

Improper ferroelectrics

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Improper ferroelectrics are considered in the review from a unified point of view on the basis of the phenomenological Landau theory of phase transitions. In such ferroelectrics, in contrast to the ordinary ones, the order parameter of the phase transition is not the polarization but another physical quantity whose transformation properties are different from those of the polarization. Spontaneous polarization arises in the phase transition as a secondary effect. Therefore, the dielectric anomalies in the improper ferroelectrics are significantly different from the dielectric anomalies in the ordinary ferroelectrics. In particular, the temperature dependence of the permittivity does not obey the Curie-Weiss law, an electric field does not suppress the phase transition, etc. The dielectric anomalies are derived by analyzing a definite form of the thermodynamic potential with a two-component order parameter. Such an analysis turns out to be sufficient for the discussion of the available experimental data. The domain structure of the improper ferroelectrics also possesses specific properties: In particular, there exist domains which do not differ in their polarizations. Since the loss of stability in an improper ferroelectric phase transition occurs not with respect to polarization, the soft mode in the nonpolar phase is inactive in the infrared spectrum. Other distinctive features of the phonon spectrum in the phase-transition region are also considered. The experimental data on improper ferroelectrics are discussed. For the rare-earth molybdates, the theory is in quantitative agreement with experiment. In certain other improper ferroelectrics the phase transitions are of first order and nowhere near to being of second order. The quantitative description of such transitions requires additional experimental data and further development of the theory.

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1. THERMODYNAMIC THEORY

a) Definition. The phenomenological Landau theory of phase transitions^[1], which was first applied to ferroelectric transitions by Ginzburg^[2], has been successfully used to explain the dielectric anomalies and other characteristics of quite a number of ferroelectrics (see, for example,^[3,4]). The role of order parameter in the Ginzburg theory is played by polarization. There can, however, be ferroelectric phase transitions for which the polarization is not the order parameter. This possibility was first pointed out by Indenbom^[5].

A phase transition is called ferroelectric if spontaneous polarization arises in the transition. But it does not still follow from this that the polarization should be the order parameter of the ferroelectric transition—as a matter of fact, a quantity which is not the order parameter can arise in a phase transition. For example, the transition of barium titanate from the cubic to the tetragonal phase is accompanied by spontaneous deformation of the crystal. The order parameter here, however, is polarization, since its appearance completely accounts for the reduction in symmetry that accompanies the phase transition, while the appearance of the strain only partially accounts for this reduction. Indeed, if we polarize the cubic phase along a cubic edge, we obtain a tetragonal phase of the same symmetry as the experimentally observed phase, even when the crystal is clamped. If, on the other hand, the cubic phase is deformed, we obtain a tetragonal phase of higher symmetry: any uniform deformation preserves the center of inversion, which is absent in the tetragonal phase of barium titanate, since the phase is polar (Fig. 1). The spontaneous strain that arises in barium titanate is a consequence of the spontaneous polarization, and is a

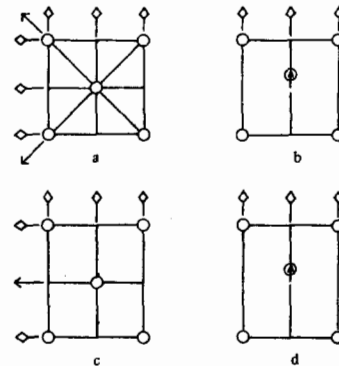


FIG. 1. Schematic representation of the unit cell of an ordinary ferroelectric (barium titanate): a) The initial cubic phase; b) after a distortion describable by a polarization order parameter; c) after its deformation; d) the tetragonal phase.

second-order effect (the components u_{ij} of the strain tensor and the polarization vector P_i are connected by relations of the form $u_{zz} \sim P_z^2$).

It is also natural for spontaneous polarization to arise in a phase transition as a second or higher order effect accompanying a more complicated change in the crystal (or magnetic) structure of a substance. The order parameter in this case is not the polarization, but a quantity having another physical meaning. If now we polarize the initial phase of the crystal in the requisite direction, we obtain a polar phase of symmetry higher than that of (and therefore structurally different from) the phase that arises in the phase transition (Fig. 2). In other words, the transition is not to the maximal polar subgroup of the space group of the initial phase^[5].

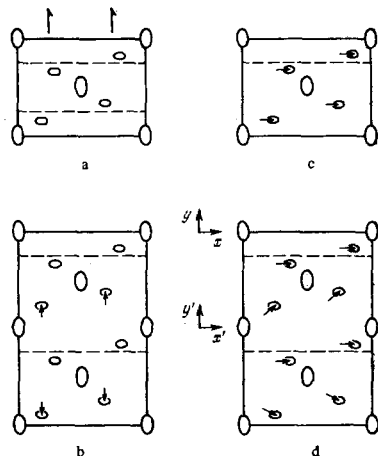


FIG. 2. Schematic representation of the unit cell of an improper ferroelectric (the phase transition $C_{2h}^5 \leftrightarrow C_2^2$): a) The initial phase; b) after a distortion describable by the order parameter; c) after its polarization along the x axis; d) the asymmetric phase. The order parameter is proportional to the ionic displacements in Fig. b). The pattern of possible displacements is simplified. The ions are assumed to be undeformable. The phases in Figs. a) and c) have a higher symmetry than the phases in Figs. b) and d). When we go over from the coordinate system (x, y) to the system (x', y') (which is equivalent to choosing a different unit cell), the signs of the ionic displacements along the y axis change, while those of the displacements along the x axis remain unchanged. It follows from this that the polarization is proportional to the square of the order parameter.

Ferroelectric phase transitions for which the order parameter is not the polarization, but a quantity having another physical meaning and possessing other transformation properties (see Sec. b), are called improper ferroelectric phase transitions. Ferroelectrics with such transitions are called improper¹⁾ ferroelectrics. Improper ferroelectrics differ significantly in many of their properties (dielectric anomalies, characteristics of the phonon spectrum near the transition point, the nature of the twinning, etc.) from the ordinary ferroelectrics.

Notice that if the polarization and some other quantity are linearly related, then they can arise in a phase transition as effects of the same order. Which of the quantities in this case can be appropriately regarded as the order parameter is usually determined from additional considerations. Even if such a quantity does not turn out directly to be the polarization—for example, in potassium dihydrophosphate it is the degree of proton ordering—the phase transition should not be classified as an improper transition. Indeed, the quantity playing the role of order parameter possesses the same transformation properties as the polarization, the transition is to the maximal polar subgroup of the symmetry group of the initial phase, and the dielectric anomalies and the other properties are essentially the same as in the case when the role of order parameter is played directly by the polarization.

The existence of improper ferroelectric phase transitions was theoretically predicted relatively long ago^[5]. An example of such a transition can actually be found in Lyubarskii's book^[7], although the distinctive features of the transition are not pointed out. In^[5] the main attention was given to the problems of symmetry. The thermodynamic theory of the dielectric anomalies of improper ferroelectrics was developed in^[6]. The first ferroelectric which, on the

basis of experimental data, could safely be classified as an improper ferroelectric was gadolinium molybdate^{[9,10] 2)}. At present, quite a number of improper ferroelectrics are known. It is therefore quite opportune to consider their basic properties in greater detail and to compare the theoretical results with the experimental data. It is natural in doing this to lay emphasis on the phenomenological theory, which is based on the Landau theory of phase transitions^[11]—it enables us to consider from a unified standpoint the most characteristic properties of the improper ferroelectrics³⁾.

b) The order parameter. The crystal and magnetic structures of a crystal are respectively determined by the charge- and current-density functions $\rho(\mathbf{r})$ and $\mathbf{j}(\mathbf{r})$. In a phase transition, the symmetry of the crystal changes, i.e., the symmetry of the function $\rho(\mathbf{r})$ or $\mathbf{j}(\mathbf{r})$ changes. The order parameter in the Landau theory is the quantity that characterizes the change in either function. It is convenient to represent a change in crystal structure⁴⁾ as the result of a sublattice displacement (a displacive type of transition), or as some ordering (an order-disorder type of transition). The (order) parameter of the transition is then the quantity characterizing the sublattice displacement (see Chap. 2) or the degree of ordering.

However, in the phenomenological theory of phase transitions, the specific physical meaning of the order parameter is not important, i.e., it does not matter which atoms are displaced or ordered and in what manner. Only the transformation properties of the order parameter (i.e., how it transforms under the symmetry operations of the initial phase) are important.

The order parameter transforms according to one of the irreducible representations of the symmetry group of the initial phase of the crystal. The number of components of the order parameter is equal to the dimensionality of the corresponding representation. The irreducible representation in question, if it is multidimensional, can, generally speaking, be responsible for transitions to several phases (of different symmetries). Actually, the phase that corresponds to the minimum of the thermodynamic potential at the given values of the crystal constants is realized.

Notice that in all the presently known improper ferroelectric phase transitions the translational symmetry of the crystal changes. This means that the (order) parameter of the phase transition is not invariant under certain translations, i.e., it transforms according to one of the irreducible representations of the space symmetry group of the initial phase. There are, however, improper ferroelectric phase transitions that do not change the translational symmetry of the crystal^[5]. The order parameter in this case transforms according to one of the irreducible representations of the point group of the initial phase of the crystal, i.e., it is a tensor quantity.

c) The thermodynamic potential. The Landau phenomenological theory is based on the expansion of the thermodynamic potential in a power series in the components of the order parameter and other physical quantities. The thermodynamic potential can depend only on the invariant combinations of the indicated quantities. The specific form of these invariants is determined by the transformation properties of the order parameter and the other quantities, i.e., by those representations of the symmetry group of the initial phase of the crystal

according to which they transform. Let us first consider the possible dependence of the thermodynamic potential on the components of the order parameter.

The case of the one-component order parameter is, from the point of view of the improper ferroelectric phase transition, uninteresting (see Sec. d). Let us discuss in detail the case of the two-component order parameter (which transforms according to a two-dimensional irreducible representation). Let us denote the components by η and ξ . To describe the presently available experimental data on the improper ferroelectrics (see Chap. 3), it is in practice sufficient to consider the two forms of the thermodynamic potential respectively investigated in ^[8,12,13]:

$$\Phi = \frac{\alpha}{2}(\eta^2 + \xi^2) + \frac{\beta_1}{4}(2\eta\xi)^2 + \frac{\beta_2}{4}(\eta^2 - \xi^2)^2 + \frac{\gamma}{6}(\eta^2 + \xi^2)^3 + \frac{\delta}{8}(2\eta\xi)^4, \quad (1)$$

$$\Phi = \frac{\alpha}{2}(\eta^2 + \xi^2) + \frac{\beta_1}{4}(2\eta\xi)^2 + \frac{\beta_2}{4}(\eta^2 - \xi^2)^2 + \frac{\beta_3}{4}2\eta\xi(\eta^2 - \xi^2) + \frac{\gamma}{6}(\eta^2 + \xi^2)^3. \quad (2)$$

In the expressions (1) and (2) we give the invariants essential to what follows—in particular, we give only one sixth-order and one eighth-order (1) invariants. Allowance for the other sixth- and eighth-order, as well as for higher order, invariants will practically not change the results.

Let us explain how the expressions (1) and (2) are obtained. There are no first-order invariants in η and ξ , since by implication the order parameter cannot be an invariant quantity ^[1]. There is only one second-order invariant for any irreducible representation ^[11]: $\eta^2 + \xi^2$. There can be one, two (1), and three (2) fourth-order invariants in η and ξ .

