niobium and tantalum are so close in their chemical properties and ionic radii that when they are substituted for one another no phase separation of the solid solution occurs, at any concentration of the components. Therefore, when considering macroscopic experiments we

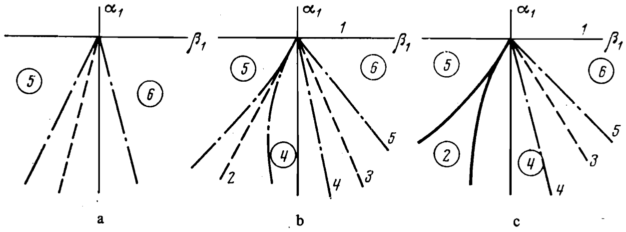

FIG. 1. Possible types of phase diagram near a five phase point for a three-component order parameter ($L = O_h$). The phase labels corresponding to (1)–(6) are ringed by circles. The solid lines are second-order transition lines; lines of first-order transitions between nonsymmetric phases are shown by dashed lines, and the stability boundaries of phases by dashed-dotted lines.

can assume that, in the substitution, there is simply a change in a certain crystal-averaged characteristic. In pure $KNbO_3$ the order parameter transforms according to a vector representation of the symmetry group (O_h^1) of the paraphase, i.e., $KNbO_3$ is an intrinsic ferroelectric. Addition of tantalum leads to a uniform change in the temperatures of the ferroelectric transitions. In this situation, the tantalum concentration can be regarded as a scalar thermodynamic parameter, analogous to the temperature or pressure. Consequently, e.g., all the formulas (24)–(29) remain valid for this case, if p is replaced by x.

It follows naturally from symmetry considerations that in $KTa_xNb_{1-x}O_3$ there should exist a scalar coefficient of proportionality ν between the order parameter and the polarization of the crystal: $P_i = \nu\eta_i$; we shall assume that this coefficient has no singularities near $\Phi_1 = 0$ and $\Phi_2 = 0$. From dimensionality arguments it is obvious that the parameter ν does not appear in the final formulas describing the thermal and dielectric properties of the crystal. Also unchanged are the relations determining the phase-transition lines in the phase diagrams. In fact, the replacement of η_i by P_i in the potential (12) corresponds to the following transformation of the coefficients of the potential: $\alpha_1 \to \alpha_1'/\nu^2$, $\beta_1 \to \beta_1'/\nu^4$. For the line 1 (Fig. 1), e.g., we obtain $A_2/A_1 = A_2'/A_1' = -k_1$, for the specific-heat discontinuity on the line 1 we have $TA_1^2/2(\alpha_2 + \beta_1) = TA_1'^2/2(\alpha_2' + \beta_1')$, etc. Therefore, we can simply replace η_i by P_i in (12) and regard the coefficients in all the formulas obtained above as coefficients of the expansion of Φ in P_i.

We shall write out those relations between measurable parameters that make it possible to determine the coefficients of the thermodynamic potential. The coefficient α_1 is determined from data on the dielectric permittivity of the crystal in the paraphase ($\chi^{-1} = 2\alpha_1$). The ratio of the discontinuities in the square of the polarization in the (6)–(4) and (5)–(4) phase transitions:

$$\Delta(6,4) \equiv P_6^2 - P_4^2 = \frac{\alpha_1^2 c_{12}}{48\alpha_2^3}\left(1 - \frac{2}{9}R\right)$$

$$\Delta(5.4) \equiv P_5^2 - P_4^2 = -\frac{\alpha_1^2 c_{12}}{16\alpha_2^3}, \tag{30}$$

makes it possible to determine

$$R = \frac{9}{2}\left(1 - \frac{3\Delta(6,4)\alpha_1^2(5,4)}{\Delta(5.4)\alpha_1^2(6.4)}\right). \tag{31}$$

Here $\alpha_1(5, 4)$ is the value of α_1 at the (5) – (4) transition point,

$$\chi_\parallel^{-1}(4) - \chi_\parallel^{-1}(5) = \frac{\alpha_1^2 c_{12}}{2\alpha_2^3} = \frac{\alpha_1^2(5,4)}{2\alpha_2}u. \tag{32}$$

The relations (25) enable us to determine B_1/α_2 and B_2/α_2. The ratio α_3/α^2 is determined from any value of $\chi_\parallel^{-1}$; e.g., in the phase (5),

$$\chi_\parallel^{-1}(5) = 4\alpha_1[-1 + {}^3/_4\alpha_1(\alpha_3/\alpha_2^2 + u)]. \tag{33}$$