To show this, let us consider the representation according to which the three quantities η^2 , $2\eta\xi$, and ξ^2 transform. This is a three-dimensional representation (called the symmetrized square of the original representation), which is reducible, since it must contain the unit representation according to which the quantity $\eta^2 + \xi^2$ transforms. To the unit representation corresponds the fourth-order invariant in η and ξ : $(\eta^2 + \xi^2)^2$. The remaining two-dimensional representation (its basis functions are $2\eta\xi$ and $\eta^2 - \xi^2$) may be either irreducible or reducible. If it is irreducible, then to it corresponds one invariant $(2\eta\xi)^2 + (\eta^2 - \xi^2)^2 = (\eta^2 + \xi^2)^2$, which coincides with the previously obtained invariant. Thus, there is only one fourth-order invariant in η and ξ . This case (to it corresponds several different possible forms of the thermodynamic potential ^[14]) will not be considered below (see Sec. d). If the two-dimensional representation is reducible, then it is reducible into two one-dimensional representations, which may be different or equivalent. If they are different, then to one of them will correspond the invariant $(2\eta\xi)^2$, and to the other the invariant $(\eta^2 - \xi^2)^2$. In all, however, there will be two linearly independent fourth-order invariants in η and ξ , see the expression (1). If the one-dimensional representations are equivalent, then there will clearly be another invariant $2\eta\xi(\eta^2 - \xi^2)$, giving in all three linearly independent fourth-order invariants in η and ξ (see the expression (2)). This exhausts all the possible cases for the fourth-order invariants.

As can be shown, the two thermodynamic potentials (1) and (2) cannot contain odd-order—in particular, third-order—invariants.

Order parameters having three or more components will not be considered here. Although improper ferroelectric phase transitions with six-component order

parameters are known, these transitions can in fact be described with the aid of two-component order parameters (see Sec. b of Chap. 3).

d) Mixed invariants. In order to investigate the dielectric anomalies peculiar to the improper ferroelectrics, it is necessary to take into account the dependence of the thermodynamic potential on the components P_i of the polarization vector. The most reliable experimental data available are for those improper ferroelectric phase transitions that give rise to spontaneous polarization along only one crystallographic axis. Therefore, we shall henceforth restrict ourselves to the consideration of only one polarization-vector component P_i (e.g., P_z , which will be denoted by P), which transforms according to a one-dimensional representation of the symmetry group of the initial phase of the crystal.

The second-order invariant in P has the form P^2 ; in contrast to the ordinary ferroelectrics, the higher-order invariants are not important here. Let us discuss in greater detail the mixed invariants, which simultaneously depend on P and the components of the order parameter. Of primary interest are those invariants into which P enters linearly—they are precisely the terms that are responsible for the appearance of the spontaneous polarization in the phase transition ^[5].

Let us first show that an improper ferroelectric phase transition cannot have a one-component order parameter. Indeed, otherwise the combination ηP , where η is the order parameter, will be the only possible mixed invariant linear in P . The presence of such an invariant will imply that η and P transform according to one and the same one-dimensional representation, i.e., that they possess the same transformation properties. The ferroelectric phase transition will, consequently, not be an improper transition (see Sec. a).

Let us consider the two-component order parameter (η, ξ) . There are no mixed invariants linear in η or ξ . (The contrary would imply that η and ξ transform in the same way as the components P_i of the polarization vector.) The mixed invariants that are quadratic in η and ξ may have the form $2\eta\xi P$ and $(\eta^2 - \xi^2)P$.

In the case of the thermodynamic potential (1), when the quantities $2\eta\xi$ and $\eta^2 - \xi^2$ transform according to different one-dimensional representations, we can have only one of these invariants—either $2\eta\xi P$ or $(\eta^2 - \xi^2)P$. The two possibilities are equivalent, since the corresponding thermodynamic potentials are transformed into each other by making the change of variables: $\eta' + \xi' = \sqrt{2}\eta$ and $\eta' - \xi' = \sqrt{2}\xi$.

Thus, to allow for the dependence of the thermodynamic potential on P and E , we must add to the expression (1) the terms

$$\frac{\kappa}{2} P^2 + 2a\eta\xi P - PE + \frac{\kappa'}{2} Q^2 + a'(\eta^2 - \xi^2)Q, \quad (3)$$

where E is the strength of the electric field along P , and Q is some tensor component (the introduction of Q is necessary for what follows). In particular, Q can be another component of the vector P_i , the other component being, of course, P .

In the case of the thermodynamic potential (2), when the quantities $2\eta\xi$ and $\eta^2 - \xi^2$ transform according to equivalent one-dimensional representations, the presence of the mixed invariant $2\eta\xi P$ implies at the same time the presence of the mixed invariant $(\eta^2 - \xi^2)P$.

Thus, it is necessary to add to the expression (2) the terms

$$\frac{\kappa}{2} P^2 + 2a_1 \eta \xi P + a_2 (\eta^2 - \xi^2) P - PE. \quad (4)$$

In the case of the thermodynamic potential (1), it may also be that there are no mixed invariants that are quadratic in η and ξ , but there is one that is of fourth order in η and ξ : $2\eta\xi(\eta^2 - \xi^2)P$. The corresponding improper ferroelectric phase transitions will not be considered.

When the quantities $2\eta\xi$ and $\eta^2 - \xi^2$ transform according to a two-dimensional irreducible representation (one invariant that is of fourth order in η and ξ ; see Sec. 2), the mixed invariant that is quadratic in η and ξ can only be of the type $2\eta\xi P_x + (\eta^2 - \xi^2)P_y$. It exists if the components P_x and P_y transform according to the same two-dimensional irreducible representation. Spontaneous polarization arises in the corresponding ferroelectric transition along two crystallographic axes. Such a case, as has already been noted, will not be considered.

e) The phases and phase diagrams. It is convenient, when investigating the thermodynamic potentials (1), (3) or (2), (4), to go over in the (η, ξ) plane to the polar coordinates ρ and φ :

$$\eta = \rho \cos \varphi, \quad \xi = \rho \sin \varphi. \quad (5)$$

Then the expressions (1), (3) and (2), (4) assume respectively the following forms:

$$\Phi = \frac{\alpha}{2} \rho^2 + \frac{\beta_1}{4} \rho^4 \sin^2 2\varphi + \frac{\beta_2}{4} \rho^4 \cos^2 2\varphi + \frac{\gamma}{6} \rho^6 + \frac{\delta}{8} \rho^8 \sin^4 2\varphi + \frac{\kappa}{2} P^2 + aP\rho^2 \sin 2\varphi - PE + \frac{\kappa'}{2} Q^2 + a'Q\rho^2 \cos 2\varphi, \quad (6)$$

$$\Phi = \frac{\alpha}{2} \rho^2 + \frac{\beta_1}{4} \rho^4 \sin^2 2\varphi + \frac{\beta_2}{4} \rho^4 \cos^2 2\varphi + \frac{\beta_3}{4} \rho^4 \sin 2\varphi \cos 2\varphi + \frac{\gamma}{6} \rho^6 + \frac{\kappa}{2} P^2 + a_1 P \rho^2 \sin 2\varphi + a_2 P \rho^2 \cos 2\varphi - PE. \quad (7)$$

Let us consider in detail the thermodynamic potential (6) [9], neglecting, for the time being, the eighth-order invariant (it will be taken into account below, in Sec. g). The equilibrium values of ρ , φ , and P are determined from the conditions for a minimum of the thermodynamic potential (6). The system of equations $\partial\Phi/\partial\rho=0$, $\partial\Phi/\partial\varphi=0$, and $\partial\Phi/\partial P=0$ has three different types of solutions, which correspond to three phases—the initial 0 and two asymmetric phases 1 and 2:

$$0 \quad \rho=0, \quad P=-\frac{1}{\kappa} E, \quad Q=0; \quad (8)$$

$$1 \quad \rho^2 = \frac{1}{2\gamma} \{-\beta_1 + [\beta_1^2 - 4\gamma(\alpha \mp e)]^{1/2}\}, \quad \sin 2\varphi = \mp 1 \quad (\eta = \mp \xi), \\ P = \pm \frac{a}{\kappa} \rho^2 + \frac{1}{\kappa} E, \quad \chi = \frac{1}{\kappa} \left(1 + \frac{\Delta}{[\beta_1^2 - 4\gamma(\alpha \pm e)]^{1/2}}\right), \quad Q=0; \quad (9)$$

$$2 \quad \rho^2 = \frac{1}{2\gamma} \{-\beta_2 + [\beta_2^2 - 4\gamma\alpha]^{1/2}\}, \quad \sin 2\varphi = -\frac{e}{\beta_2} \\ (\eta\xi = -\frac{e}{2\beta}), \quad P = \frac{1}{\kappa} \left(1 + \frac{\Delta}{\beta}\right) E, \quad Q = -\frac{a'}{\kappa'} \rho^2 \cos 2\varphi; \quad (10)$$

here we have used the notations

$$\beta = \beta_1 - \beta_2, \quad \beta_1 = \beta_1' - \Delta, \quad \beta_2 = \beta_2' - \Delta', \quad \Delta = \frac{2a^2}{\kappa}, \quad \Delta' = \frac{2a'^2}{\kappa'}, \quad e = \frac{2\alpha}{\kappa} E. \quad (11)$$

The expression for the dielectric susceptibility $\chi = dP/dE$ is given only in (9); it is obvious in (8) and (10). The phase 1 is polar, while the phase 2 is nonpolar. The phase 2 could also be polar (see the text after the formula (3)). Such a case is considered in [15].

Which of the solutions (8)–(10) corresponds to the minimum of the thermodynamic potential, i.e., which

of the phases is stable, is determined by analyzing the second derivatives of the thermodynamic potential (6). Such an analysis leads to the following inequalities, which characterize the limits of stability of the phases:

$$\left. \begin{array}{l} 0 \quad \alpha \geq \alpha_0, \\ 1 \quad \alpha \leq \alpha_0 (\beta_1 > 0), \quad \alpha \leq \alpha_0 + \frac{\beta_1^2}{4\gamma} \quad (\beta_1 < 0), \quad \beta \leq \beta_-, \quad \beta \geq \beta_+ \quad (\beta > 0), \\ 2 \quad \alpha \leq \beta_2^2/4\gamma, \quad \beta \geq \beta_-, \end{array} \right\} \quad (12)$$

where

$$\alpha_0 = |e|, \quad \beta_{\pm} = \frac{|e|}{2\alpha} \{-\beta_2 \pm [\beta_2^2 - 4\gamma\alpha]^{1/2}\}.$$

Notice that the number of different solutions in the phase 1, (9), and in the phase 2, (10), is equal to four ($\varphi = \pi/4, 3\pi/4, 5\pi/4, \text{ and } 7\pi/4$ in the phase 1 and $\varphi = 0, \pi/2, \pi, \text{ and } 3\pi/2$ in the phase 2 for $E=0$). Each of the four solutions corresponds (for $E=0$) to the same value of the thermodynamic potential (6). This means that in the asymmetric phases 1 and 2 the crystal can be divided into four types of domains.

Let us consider the thermodynamic potential (7) [13]. In contrast to the thermodynamic potential (6), there will now be two different types of solutions, which correspond to two phases—the initial phase (8) and one asymmetric phase. The solutions for the asymmetric (polar) phase have for $E=0$ the form

$$\rho^2 = \frac{1}{2\gamma} \{-\beta + [\beta - 4\gamma\alpha]^{1/2}\}, \quad (13a)$$

$$\beta = \beta_1 \sin^2 2\varphi + \beta_2 \cos^2 2\varphi + \beta_3 \sin 2\varphi \cos 2\varphi, \quad (13b)$$

$$\lg 4\varphi = \frac{\beta_3}{\beta_3 - \beta_1}, \quad P = -\frac{a_1}{\kappa} \rho^2 \sin 2\varphi - \frac{a_2}{\kappa} \rho^2 \cos 2\varphi, \quad (13c)$$

where

$$\beta_1 = \beta_1' - \frac{2a_1^2}{\kappa}, \quad \beta_2 = \beta_2' - \frac{2a_2^2}{\kappa}, \quad \beta_3 = \beta_3' - \frac{4a_1 a_2}{\kappa}.$$

It is impossible to obtain the solutions for $E \neq 0$ in explicit form. In all, there are eight different solutions to (13). However, the number of stable solutions to (13) for any fixed values of the coefficients of the thermodynamic potential (7) is equal to four. Thus, in the asymmetric phase (13), there can be four different domains (as in the phases 1 and 2).

Let us emphasize that the thermodynamic potentials (6) and (7) do not have the same number of asymmetric phases. In the case (6) there are (as will be shown below in Sec. g) several—three: 1, 2, and 3, to be exact—asymmetric phases, while in the case (7) there is one. The latter is due to the fact that the two-dimensional representation according to which, in the case (7), the components η and ξ of the order parameter transform is mathematically reducible and decomposes into two one-dimensional complex conjugate representations. Notice that since different forms of the thermodynamic potential (e.g., (6) and (7)) correspond to different types of irreducible representations, the number of phases could be found not from the thermodynamic potential, but directly by analyzing the properties of the matrices corresponding to the irreducible representations. Such an approach was essentially used in [14].

f) The dielectric anomalies. Let us consider the dielectric anomalies arising in the ferroelectric phase transition $0 \rightarrow 1$. This transition is a second-order transition if $\beta_1 > 0$ (11), and a first-order transition if $\beta_1 < 0$. When the transition is of second order, we can neglect in the thermodynamic potential (6) the sixth-order invariant. The expressions (8) for ρ^2 and χ then get simplified and assume the form

$$1 - \rho^2 = -\frac{\alpha \mp e}{\beta_1}, \quad \chi = \frac{1}{\kappa} \left(1 + \frac{\Delta}{\beta_1} \right). \quad (14)$$

Figure 3 shows the temperature anomalies in P and χ given by (14) and (9). They were obtained under the usual assumptions made in the Landau theory [1] that only one coefficient α in the thermodynamic potential (6) depends on the temperature T and, besides, linearly: $\alpha = \tilde{\alpha}(T - \theta)$. Figure 3, like Figs. 4 and 8 below, does not show the metastable solutions (14) and (9) for $E \neq 0$. The dependence of P on E in the phase 1 ($\alpha < 0$) has the form of a hysteresis loop whose maximum width is determined by the value $E = |\kappa\alpha\beta/2a\beta_2|$.

It can be seen from Fig. 3 and the relations (14) and (9) that the phase transition under consideration differs from the usual ferroelectric transition in possessing the following peculiarities. The spontaneous polarization P_S depends on the temperature T not as $|T - \theta|^{1/2}$, but linearly: $\sim |T - \theta|$. In an electric field E, the transition is not smeared out, but maintains its sharpness, shifting toward the higher-temperature region. The dielectric susceptibility χ changes discontinuously at the transition temperature θ , and does not obey the Curie-Weiss law.

Let us explain these properties. The linear dependence $P_S(T)$ follows (as has already been noted in [5]) simply from the fact that the mixed invariant $\eta\xi P$ in the thermodynamic potential (6) is linear in P and quadratic in η and ξ . Therefore, $P_S \sim \eta_S \xi_S$, and both η_S and ξ_S vary with temperature as $|T - \theta|^{1/2}$ (i.e., as, according to the Landau theory, the components of the order parameter of any second-order phase transition vary). The phase transition maintains its sharpness in an electric field, since in the improper ferroelectrics, in contrast to the ordinary ones, the field does not remove the difference in symmetry of the phases (see Sec. a). The dependence of χ on T does not obey the Curie-Weiss law, since χ is not determined, as in ordinary ferroelectrics, by a coefficient α that vanishes at the phase transition point. The discontinuous increase of χ at the transition point is due to the fact that η and ξ , under the action of E, do not change in the initial phase, but change in the polar phase, making an additional contribution to the polarization.

Let us emphasize that the above-considered dielectric anomalies in the improper ferroelectrics are similar to, for example, the elastic anomalies in the ordinary ferroelectrics that are not piezoelectric in the initial phase. Indeed, the thermodynamic potentials contain mixed invariants $\eta\xi P$ and, for example, $P_x P_y u_{xy}$, respectively, that are identical in form.

It follows, in particular, from this that the complex dielectric susceptibility in the polar phase 1 is described by an expression similar to the Landau-Khalatnikov formula [16]:

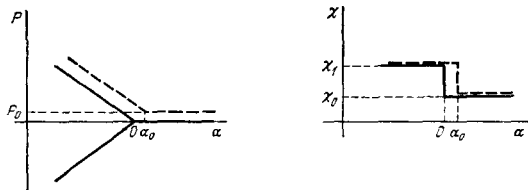


FIG. 3. The dependence of P and χ on T ($\alpha = \tilde{\alpha}(T - \theta)$) for the second-order ($\beta_1 > 0$) phase transition $0 \leftrightarrow 1$ ($\beta < 0$). The dashed lines represent the dependences for $E \neq 0$; $\alpha_0 = |e|$, $P_0 = |E|/\kappa_0$, $\chi = 1/\kappa$, $\chi_1 = [1 + (\Delta/\beta_1)]/\kappa$.

$$\chi = \chi' + i\chi'' = \frac{1}{\kappa} \left(1 + \frac{\Delta/\beta_1}{1 - i\omega\tau} \right), \quad \tau = \frac{\nu}{2|\alpha|}, \quad (15)$$

where ω is the frequency, τ the relaxation time, and ν the coefficient of friction, i.e., the coefficient in front of $d\rho/dt$ in the equation of motion. In deriving the formula (15) we neglected in the equations of motion the inertial terms $\sim d^2\rho/dt^2$ and $\sim d^2P/dt^2$ (the formula (14) is valid for not too high frequencies), as well as the dissipative term $\sim dP/dt$. At low frequencies ($\omega \ll 1/\tau$) the dielectric losses χ'' are proportional to the relaxation time τ , which increases, as we approach the transition temperature θ , as $|T - \theta|^{-1}$ [17].

The dependence on ω and T of the complex elastic compliances corresponding to those strain tensor components that enter linearly into the mixed invariants that are quadratic in η and ξ is similar to (15).

Allowance for fluctuations in the order parameter (see Sec. h) leads to an additional temperature and frequency dependence of χ . Near θ , in first-order perturbation theory, the variation of χ'' with T for low frequencies ($\omega \ll 1/\tau$) has the form $\chi'' \sim |T - \theta|^{-3/2}$ in both phases [17].

For $\beta_1 < 0$, (11), the phase transition $0 \leftrightarrow 1$ is a first-order transition. The temperature anomalies of P and χ and the dependence P(E) at different T are shown in Figs. 4 and 5.

Let us emphasize the difference between such anomalies and the anomalies that arise in first-order phase transitions in ordinary ferroelectrics. The spontaneous polarization P_S depends on T in the same manner as P_S^2 depends on T in the ordinary ferroelectrics. The discontinuity in P_S at the transition point remains unchanged in an electric field, or, more precisely, it changes slightly, depending on E only quadratically (this variation can be found by allowing in the thermodynamic potential for mixed invariants of higher order in P, e.g., for invariants of the form $(\eta^2 + \xi^2)P^2$). Similarly, the thermal hysteresis depends only weakly

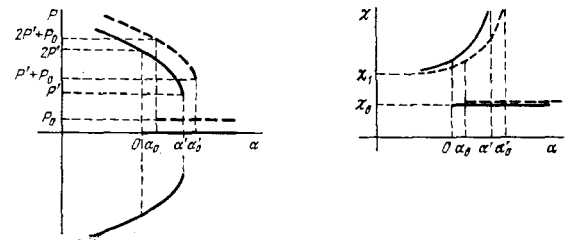


FIG. 4. Dependence of P and χ on T ($\alpha = \tilde{\alpha}(T - \theta)$) for the first-order ($\beta_1 < 0$) phase transition $0 \leftrightarrow 1$ ($\beta < 0$). The dashed lines represent the dependences for $E \neq 0$; $\alpha' = \beta_1/4\alpha$, $\alpha_0 = |e|$, $\alpha'_0 = \alpha' + \alpha_0$, $P_0 = |E|/\kappa$, $P' = |a\beta_1|/2\kappa\gamma$, $\chi_0 = 1/\kappa$, $\chi_1 = [1 + (\Delta/\beta_1)]/\kappa$.

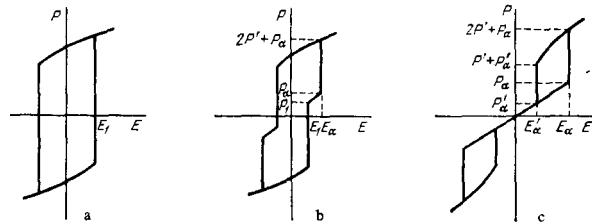


FIG. 5. Dependence of P on E at different T for the first-order ($\beta_1 < 0$) phase transition $0 \leftrightarrow 1$ ($\beta < 0$) (see Fig. 4): a) $\alpha < (7/8)\alpha'$; b) $(7/8)\alpha' < \alpha < \alpha'$; c) $\alpha' < \alpha$, $\alpha' = \beta_1/4\gamma$, $E_\alpha = \kappa\alpha/2|a|$, $E'_\alpha = \kappa(\alpha - \alpha')/2|a|$, $E_1 = \kappa|\beta|(-\beta_2 + [\beta_2^2 - 4\gamma\alpha]^{1/2})/4|a|\gamma$, $P_\alpha = E_\alpha/\kappa$, $P'_\alpha = E'_\alpha/\kappa$, $P_1 = E_1/\kappa$, and $P' = |a\beta_1|/2\kappa\gamma$.

(quadratically) on E . As the temperature T increases, the double hysteresis loop in the phase 0 (see Fig. 5) does not vanish, but shifts toward the region of higher E values, slightly changing in width in the process.

The $\chi(T)$ dependence does not, in general, exist in the initial phase 0, and in the polar phase 1 the closer the transition is to being a second-order phase transition, i.e., the smaller the coefficient β_1 is, the more important this dependence is. Near the tricritical point, where the first- and second-order phase transition lines meet, $\chi \sim |T - \theta|^{-1/2}$ and $P \sim |T - \theta|^{1/2}$ in the polar phase. The temperature dependence of χ in the polar phase will also be pronounced in the case of a second-order phase transition if the transition is nearly of first order, i.e., if the coefficient β_1 is small but greater than zero (the dependence $\chi(T)$ shown in Fig. 3 was computed without allowance for γ , i.e., for large values of β_1).

The dielectric anomalies arising in the ferroelectric transition between the phases (8) and (13)—a transition which is described by the thermodynamic potential (7)—are similar^[13] to the above-considered anomalies arising in the phase transition $0 \leftrightarrow 1$. Therefore, the results of the corresponding computations, which, moreover, are very unwieldy, are not given here (see^[13]).

The dielectric anomalies were considered above because they are precisely the properties that typify ferroelectric phase transitions. The anomalies in the other quantities are not typical of these transitions. Only the obvious difference between the electric-field (polarization) dependences of these quantities in the ordinary and improper ferroelectrics is of interest. Indeed, in the ordinary ferroelectrics the field directly influences the order parameter, i.e., the polarization (it is a force conjugate to the order parameter), while this is not so in the improper ferroelectrics. Therefore, the relation between the quantities (e.g., those characterizing the elastic or optical properties) and the polarization induced by the field in the paraelectric phase, and the relation between the spontaneous values of those same quantities and the spontaneous polarization in the polar phase in the improper ferroelectrics, in contrast to the ordinary ones, are different. This circumstance can serve as an additional experimental confirmation of the fact that a given ferroelectric is an improper ferroelectric.