The coefficient ratios found (R, u, B_1/α_2, B_2/α_2 and α_3/α_2^2) make it possible to predict completely the temperature dependence of the susceptibilities in the low-symmetry phases:

$$\chi_\perp^{-1}(5) = 2\alpha_1\left(\frac{\beta_1}{\alpha_2} - \frac{\alpha_1 u}{2}\right),$$

$$\chi_\parallel^{-1}(4) = 4\alpha_1\left[-1 + \frac{3}{8}\alpha_1\left(2\frac{\alpha_3}{\alpha_2^2} + u\right)\right],$$

$$\chi_{zz}^{-1}(4) = \alpha_1\left[\frac{\beta_1}{\alpha_2} - \frac{\alpha_1 u}{2}\left(1 - \frac{1}{4}R\right)\right],$$

$$\chi_{\perp xy}^{-1}(4) = -2\alpha_1\left(\frac{\beta_1}{\alpha_2} - \frac{\alpha_1 u}{2}\right),$$

$$\chi_\parallel^{-1}(6) = 4\alpha_1\left[-1 + \frac{\alpha_1}{36}\left(27\frac{\alpha_3}{\alpha_2^2} + 9u + Ru\right)\right]. \tag{34}$$

Hence it can be seen that the number of experimentally determinable relationships considerably exceeds the number of parameter combinations introduced. Naturally, these combinations of parameters can also be determined from other relations, e.g., relations taken from (34).

The absolute values of the coefficients of the thermodynamic potential can be found if we know the absolute values of the polarization in any of the phases, or the latent heats of the transitions between the phases. In fact, the value of α_2 is determined from any one of the relations

$$P_6^2 = \frac{\alpha_1}{2\alpha_2}\left[-1 + \frac{\beta_1}{3\alpha_2} - \frac{3\alpha_3\alpha_1}{4\alpha_2^2} - \frac{\alpha_1}{4}u\left(1 + \frac{1}{9}R\right)\right],$$

$$P_4^2 = \frac{\alpha_1}{2\alpha_2}\left[-1 + \frac{\beta_1}{2\alpha_2} - \frac{3\alpha_3\alpha_1}{4\alpha_2^2} - \frac{\alpha_1}{4}u\right],$$

$$P_5^2 = \frac{\alpha_1}{2\alpha_2}\left[-1 + \frac{\beta_1}{\alpha_2} - \frac{3\alpha_3\alpha_1}{4\alpha_2^2} - \frac{\alpha_1}{4}u\right], \tag{35}$$

$$Q(5,4) = T(5.4)\frac{\alpha_1^2(5,4)}{8\alpha_2^2}\left(-\frac{A_1 u\alpha_2}{2} + B_1\right),$$

$$Q(6.4) = T(6.4)\frac{\alpha_1^2(6,4)}{24\alpha_2^2} \times \left[\frac{-\alpha_2 A_1 u}{2}\left(1 - \frac{4}{9}R\right) + B_1\right]. \tag{36}$$

The other relations from (35) and (36) can be regarded as checks.

After determining the absolute values of the coefficients it is easy to find the critical point lying on the intersection of the lines $\alpha_1 = 0$ and $\beta_1 + 2\alpha_2 = 0$.

It follows from the data of[9] on the dielectric susceptibility that the approximation linear in ΔT and Δx, which we took above in (24), is valid. The coordinates of the four-phase point for KTN are $x_0 = 0.88$ and T = 135 K. From the experimental phase diagram of[9] (Fig. 2) we find $k_1 = -625$ deg, $k_2 = 375$ deg, $k_3 = 160$ deg.

Then, according to the relations (29),

$$k_4 = 240 \text{ deg}, \quad k_5 = 105 \text{ deg}. \tag{37}$$

The temperature hysteresis of the transitions has been investigated experimentally for x = 0.8. The observed values of the hysteresis between the phases (5)

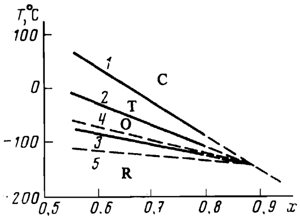

FIG. 2. T-x phase diagram of KTN. The solid lines are plotted from the data of paper [9]. The dashed lines are those obtained as a result of the calculation. The letters denote the symmetries of the corresponding phases: cubic (C), tetragonal (T), orthorhombic (O) and rhombohedral (R).

and (4) cannot be distinguished from zero experimentally, and a value ~3 deg was obtained for the (4)—(6) transition. Estimates from (37) give 0.3 and 10.8 deg, respectively, for the maximum possible values of the hysteresis. These results should correspond to the difference in the Curie temperatures defined with respect to the corresponding component of the dielectric-permittivity tensor rather than with respect to the observed hysteresis.

The analysis carried out above can be applied without change to the p-T phase diagram of $BaTiO_3$. Using the experimental data of[10], we find that the four-phase point in the p-T diagram of $BaTiO_3$ should have coordinates p = 50 kbar, T = 140 K. There should be analogous four-phase points in the phase diagrams of $KNbO_3$, $PbTi_xHf_{1-x}O_3$, etc.

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Translated by P. J. Shepherd
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