For example, the components of the strain tensor u_{ij} and the polarization vector P_i are connected in the paraelectric phase by relations of the form $u = \lambda P + qP^2$, where λ and q are the corresponding piezoelectric and electrostriction coefficients. In the ordinary ferroelectrics, the same relations remain valid for the spontaneous values u_S and P_S in the polar phase. In the polar phase of the improper ferroelectrics, the quantities u_S are, in the final analysis, determined by the spontaneous values of the components of the order parameter. It is possible here to express u_S in terms of P_S , but this relation will be different from $u_S = \lambda P_S + qP_S^2$. If the component u is linearly related to P : $u = \lambda P + R\eta\xi$, then in the paraelectric phase, in which E induces P and $\eta = \xi = 0$, we shall have $u = \lambda P$; in the polar phase, $u_S = \lambda P_S + R\eta_S\xi_S$, $P_S = (2|a|/\kappa)\eta_S\xi_S$, and therefore $u_S = \lambda'P_S$, where $\lambda' = \lambda + \kappa R/2|a|$. If the component u is not linearly related to P : $u = qP^2 + R'(\eta^2 + \xi^2)$, then in the paraelectric phase $u = qP^2$, while in the polar phase $u_S = qP_S^2 + R'(\eta_S^2 + \xi_S^2) = qP_S^2 + \lambda''P_S$, where $\lambda'' = \kappa R'/|a|$.

Similar relations are clearly valid for the permittivity tensor ϵ_{ij} (in place of u_{ij}), which describes the optical properties of the crystal.

As another example, we can cite the anomaly in the relaxation sound absorption coefficient Γ , which is proportional to τ , the order-parameter relaxation time. In the ordinary ferroelectrics, $\tau \sim \chi$ and, consequently, $\Gamma \sim \chi$. For the improper ferroelectrics, such a relation does not exist between Γ and χ .

g) Phase transitions between asymmetric phases. The theory of the ordinary ferroelectrics with several polar axes (e.g., barium titanate) considers transitions not only from the paraelectric to a polar phase, but between the various polar phases as well. Similarly, it is expedient in the theory of the improper ferroelectrics to consider transitions between different asymmetric phases.

The phase transition $2 \leftrightarrow 1$ is a ferroelectric transition (the phase 2 is nonpolar), but it differs in its properties from the ordinary (and from the improper) ferroelectric transitions. Let us consider it in greater detail.

Let us point out that the solutions (9), $\sin 2\varphi = \mp 1$, corresponding to the phase 1 cannot be arrived at from the solutions (10), $\sin 2\varphi = 0$ (for $E = 0$), corresponding to the phase 2 by an infinitesimal change in the quantity φ . The phase transition $2 \leftrightarrow 1$ can only be a first-order transition. It also follows from this that the symmetry group of the phase 1 is not a subgroup of the symmetry group of the phase 2, and vice versa. Therefore, we cannot introduce a characteristic parameter for the phase transition $2 \leftrightarrow 1$, i.e., we cannot consider it on the basis of the Landau theory with the phase 2 or 1 as the initial phase. We can, however, as the initial phase for the transition $2 \leftrightarrow 1$, take the phase 0 (the phase 0 may not be experimentally observable).

The quantity φ changes discontinuously in the phase transition $2 \leftrightarrow 1$. The thermodynamic potential (6) with up to sixth-order (in the order-parameter components η and ξ) invariants contains only $\sin^2 2\varphi$. Therefore, it is natural to take into account the eighth-order invariant with the coefficient δ (see (6)), which contains $\sin^4 2\varphi$. And, consequently, allowance for this invariant will significantly affect the results.

If in the thermodynamic potential (6) the coefficient $\delta > 0$, then besides the solutions (8)–(10) corresponding to the phases 0, 1, and 2 there will be come more solutions corresponding (for $E = 0$) to a new asymmetric (polar) phase 3^[12]:

$$\begin{aligned} 3 \quad \rho^2 &= \frac{1}{2\gamma} \{-\beta_2 + [\beta_2 - 4\gamma\alpha]^{1/2}\}, \quad \sin^2 2\varphi = \frac{|\beta|}{8\alpha^2} \quad (\eta \neq \xi \neq 0), \\ \rho &= -\frac{\alpha}{x} \rho^2 \sin 2\varphi, \quad \chi = \frac{1}{x} \left(1 + \frac{\Lambda}{2|\beta|}\right), \quad Q = -\frac{\alpha'}{x} \rho^2 \cos 2\varphi. \end{aligned} \quad (16)$$

Figure 6 shows the boundaries of stability of the phases 0, 1, 2, and 3 for second-order ($\beta_2 > 0$) transitions from the phase 0 in the case when $E = 0$. As can be seen from Fig. 6, the phase transition $0 \leftrightarrow 3$ can occur at only one point. For such a transition to occur, it is necessary for two quantities, ρ and φ , to become different from zero at once. For this to happen, it is, in its turn, necessary for two coefficients, α and β , of the thermodynamic potential (6) to simultaneously change their signs, which determines the point in the (α, β) plane and, consequently, the point in the pressure-tempera-

ture plane. For the first-order ($\beta_2 < 0$) transitions from the phase 0, there is a line of demarcation between the phases 3 and 0.

Thus, the phase 3 is wedged between the phases 1 and 2. The number of different solutions (16) is equal to eight, i.e., there can be eight different domains in the phase 3. The dielectric anomalies for the $0 \leftrightarrow 3$ phase transition are similar in nature to the dielectric anomalies for the $0 \leftrightarrow 1$ transition that are shown in Figs. 3-5.

In Fig. 7, for clarity, we represent the solutions (8)-(10) and (16) for $E=0$ by points. As can be seen from this figure, the phase 3 can be reached from the phases 0, 1, and 2 through any arbitrarily small change in the quantities ρ and φ . It follows from this that the symmetry group of the phase 3 is a subgroup of the symmetry groups of all the remaining phases 0, 1, and 2, i.e., the phase 3 is the most asymmetric of the phases. By varying the coefficients of the thermodynamic potential (6), we can pass through all the points in the (ρ, φ) plane that correspond to the four phases 0, 1, 2, and 3. Therefore, allowance for higher-order invariants will not lead to the appearance of new phases.

The phase transition $2 \leftrightarrow 3$ is an ordinary ferroelectric transition. The order parameter for it, if as the initial phase we take the phase 2, is the component P. The phase transition $1 \leftrightarrow 3$ is a transition from a polar phase to a polar phase (the order parameter is the quantity Q).

If the coefficient $\delta < 0$, then the phase 3 is unstable. Therefore, passing the phase 3, the ferroelectric phase transition $2 \leftrightarrow 1$ will inevitably occur as a first-order transition. Notice that the obvious requirement that the thermodynamic potential should not have a minimum at $\rho \rightarrow \infty$ is also satisfied when $\delta < 0$ if $\delta + \delta_1 > 0$ and $\delta_1 + \delta_2 > 0$, where δ_1 and δ_2 are the coefficients attached to two other eighth-order invariants: $\delta_1(\eta^2 + \xi^2)^4/8$ and $\delta_2(\eta^2 - \xi^2)^4/8$.

The dielectric anomalies arising in the $2 \leftrightarrow 1$ ($\delta < 0$) transition are shown in Fig. 8. They are practically similar to the dielectric anomalies in the phases 2 and 1 arising in the transitions $2 \leftrightarrow 3 \leftrightarrow 1$. The dependence $P(E)$ for different T has a form similar to that shown in Fig. 5. If we set $\delta=0$, then the thermal hysteresis and the double hysteresis loop in the phase 2 will vanish in the transition $2 \leftrightarrow 1$.

h) Applicability of the Landau theory of phase transitions. It is well known that the Landau theory of phase transitions^[1] is valid only in a limited temperature range. It is not applicable both in the immediate neighborhood of, and far from, the transition point. In this theory, the thermodynamic potential is represented in the form of a power series in the order parameter η of the phase transition. It follows from the very fact of the existence of the phase transition that the coefficient α attached to η^2 changes sign at the transition point θ . All the coefficients α, β, γ , etc. of the thermodynamic potential are expanded in power series in $(T - \theta)$, and only the first terms of the expansions are considered, i.e., the simplest temperature dependence is assumed for these coefficients.

It is clear that at a point sufficiently far from the transition point we cannot limit ourselves to the first terms of the power-series expansions in $(T - \theta)$ of the coefficients α, β, γ . Furthermore, in the asymmetric

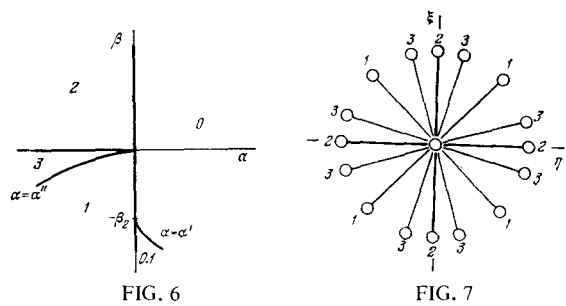


FIG. 6. Stability boundaries of the phases 0, 1, 2, and 3 ($E=0$) in the (α, β) plane for the second-order ($\beta_2 > 0$) transitions. $\alpha'' = (\beta\gamma/\delta) - (|\delta|\beta_2^2/\delta)^{1/2}$ and $\alpha' = \beta_2/4\gamma$.

FIG. 7. The solutions (8) - (10) and (16) corresponding to the phases 0, 1, 2, and 3 in the (η, ξ) plane.

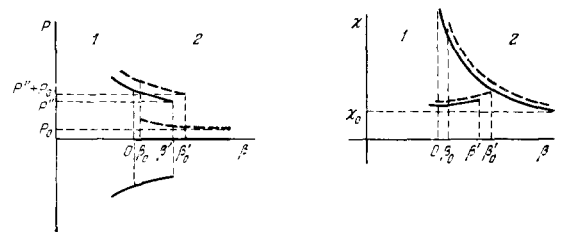


FIG. 8. The dependence of P and χ on T through $\beta = \tilde{\beta}(T - \theta)$ for the phase transition $2 \leftrightarrow 1$ ($\alpha < 0$). The dashed curves represent the dependences for $E \neq 0$. It is assumed that $\beta_2 > 0$, $\gamma = 0$, and $\delta < 0$. $\beta' = |\delta|\alpha^2/\beta_2^2$, $\beta_0 = (\Delta/\delta|E^2/2\kappa)^{1/3}$, $\beta'_0 = \beta' + \Delta\beta_2|E|/|\alpha|$, $P_0 = |E|/\kappa$, $P'' = |\alpha|/\kappa\beta_2$, and $\chi_0 = 1/\kappa$.

phase, in which the spontaneous value of η increases with $|T - \theta|$, we cannot restrict ourselves to only a few terms in the expansion of the thermodynamic potential in a power series in η . Therefore, we cannot, in particular, describe on the basis of the Landau theory pronounced first-order phase transitions, i.e., transitions in which the atomic displacements are comparable to the interatomic distances and the transition temperature T_c is, generally speaking, far from the point θ where the symmetric phase loses its stability. How wide the temperature range in which the Landau theory is valid is, strictly speaking, determined by the specific properties of the interaction in the crystal, and may be of the order of θ , or of the order of another characteristic temperature. Thus, in describing first-order transitions (or second-order ones in a sufficiently wide range of temperatures), we must take into account the specific properties of the concrete substance.

For second-order phase transitions, or for the first-order ones that are nearly of second order, the Landau theory makes definite inferences about the symmetry change that occurs in a transition; namely, the change in symmetry is described with the aid of one irreducible representation of the symmetry group of the initial phase^[1]. For a pronounced first-order phase transition, the change in symmetry can, generally speaking, be described by several irreducible representations. In other words, as a result of the loss of stability with respect to one representation, there arise such large displacements that stability with respect to another representation is lost. Such cases are apparently encountered in the improper ferroelectrics (see Secs. b and c of Chap. 3).

The Landau theory is also inapplicable in the immediate neighborhood of the transition point. This neighbor-

hood is different for different types of phase transitions. For example, it is negligibly small for transitions to the superconducting state, and encompasses in transitions to the superfluid state the entire temperature region that is of interest^[18]. For phase transitions with a change in crystal structure, to which ferroelectric transitions pertain, the temperature range in which the Landau theory is invalid can be considerable.

The physical cause of the inapplicability of the Landau theory is the spatially inhomogeneous fluctuations in the order parameter (i.e., the correlation effects)^[18,19]. They grow as the transition point is approached because of the increasing pliability of the crystal with respect to those distortions of its structure that arise in the phase transition.

Because of the fluctuations in the order parameter, the temperature dependences of the coefficients α , β , γ turn out to be more complicated than in the Landau theory. In the temperature region where the fluctuations are large, all the coefficients of the thermodynamic potential essentially depend on the temperature. At the second-order phase-transition point itself, they vanish (or become infinite). In other words, the thermodynamic potential cannot be validly expanded at the phase transition point in a power series in the order parameter, i.e., it is singular at the point itself^[1].

The fluctuations in the order parameter can also lead to a marked temperature dependence of the other coefficients of the thermodynamic potential. Correspondingly, the anomalies in the various physical quantities will change in the temperature region where the fluctuations play a major role. In the Landau theory, such quantities as, for example, the specific heat or the compressibility undergo a discontinuity in a second-order phase transition, remaining constant as the transition point is approached^[1]. Allowance for the fluctuations in the order parameter leads to the growth of these quantities according to a weak power or logarithmic law (see, for example,^[20]). As has already been noted, in improper ferroelectric transitions the anomaly in the dielectric susceptibility is similar to, for example, the anomaly in the compressibility. The fluctuation-induced changes in the anomalies of these quantities will also be similar in nature.

In crystals, spatially inhomogeneous fluctuations in the order parameter also lead to a situation in which a second-order phase transition becomes impossible; it is transformed into a first-order transition^[21]. This circumstance is due to the special role played by the inhomogeneous shear strains that arise as a result of the inhomogeneous fluctuations in the order parameter. For second-order phase transitions, the coefficient β in the thermodynamic potential should, upon allowance for the fluctuations, vanish at the same point as the coefficient α . Allowance for the shear strains leads to a case in which the coefficient β passes through zero earlier than the coefficient α . Thus, β becomes negative and, consequently, the phase transition becomes a first-order transition. The wider the temperature range in which the fluctuations are substantial, and the stronger the coupling between the strains and the order parameter, the stronger such an effect. In some cases, e.g., in ferromagnets, it is practically negligible; in others, it is important^[21]. Notice that all the known improper ferroelectric phase transitions are first-order transitions. It is not impossible that this will,

in a number of cases, be due to the fluctuations in the order parameter (see Sec. a of Chap. 3). The elucidation of this connection will require a more complete and thorough investigation of the improper ferroelectrics.

1) **The domains.** As was noted above, the polar phase 1 contains four different domains corresponding to the four equivalent (with the same value of the thermodynamic potential) solutions (9). These domains differ in the spontaneous values of the order-parameter components η and ξ (see Fig. 7). Furthermore, two of the domains differ from the other two in the sign of P . It is clear that any domain can be transformed into another by the action on it of one of those symmetry elements of the initial phase that are lost in the transition to the polar phase. Therefore, for each twin arising in the phase transition, we can find a symmetry element of the initial phase that transforms one domain of the twin into another (there may be several such elements for a given twin).

If the components of the order parameter are not tensor quantities, i.e., if they transform according to an irreducible representation of the space (and not the point) group of the initial phase, then the set of symmetry elements lost in the phase transition will contain a translation. This translation is a twinning element for the domains with identical P (domains that differ in the signs of both η and ξ corresponding to them). Such domains (they are called antiphased domains) do not differ in any of their tensor, i.e., macroscopic, properties. A given domain forms two twins with domains whose polarizations P differ in sign. The corresponding twinning elements act in like manner on P and differently on η and ξ . The energy and thickness of the boundaries of these two twins are different, and can, generally speaking, coincide only when the boundaries have certain orientations in the crystal. All the foregoing is valid for the phase (13). The phase 3, (16), contains eight different domains. These domains form translational twins (if η and ξ are not tensor quantities), twins which differ in the sign of P , in the sign of Q , and in the signs of both P and Q (in this case all the domains differ in the spontaneous values of η and ξ ; see Fig. 7).

The equilibrium domain structure in ferroelectrics is, as is well known, determined by a relation between two energies—the energy of the electric field produced by the spontaneous polarization and the energy of the domain walls. The temperature dependence of the spontaneous polarization and, consequently, of the electrostatic energy (when the crystal is not short-circuited) in the ordinary ferroelectrics is different from the dependence in the improper ferroelectrics. The temperature dependence of the domain-wall energy, on the other hand, is the same in both cases (it is the same for any twin boundaries that arise in second-order phase transitions); whence the equilibrium domain widths in the ordinary and improper ferroelectrics will vary differently with temperature.

Let us estimate the electrostatic energy for a plane-parallel plate, whose thickness is L and which is divided into domains of transverse dimension l . If $l \ll L$, then the electric field E produced by the spontaneous polarization P_s penetrates the plate to a depth $\sim l$, and has a magnitude $E \sim -4\pi P_s$. Hence we obtain for the energy per unit plate-surface area the expression

$$U_1 \sim P_s E l \sim P_s^2 l \sim \left(\frac{a}{\kappa} \rho_s\right)^2 l \sim \left(\frac{a}{\kappa} \frac{|\alpha|}{\beta_1}\right)^2 l. \quad (17)$$

For the energy per unit domain-wall surface area, we obtain

$$U_2 \sim \Phi_s d \sim |\alpha| \rho_s^2 d \sim \frac{\alpha^2}{\beta_1} d \sim \frac{|\alpha|^{3/2} \sigma^{1/2}}{\beta_1}, \quad (18)$$

where $d \sim (\sigma/|\alpha|)^{1/2}$ is the effective thickness of the domain wall and σ is the coefficient attached to gradient terms of the form $\sigma[(\nabla\eta)^2 + (\nabla\xi)^2]$ in the thermodynamic potential. The equilibrium domain dimension l_0 is determined from the condition for a minimum of the total energy $U_1 + (U_2 L/l)$ per unit plate-surface area^[17]:

$$l_0 = \left(\frac{U_2 L}{U_1 l} \right)^{1/2} \sim \frac{\alpha \beta_1^{1/2} \sigma^{1/4} L^{1/2}}{\kappa |\alpha|^{1/4}} \sim |T - \theta|^{-1/4}. \quad (19)$$

As a similar estimate shows, in the ordinary ferroelectrics, l_0 does not depend on temperature. It follows from this, in particular, that it is more complicated to obtain the equilibrium domain structure in the improper ferroelectrics than in the ordinary ones, since in order to maintain it in the improper ferroelectrics as the temperature is lowered, it is necessary that new domains be continuously formed.

As can be seen from the relation (19), l_0 increases without restriction as we approach the transition temperature θ , and although this relation is valid only when $l_0 \ll L$, we can draw from it the conclusion that in contrast to the ordinary ferroelectrics, the improper ferroelectrics can become unstable with respect to the transition to the single-domain state^[6]. Let us explain this further in the following manner. In an ordinary ferroelectric, a second-order phase transition occurs when the coefficient α in the term $\alpha P^2/2$ of the thermodynamic potential becomes equal to zero. If the crystal is not electrically short-circuited, then there arises an electric field (called a depolarization field) equal in the case of a homogeneous polarization in the plate to $-4\pi P$. It is then necessary to add to the thermodynamic potential the long-range dipole-dipole interaction energy $-PE/2$ (the electrostatic energy), and, consequently, the coefficient in front of $P^2/2$ will not be α , but $\alpha + 4\pi$. This coefficient does not vanish. Therefore, the phase transition cannot be to the single-domain state, but to a polydomain state in which the depolarization field is weak.

In the improper ferroelectrics, the energy of the depolarization field $-PE/2$ leads to a change by 4π not in the coefficient α , but in the coefficient κ in the term $\kappa P^2/2$ of the thermodynamic potential (6). Therefore, the appearance in an electrically open crystal of a single-domain state is possible upon a change in sign of α . This state is metastable, since the partition into domains is energetically advantageous.

The process of polarization reversal in the improper ferroelectrics, in comparison with the ordinary ones, does not possess obvious specific properties. Indeed, as is well known, polarization reversal occurs on account of the motion of the domain boundaries. The resistance to the boundary motion is due largely to the difference in the spontaneous deformations of the neighboring domains and the existence of inhomogeneous strains at the domain boundaries, which interact with the defects of the crystal lattice. These and the other strains have similar character in ordinary and improper ferroelectrics. Notice that the spontaneous polarization P_S in an improper ferroelectric is, as a rule, weaker than the polarization in an ordinary ferroelectric (i.e., it is a quantity of higher order in smallness), and that the force exerted by the

electric field on a domain boundary is proportional to P_S . This must be taken into account when comparing the mobility of the domain boundaries of different ferroelectrics.

2. THE VIBRATIONAL SPECTRUM OF A CRYSTAL NEAR THE PHASE-TRANSITION POINT

a) **Normal coordinates and the order parameter.** Remaining in the framework of the phenomenological theory, we not only can describe the anomalies in the thermodynamic quantities, but also determine the nature of the changes that occur in the spectrum of the elementary excitations of the crystal in the neighborhood of the phase transition. For this purpose, we must relate the components of the order parameter to the change that occurs in the positions of the atoms in the crystal lattice during the phase transition. The physical meaning of the order parameter is elucidated at the same time. With that end in view, let us use the approach in which the phenomenological theory of phase transitions is expounded in the language employed in the dynamical theory of the ideal crystal lattice. By this token, we shall consider only the displacive-type phase transitions: the changes in the vibrational (phonon) spectrum of the crystal in the neighborhoods of the critical points of such transitions are experimentally the most noticeable. The indicated approach to the description of ferroelectric phase transitions was used by Ginzburg in his papers^[2], and subsequently more fully by Anderson^[22] and Cochran (see, for example, ^[23]).

A change in structure occurs in a displacive-type phase transition as a result of the displacement of the ions (atoms) in the crystal lattice. We shall, for simplicity, consider the ionic displacements corresponding to only the optical (and not the acoustic) branches of the vibrations, i.e., we shall neglect the deformation of the crystal, fixing the positions of ions of the same kind (i.e., of ions forming a Bravais lattice).

If the translational symmetry of the crystal does not change in the phase transition, then the resulting ionic displacements are the same in all the unit cells (i.e., correspond to the wave vector $k=0$). The structure of the crystal can then be described with the aid of $3N-3$ (N is the number of atoms in a unit cell) coordinates x_i , which are conveniently measured from the equilibrium positions of the ions in the initial phase.

The thermodynamic potential is a function of the coordinates x_i of the ions. However, the variables x_i are inconvenient, since they are all coupled to each other: because of the interaction between them, the displacement of one ion leads to the displacement of the rest. By means of a linear transformation we can go over to new variables—normal coordinates q_i , which, in the harmonic (quadratic in q_i) approximation, are not coupled to each other. The thermodynamic potential in the variables q_i is a diagonal quadratic form: it does not contain terms of the form $q_i q_j$ with different i and j .

The coordinates x_i form a basis for the representation of the point group of the initial phase, i.e., they transform into each other under the symmetry operations. The transition to the new basis q_i leads to the decomposition of the representation into irreducible representations. In other words, the q_i break up into separate sets and transform into each other only within each such set.

The thermodynamic potential can be represented in the form

$$\Phi = \sum_n \alpha_n \sum_r q_{nr}^2.$$

The normal coordinates q_{nr} with a given n transform according to one irreducible representation (the number of different r is equal to the dimensionality of the corresponding representation).

In the initial phase, all $q_{nr} = 0$ ⁶⁾. The stability condition for this phase amounts to the requirement that all coefficients $\alpha_n > 0$. We shall for definiteness henceforth speak of second-order phase transitions. In order for the transition to occur, the initial phase should become unstable, i.e., one of the coefficients α_n (let us denote it by α_m) should become negative, having passed through zero at the transition point itself. Some of the q_{mr} become different from zero when $\alpha_m < 0$. The ionic displacements corresponding to these q_{mr} arise in the phase transition, changing the symmetry of the crystal. The components of the order parameter in the Landau theory for the displacive type of transitions are, by their physical meaning, the normal coordinates q_{mr} .

In order to not only describe the loss of stability, but also find the coordinates of the ions in the asymmetric phase, it is necessary to take into account in the thermodynamic potential invariants of order in q_{mr} higher than the quadratic (i.e., allow for anharmonicity). In this case there will also appear mixed invariants in the form of products of powers of q_{mr} and other q_{nr} . The ionic displacements corresponding to those normal coordinates q_{nr} that enter into the mixed invariants linearly (let us denote them by q_{lr}) can also arise in the phase transition.

The above-considered order-parameter components η and ξ have the meaning of normal coordinates q_{m1} and q_{m2} . The role of the coordinate q_l ($r=1$), which transforms according to a (one-dimensional) representation that is different from that according to which q_{mr} transforms, was played by P , which entered linearly into the corresponding mixed invariant $\eta\xi P$.

The foregoing analysis can easily be extended in its entirety to the case when the translational symmetry of the crystal changes in the phase transition. In such transitions, the ions in neighboring unit cells are not displaced equally. Therefore, we must consider normal coordinates with wave vectors k different from zero. For those normal coordinates that play the role of order-parameter components, the wave vectors can terminate only at certain points of the Brillouin zone. This is connected with the requirement that the phase transition lead to a homogeneous, and not a layered, crystal^[11].

b) The normal modes. In the equations of motion that describe the normal modes of the crystal lattice, the role of the potential energy is played by the thermodynamic potential, which depends on the normal coordinates. Therefore, definite conclusions about the vibrational spectrum of the crystal in the phase-transition region can be drawn in the frame-work of the phenomenological Landau theory. Thus, for example, the vanishing of the frequency of the soft mode at the second-order phase transition point follows from the following simple arguments. The coefficients α_n in the thermodynamic potential have the meaning of "elastic" constants for the normal coordinates q_{nr} . Therefore, if the damping is weak, then $\omega_n^2 \sim \alpha_n$, where ω_n is the frequency of

the corresponding normal mode. The coefficient α_m vanishes at the phase-transition point; therefore, the frequency ω_m of the normal coordinate q_{mr} also vanishes. It is this vibration that is called the soft mode.

Let us consider the vibrational spectrum of a crystal that undergoes an improper ferroelectric phase transition. In the ordinary ferroelectrics, the soft modes in both phases are active modes in the infrared spectrum, i.e., their vibrations are accompanied by polarization oscillations. In the improper ferroelectrics, the soft mode in the initial phase is inactive in the infrared spectrum (the quantities η and ξ are not polarization-vector components). In the polar phase, we should in considering the crystal-lattice vibrations reckon η , ξ , and P not from zero, as is done in the initial phase, but from the spontaneous values η_S , ξ_S , and P_S . In this case the deviations $\eta' = \eta - \eta_S$, $\xi' = \xi - \xi_S$, and $P' = P - P_S$ will not be normal coordinates, since the corresponding quadratic form will not be diagonal. Indeed, because of the presence of the mixed invariant $\eta\xi P$, there will appear terms of the form $P_S \eta' \xi' + \xi_S \eta' P' + \eta_S \xi' P'$. The normal coordinates will now be some linear combinations of the quantities η' , ξ' , and P' . In other words, all the three quantities η' , ξ' , and P' will, generally speaking, participate in any of the three normal vibrations. However, the coefficients attached to the mixed terms $\eta' P'$ and $\xi' P'$ vanish at the transition point and are consequently small near this point in comparison with the coefficient attached to P'^2 . Therefore, it makes sense to speak of η' and ξ' modes with an admixture of the P' mode. This admixture (the oscillator strength) thus decreases as we approach the phase-transition point and vanishes at the point itself^[24].

The computation performed for the thermodynamic potential (6) with the coefficients $\gamma = \delta = 0$ leads to the results shown in Fig. 9 for the temperature dependence of the normal-mode frequencies near the second-order phase-transition point. In the initial phase the mode corresponding to the polarization vibrations has a frequency $\omega_P^2 = \kappa/\mu'$, where μ' is the coefficient attached to $\dot{P}^2/2$ in the expression for the kinetic energy (a coefficient that plays the role of a generalized mass). The two other modes (which are inactive modes in the infrared spectrum) have the same frequency $\omega_\eta^2 = \omega_\xi^2 = \alpha/\mu$, where μ is the coefficient attached to $(\dot{\eta}^2 + \dot{\xi}^2)/2$ (the soft mode is two-fold degenerate). In the polar phase one of the two soft modes is inactive in the infrared spectrum, its frequency being given by $\omega_1^2 = 2|\alpha||\beta|/\beta_1\mu$, while the other mode, whose frequency in the vicinity of the transition point for $|\alpha|\mu' \ll \kappa\mu$ is $\omega_2^2 = 2|\alpha|/\mu$, is an active mode; the frequency of the third mode is given by $\omega_3^2 = (\kappa/\mu') + (2|\alpha|\Delta/\beta_1\mu)$. The dielectric susceptibility $\chi = dP'/dE$ is determined by the relation

$$\chi = \frac{(1/\mu') - 2\Delta|\alpha|/\beta_1\kappa\mu}{\omega_3^2 - \omega^2} + \frac{2|\alpha|\Delta/\beta_1\kappa\mu}{\omega_2^2 - \omega^2}, \quad (20)$$

from which it can be seen that the oscillator strength of the soft-mode vibrations, which is equal to $2|\alpha|\Delta/\beta_1\kappa\mu$, decreases according to the law $\sim |T - \theta|$ as we approach the transition temperature θ .

For a first-order phase transition, the square of the soft-mode frequency does not vanish at the transition point, the varies linearly with temperature in the initial phase and according to a more complicated law in the polar phase^[25].

In the phase transition $2 \leftrightarrow 1$, the vanishing of the frequencies of the soft modes occurs in both phases at

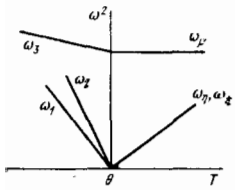


FIG. 9. The temperature dependences of the frequencies of the various vibrational modes in the vicinity ($|\alpha|\mu' \ll \kappa\mu$) of the second-order ($\beta_1 > 0$) phase transition $0 \leftrightarrow 1$ ($\beta < 0$).

the points where these phases lose their stability. Let us emphasize that the soft modes correspond to different branches of the phonon spectrum. In the phase 2 the soft mode is the oscillation of the polarization component P, while in the phase 1 the soft mode is the oscillation of another tensor quantity Q (3).

In the case of the thermodynamic potential (7), the nature of the temperature dependence of the normal-mode frequencies will be similar to that of the temperature dependence shown in Fig. 9, except that now in the polar phase both soft modes will be active in the infrared spectrum.

If the phase transition occurs without a change in the number of atoms in the unit cell, then all the frequencies represented in Fig. 9 correspond to oscillations with $k=0$. If the transition occurs with a change in the translational symmetry of the crystal, then the two frequencies in the initial phase correspond to η and ξ vibrations with a non-zero wave vector k . In the polar phase all the frequencies correspond to $k=0$. The number of branches in this phase naturally increases, which is not shown in Fig. 9.

Notice that Fig. 9 essentially shows the temperature dependences of the "elastic" constants α_n of the normal modes. The squares of the frequencies have similar dependences only in the case when the damping of the vibrations is weak. If the damping is not weak, then we cannot, strictly speaking, use the normal-mode language. However, the form of the thermodynamic potential, on the basis of which all the results are obtained, does not depend on the presence of damping and, consequently, the entire analysis can be carried out in the same way as was done above. Naturally, the results obtainable here will be different. For example, when the damping is so strong that instead of vibrations we have relaxation, then what will vanish at the phase-transition point is not the frequency, but the inverse relaxation time.

We have assumed above that $P \sim q_l$, i.e., that P arises as a result of the ionic displacements corresponding to one normal mode of the initial phase of the crystal. Contributions to P can, however, be made by the ionic displacements corresponding to several normal modes (i.e., corresponding to coordinates q_l with different l , but transforming according to one irreducible representation), as well as by purely electronic displacements. Allowance for this will not change any of the above results, since they were essentially obtained on the basis of a phenomenological analysis (only the microscopic meaning of the coefficients κ and a of the thermodynamic potential will change).

The most complete data on the frequencies of the normal modes—in particular, the soft modes—of a crystal can be obtained from inelastic neutron scattering experiments. This method allows us, in principle, to measure the frequency of any vibration of the crystal.

The method of (first-order) Raman light scattering allows us to investigate only those normal modes which

have small wave vectors k (of the order of the wave vector of the light wave), and for which the refractive index (or, more precisely, each component of the permittivity tensor ϵ_{ij} at optical frequencies) varies in proportion to the corresponding normal coordinates. In the initial phase of an improper ferroelectric, the components of the tensor ϵ_{ij} are quadratic in the normal coordinates of the soft mode, e.g., η and ξ . Therefore, the soft mode does not contribute to the Raman light scattering. In the polar phase the quantities η and ξ have the spontaneous values η_S and ξ_S . Therefore, the relation between the change in ϵ_{ij} and η' , ξ' —the deviations of η , ξ from η_S , ξ_S —becomes linear.

If the long-wave normal modes of the crystal lattice are accompanied by oscillations of the electric dipole moment P, then they give an absorption line in the infrared region of the spectrum (i.e., they are active in the infrared spectrum). In the improper ferroelectrics, as was noted above, the soft modes can be active in the infrared spectrum only in the polar phase. The infrared absorption lines corresponding to the soft modes shift toward the low-frequency region, and their intensity decreases as we approach the transition point.

3. DISCUSSION OF THE EXPERIMENTAL DATA

a) The rare-earth molybdates. Let us now proceed to discuss the experimental data. We did not find it expedient to give here a complete review of the large number of papers on the improper ferroelectrics. We do not cite papers containing experimental data that are insufficient for their unique interpretation, or that essentially duplicate results obtained by other methods, or that bear no direct relation to the above-exposed theory.

Let us begin the discussion with gadolinium molybdate $Gd_2(MoO_4)_3$, since the data for it are the most complete and reliable. The other rare-earth molybdates have similar properties. Gadolinium molybdate undergoes at $T \approx 159^\circ C$ a ferroelectric phase transition in which its space group changes from $D_{3d}^3(P\bar{4}2_1m)$ to $C_{2v}^8(Pba2)$. The reconstruction of the structure in the transition is such that the volume of the unit cell is doubled—certain translations in the plane perpendicular to the polar axis are lost (see, for example, ^[26,27]). The latter fact implies that gadolinium molybdate is an improper ferroelectric (the phase transition is a first-order transition that is nearly of second order—see Sec. h of Chap. 1).

The irreducible representation of the symmetry group of the initial phase D_{3d}^3 that is responsible for the transition to the polar phase C_{2v}^8 was found in ^[28]. The thermodynamic potential corresponding to this representation has the form (2), (4), or (7) ^[28]. In the paraelectric phase, gadolinium molybdate is a piezoelectric, the piezoelectric modulus coupling P_z and u_{xy} (the z axis is directed along the major axis, while the x and y axes are directed along the two-fold axes) being different from zero. In other words, P_z and u_{xy} possess the same transformation properties, i.e., they enter into the thermodynamic potential in similar fashion. Let us add to the expression (7) terms depending on $u_{xy} \equiv u$:

$$\frac{1}{2} cu^2 + \lambda Pu + 2b_1 \eta \xi u + b_2 (\eta^2 - \xi^2) u. \quad (21)$$

The anomalies in the dielectric properties of gadolinium molybdate (Fig. 10) ^[29] are well described by the

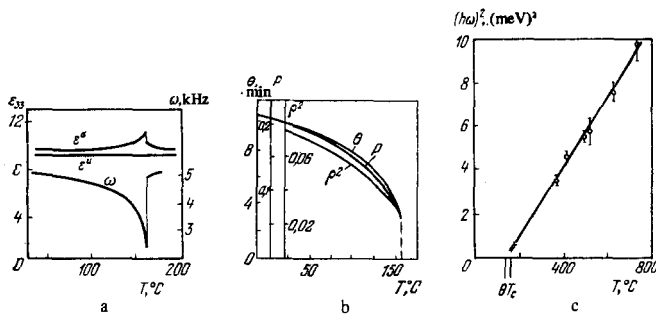


FIG. 10. Experimental data on the rare-earth molybdates. Dependences for gadolinium molybdate: a) $\epsilon_{33}(T)$, $C_{66}(T)$, $C_{66} \sim \omega^{[29]}$ and b) $\rho^2(T)^{[27]}$, $P(T)$ ($\mu\text{C}/\text{cm}^2$), $u_{xy}(T)$, $u_{xy} \sim \theta^{[29]}$, and c) the dependence of the frequency ω of the soft mode with $\mathbf{k} = (\frac{1}{2}, \frac{1}{2}, 0)$ on T for terbium molybdate: $\omega^2 = A(T - \theta)$ ($\theta = 149^\circ\text{C}$, $T_C = 159^\circ\text{C}$, and $A = 0.0165$ meV/deg) $^{[25]}$.

above-expanded theory (see Figs. 3 and 4). It is precisely this circumstance that allowed in its time the classification of gadolinium molybdate as an improper ferroelectric $^{[9]}$. Indeed, the anomaly in the permittivity ϵ_{33} is relatively weak. In the paraelectric phase, ϵ_{33} does not obey the Curie-Weiss law and is almost temperature independent.

For a mechanically compressed crystal, there is practically no anomaly in ϵ_{33} . This means that the coefficients a_1 and a_2 attached to the mixed invariants in the thermodynamic potential (7) are very small: $a_1 \approx 0$, $a_2 \approx 0$. The appearance of the spontaneous polarization in the phase transition is thus due not to the direct coupling of P to the order-parameter components η and ξ , but to the coupling of P to u and u to η and ξ .

The temperature dependences of the spontaneous values of ρ^2 , P_z , and u_{xy} (Fig. 10) are identical, which is evident from the form of the thermodynamic potential (7), (21). Similarly, the anomalous parts of the elastic modulus C_{66} and the inverse dielectric susceptibility χ_{33}^{-1} have the same temperature dependence. Numerically, the anomaly in C_{66} is quite high.

Two types of twin boundaries—ferroelectric and translational or antiphase—arising in the phase transition in gadolinium molybdate have apparently been observed (with the aid of the method of selective etching) in $^{[30]}$.

The quantitative comparison of the experimental data with the theory can be done on the basis of a simplified thermodynamic potential obtained by setting in (7), (21), $\beta_3 = a_2 = b_2 = 0$, since the anomalies for the thermodynamic potentials (6) and (7) practically coincide (see Sec. f of Chap. 1). The experimental data presented in Fig. 10 allow us to determine the following combinations of the coefficients of the thermodynamic potential: $a \approx 0$, $\kappa \approx 1.5$, $\lambda/\kappa \approx 2 \times 10^5$ cgs esu, $\lambda^2/c\kappa \approx 0.04$, $b|\beta_1|c\gamma \approx 10^{-3}$, $\beta_1^2/\tilde{\alpha}\gamma \approx 20$ deg, and $b^2/c|\beta_1| \approx 1$. It is significant, for example, that the last value can be obtained from the discontinuity in C and the magnitudes of, and discontinuity in, χ . The coincidence to within the limits of experimental error of these two values attests not only to the qualitative, but also to the quantitative agreement of the theory with experiment (see also $^{[9]}$). The complete determination of the coefficients of the thermodynamic potential requires experimental data on the anomalies in other quantities, e.g., the specific heat. The accuracy of such data is not yet sufficient.

The soft mode in terbium molybdate has been investigated by the inelastic neutron scattering method $^{[25]}$. In the paraelectric phase, the square of the frequency of the mode with the Brillouin-zone-edge wave vector $\mathbf{k} = (\frac{1}{2}, \frac{1}{2}, 0)$ was found to have a linear temperature dependence (see Fig. 10). This experiment directly indicates that the ferroelectric phase transition in terbium molybdate is an improper one. In the polar phase one scattering peak was observed which corresponds to two merged—as a result of damping—soft modes. The peak moved slowly and broadened with increasing temperature. The weak dependence of the frequencies of the soft modes on temperature may be due to the fact that the transition is of first order. However, the experimental data on the polar phase near the transition temperature are not sufficiently accurate for their unique interpretation $^{[25]}$.

In the experiments $^{[31]}$ on Raman light scattering in the polar phase of gadolinium molybdate, a peak having approximately the same frequency as the one in $^{[25]}$ was observed which was apparently connected with a soft mode (the peak decreased in intensity and frequency as the temperature increased).

In the experiments $^{[32]}$ on infrared light absorption in the polar phase of gadolinium molybdate, two weak peaks were observed which, as the temperature was increased, decreased in intensity and frequency, and broadened, merging at room temperature. By their appearance, these peaks correspond to soft modes. The weak intensity of the peaks can easily be explained if we allow for the fact that the infrared absorption is determined by the contribution of the soft-mode vibrations to the imaginary part of the permittivity of the clamped crystal, since the frequencies at which the absorption occurs are substantially higher than the piezoelectric-resonance frequencies. In gadolinium molybdate, this contribution is very small, to which corresponds the smallness of the coefficients a_1 and a_2 in the thermodynamic potential (7).

From the experimental data on the dielectric anomalies and the dependence $\omega(\mathbf{k})$ for the soft mode $^{[25]}$, we can estimate the role of the fluctuation effects in the phase transition. Such an estimate $^{[33]}$ shows that this role can prove to be fairly important. Therefore, it is precisely the fluctuations (see Sec. h of Chap. 1) that, possibly, make the phase transition in the rare-earth molybdates a first-order transition.

b) The boracites. The majority of the boracites—compounds with the formula $\text{Me}_3\text{B}_7\text{O}_{13}\text{X}$, where Me is a divalent metal and X is a halogen—are ferroelectrics (see, for example, $^{[33]}$). The ferroelectric phase transition occurs with a change in the space group—from $T_d^5(\bar{F}43c)$ to $C_{2v}^5(\text{Pca})$ —and a doubling of the (primitive) unit-cell length in the plane perpendicular to the spontaneous polarization axis $^{[34]}$.

The irreducible representation responsible for the $T_d^5 \leftrightarrow C_{2v}^5$ transition with a doubling of the unit-cell size has been determined in $^{[35]}$. This representation is six-dimensional, and to it correspond many other asymmetric phases. The sequence of phase transitions $T_d^5 \leftrightarrow C_{2v}^5 \rightarrow C_s \leftrightarrow C_{3v}^6$ $^{[36]}$ (the space group of the C_s phase has not been reliably established) has been experimentally observed in a number of boracites. The indicated irreducible representation is responsible not only for the transition to the phase C_{2v}^5 , but also for the transitions to the phases $C_s^4(\text{Bb})$ and $C_{3v}^6(\text{R3c})$ with a quadrupling

of the unit-cell size as compared to that of the initial phase T_d^5 [35]. This, however, does not mean that the entire chain of phase transitions in the boracites can be described on the basis of one irreducible representation. Although such a possibility is alluring, it is by no means obligatory, and does not agree with the available experimental data [37], according to which the unit cells of the C_{3v}^6 and T_d^5 phases contain the same number of atoms.

The expression for the thermodynamic potential, which depends on six order-parameter components (η , η' , ξ , ξ' , ζ , ζ') is quite unwieldy [36], and it is not expedient to give it here. Notice that this expression contains third-order invariants of the form $\eta\xi\xi' - \eta'\xi'\xi'$. Therefore, any transition from the T_d^5 phase should be a first-order transition. The mixed invariant containing the components of the polarization vector has the form: $\eta\eta'P_x + \xi\xi'P_y + \zeta\zeta'P_z$. The C_{2v}^5 phase corresponds to a solution of the type $\zeta = \pm\xi'$, $\eta = \eta' = \xi = \xi' = 0$. It follows from this that the coefficients attached to the third-order invariants do not enter into the expressions for the dielectric anomalies arising in the phase transition $T_d^5 \rightarrow C_{2v}^5$. It follows from the form of the mixed invariant and the form of the solution for the C_{2v}^5 phase that the phase transition $T_d^5 \rightarrow C_{2v}^5$ gives rise to P_x or P_y , or P_z (for a single-domain crystal). Therefore, the description of the dielectric anomalies could have been carried out for each component of the polarization vector separately on the basis of the thermodynamic potential (6). However, such a treatment does not allow the description of the observed anomalies, since the phase transition in the boracites is a pronounced first-order transition (see Sec. h of Chap. 1). Figure 11 shows a typical—for the boracites— anomaly in ϵ due to the $T_d^5 \rightarrow C_{2v}^5$ phase transition [38]. It is characteristic that ϵ undergoes a discontinuity downwards in the transition to the polar phase. We can attempt to qualitatively explain such behavior of ϵ if we take into account in the thermodynamic potential higher-order invariants in P , e.g., the invariant $d(\eta^2 - \xi^2)P^2$ [35]. To be able to do this, however, we must make special assumptions about the sign of the coefficient d and assume that this coefficient is anomalously large, or that the other coefficients of the thermodynamic potential are anomalously small.

Let us emphasize that such an explanation is by no means the only one possible. In the case of strongly pronounced first-order transitions it is generally impossible to state with certainty that the appearance of polarization in a ferroelectric phase transition that occurs with a change in the translational symmetry of the crystal is necessarily a second (and not a first) order effect. The change in the translational symmetry may be the result of the appearance of the spontaneous polarization—a spontaneous-polarization induced change in the lattice constant that is so large that structural

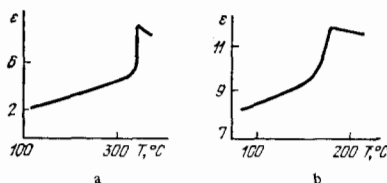


FIG. 11. The dependence $\epsilon(T)$ for: a) the Ni-I boracite at 48 MHz in the [100] direction and b) the Co-Br boracite at 100 kHz in the [111] direction [38].

changes corresponding to η and ξ become energetically advantageous (see also Sec. h of Chap. 1).

To find out whether the order parameter in the boracites is P or the two-component quantity (η, ξ) , we must investigate experimentally the T_d^5 phase under strong supercooling, i.e., close to the temperature at which this phase loses its stability.

Of special interest is the ferroelectric phase transition in the Ni-I boracite at $T \approx 64$ °K, as a result of which simultaneously with the spontaneous polarization arises, according to the data of [34,39], spontaneous magnetization. Judging from the anomaly in ϵ , the phase transition cannot be an ordinary ferroelectric transition. However, the experimental data on the Ni-I boracite are not yet sufficient for a unique description of the phase transitions that are observed in it.

c) **Rubidium and sodium trihydroselemites.** In rubidium trihydroselemitite $RbH_3(SeO_3)_2$, the anomaly in ϵ due to the ferroelectric phase transition ($T \approx -119$ °C) is weak ($\Delta\epsilon \sim 1$, $\epsilon \sim 10$), and the spontaneous polarization is very small ($P_S \sim 0.01$ $\mu C/cm^2$) [40]. The anomaly in ϵ is similar in form to the anomaly observed in gadolinium molybdate. The space group of the paraelectric phase of rubidium trihydroselemitite is $D_2^2(P2_12_1)$ [41]. It is shown in [42] that the only possible improper ferroelectric (second-order) phase transition from the group D_2^2 occurs to the group $C_2^2(P2_1)$ with a doubling of the unit-cell length in the plane perpendicular to the spontaneous polarization. The thermodynamic potential has the form (7) [42].

A curious characteristic of rubidium trihydroselemitite is the substantial decrease in the ϵ anomaly and the magnitude of P_S on the deuteration of the crystal, while the transition temperature practically remains unchanged. No ϵ or P_S anomaly is observed in the completely deuterized rubidium trihydroselemitite. Allowing for experimental error, we can assume that these quantities are at least an order of magnitude less than the values in the undeuterized substance. The indicated characteristics attest apparently to the fact that the phase transition is not directly connected with proton ordering: the ordering arises as a secondary effect, which is the cause of the spontaneous polarization [40].

Ferroelectric phase transitions accompanied by a change in the translational symmetry of the crystal lattice are observed in sodium trihydroselemitite $NaH_3(SeO_3)_2$. These transitions are strongly pronounced first-order transitions. The spontaneous polarization arises discontinuously, practically does not vary with temperature in the polar phases, and its magnitude is substantial ($P_S \sim 5$ $\mu C/cm^2$) [43]. In the paraelectric phase, ϵ is found to grow, but apparently not according to the Curie-Weiss law. The temperature-percentage deuteration-pressure phase diagram has a rather complicated shape [44]. Several phases are observed: besides the paraelectric phase, whose symmetry group is $C_{2h}^5(P2_1/b)$ [45], there are two polar phases in the symmetry classes $C_S(m)$ and $C_1(1)$ and a nonpolar phase whose structure has not yet been established. Transitions from the phase C_{2h}^5 to all the enumerated low-symmetry phases are observed at different degrees of deuteration and different pressures. The transition to the C_S phase is found to be accompanied by a doubling of the unit-cell length along the two-fold axis, while the transition to the C_1 phase leads not only to a doubling of the unit-cell length along the two-fold axis, but also to

a doubling of the length along the glide direction in the symmetry plane^[46].

A quantitative description of the anomalies and the phase diagrams on the basis of the Landau theory is not possible, since the discontinuities in the quantities at the phase-transition points are large (see Sec. h of Chap. 1). We can, however, say something about the symmetry changes that occur in the transitions. The space group of the C_S phase is found to be C_S^2 (Pb) if it is assumed that the phase transition $C_{2h}^5 \rightarrow C_S^2$ is described by the two-dimensional irreducible representation of the symmetry group C_{2h}^5 of the initial phase. The structural distortion that occurs in the phase transition $C_{2h}^5 \rightarrow C_1$ clearly cannot be described on the basis of one irreducible representation of the symmetry group of the C_{2h}^5 phase, since there occurs in this transition a doubling of the lattice constants along inequivalent axes, i.e., axes that do not transform into each other under any of the symmetry operations of the initial phase C_{2h}^5 . If such a transition were of second order, it would be realizable only at an isolated point on the phase diagram. In fact, the phase transition $C_{2h}^5 \rightarrow C_1$ is found to be realizable along a line in the temperature-percentage deuteration diagram. The symmetry group of the nonpolar phase can be uniquely established: $C_1^1(\bar{1})$, since this is the only nonpolar subgroup of the symmetry group of the C_{2h}^5 phase.

The strong influence that deuteration has on the transition temperatures is indicative of the decisive role played by proton ordering in the phase transitions. In^[47] an attempt is made to make quantitative estimates for sodium trihydroselenite with the aid of a phenomenological Hamiltonian in which the distinctive features of the specific structure change that occurs in the phase transition and the distinctive features of the interactions are taken into account.

d) **Other improper ferroelectrics.** A ferroelectric phase transition is observed in the ammonium Rochelle salt $\text{NaNH}_4\text{C}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ at $T \approx 109^\circ\text{K}$ ^[48]. The space group of the crystal changes in the transition from $D_2^3(P2_12_12_1)$ to $C_2^2(P2_1)$, and there occurs a doubling of the lattice constant along one of the screw axes^[49]. The thermodynamic potential has the form (6)^[49], the quantity $P \equiv P_z$, and the quantity $Q \equiv P_y$. The phase transition is, however, of first order. The spontaneous polarization has the magnitude $P_S \sim 0.2 \mu\text{C}/\text{cm}^2$, and practically does not vary with temperature. The components of ϵ undergo a discontinuity downwards ($\Delta\epsilon \sim 2$, $\epsilon \sim 10$) at the transition point^[48].

Ferroelectric phase transitions with weak anomalies in the permittivity ϵ are observed in two compounds with the langbeinite structure—dicadmium diammonium sulfate $\text{Cd}_2(\text{NH}_4)_2(\text{SO}_4)_3$ and dicadmium dithallium sulfate $\text{Cd}_2\text{Tl}_2(\text{SO}_4)_3$. In dicadmium diammonium sulfate, the quantity $P_S \sim 0.7 \mu\text{C}/\text{cm}^2$, and practically does not change with temperature; in the single-domain crystal, ϵ undergoes a slight discontinuity downwards ($\Delta\epsilon \sim 1$, $\epsilon \sim 10$)^[50]. The symmetry group of the paraelectric phase is $T^4(P2_13)$ ^[50]. The only irreducible representation of this group that can be responsible for the improper ferroelectric phase transition to the space group $C_2^2(P2_1)$ —a transition that is accompanied by a doubling of the lattice constant in the plane perpendicular to the spontaneous polarization—has been determined in^[51]. This transition is necessarily a first-order transition (there is a third-order invari-

ant). The representation in question is six dimensional, and there are phases of different symmetry corresponding to it. These phases are, possibly, observed in dicadmium dithallium sulfate, in which a series of several phase transition has been observed^[52].

The translational symmetry of ammonium fluoroberyllate $(\text{NH}_4)_2\text{BeF}_4$ in the polar phase ($T < -96^\circ\text{C}$) is different from the translational symmetry at room temperature^[48]. This impelled investigators to treat it as an improper ferroelectric^[11]. Such a treatment did not, however, allow the explanation of the observed^[53] dielectric anomalies. Subsequently, a specific-heat anomaly revealed a phase transition at $T \approx -90^\circ\text{C}$ ^[54]. The structure of the phase in the temperature range $-96^\circ\text{C} < T < -90^\circ\text{C}$ is unknown. It is possible that the change in the translational symmetry occurs during the phase transition with $T \approx -90^\circ\text{C}$. In^[6] it was proposed that the ferroelectric phase transition at $T \approx -96^\circ\text{C}$ be described as a transition between the asymmetric phases 2 and 1 (see Sec. g of Chap. 1). The anomalies arising in the transition $2 \rightarrow 1$ (see Sec. h of Chap. 1 (Figs. 8 and 5)) are qualitatively similar in nature to the anomalies experimentally observed in ammonium fluoroberyllate. However, it has not been possible to attain a quantitative agreement.

Furthermore, if the phase above $T \approx -90^\circ\text{C}$ is the phase 0, then there should be an appreciable anomaly in ϵ at the transition temperature $T \approx -90^\circ\text{C}$, but this has not been observed^[54]. It is possible that this transition is described by another irreducible representation. Thus, the situation is not yet clear, and we must first of all determine the structure change that accompanies the phase transitions in ammonium fluoroberyllate.

4. CONCLUSION

The purpose of the present review was to consider from a unified standpoint—on the basis of the phenomenological Landau theory—the improper ferroelectric phase transitions. It turned out that to discuss the existing experimental data it was sufficient to consider only the simplest variants of the theory. Consideration of other forms of the thermodynamic potential, of other mixed invariants, would have led to other types of dielectric anomalies, to other forms of the phase diagrams. Computations of this sort may stimulate the corresponding experimental investigations.

The development of the phenomenological theory of improper ferroelectricity may prove to be useful for the theory of ordinary ferroelectricity. For example, it is suggested in^[12] that the series of phase transitions that occurs in Rochelle salt could be treated as transitions of the type $1 \rightarrow 3 \rightarrow 2$ (see Sec. g of Chap. 1) on the basis of the thermodynamic potential of the phase 0 (which cannot be experimentally observed) that contains a mixed invariant of the form $\eta\xi(\eta^2 - \xi^2)P$ (in this case the phase 3 is polar, while the phases 1 and 2 are nonpolar). Such an approach allows us to comparatively simply explain the dielectric anomalies observed in Rochelle salt, although it is not yet clear to what extent it agrees with the structural data for the low-temperature phase. There exists quite a number of ferroelectrics with close phase-transition temperatures. They could be treated in similar fashion.

From the point of view of the microscopic theory,

ferroelectric transitions are not different from non-ferroelectric transitions that are accompanied by changes in crystal structure. This, of course, does not mean that the microscopic theory cannot lead to interesting results for the improper ferroelectrics. However, such a theory makes sense only when it is applied to specific substances or groups of similar substances. If the phase transition is of second order, or nearly of second order, then the role of the microscopic theory amounts to the determination of the coupling constants that figure with the microscopic parameters in the phenomenological theory and to the elucidation of the temperature dependence of the constants in the region far from the transition point (thereby establishing one of the limits of the region of applicability of the Landau theory). Thus, for example, for gadolinium molybdate, one of the problems of the microscopic theory is to explain the extreme smallness of the constants a_1 and a_2 of the thermodynamic potential (7).

Pronounced first-order transitions are experimentally observed in many improper ferroelectrics. Such transitions can, apparently, be described only on the basis of the microscopic theory, since the phenomenological Landau theory is practically inapplicable in this case. Notice that the existing microscopic theory is, as a rule, semiphenomenological in nature. In it is used a phenomenological Hamiltonian whose constants are not calculated, but are determined by comparing the theory with experiment. The computation of these constants is the object of a more detailed microscopic theory. As applied to specific improper ferroelectrics, the development of the microscopic theory is only just beginning.

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¹⁾This name was suggested by Dvořák [6].

²⁾The first ferroelectric that was tentatively considered to be an improper ferroelectric was ammonium fluoroborate [11] (see Sec. d of Chap. 3).

³⁾For the limitations of this approach, see Sec. h.

⁴⁾The improper ferroelectric phase transition that is accompanied by a change in the magnetic structure of the crystal occurs, possibly, in only one substance (see Sec. b of Chap. 3). Therefore, we shall, for definiteness, speak only of a change in crystal structure.

⁵⁾As always in the Landau theory, we have in mind second-order phase transitions (or first-order transitions that are nearly of second order).

⁶⁾Except the normal coordinates that transform according to the unit representation. However, they can be excluded from the present consideration, since the displacements corresponding to them do not change the symmetry of the initial phase.

⁷⁾The cited literature contains, as a rule, the more recent papers, in which references to previous papers can be found.

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