

Contribution to the Thermodynamical Theory of the Ferroelectric Properties of Barium Titanate

L. P. KHOLODENKO

(Submitted to JETP editor May 3, 1955)

J. Exptl. Theoret. Phys. USSR 31, 244-253 (August, 1956)

The question of the character of the phase transition from the nonferroelectric to the ferroelectric phase is discussed. The influence of an electric field on the temperature for the phase change is considered. It is shown that in the case of a first order phase change, a shift in the transformation point takes place, and the amount of the shift is calculated. The temperature dependence of the dielectric permeability is found for the case of a second order phase change. It is shown that in such a transformation an "induced" piezoeffect" must appear, which consists in the appearance of piezoelectric properties under application of an electric field. The "induced piezomoduli" are calculated.

1. INTRODUCTION

IN spite of the large number of works devoted to the theory of barium titanate, it is still far from completion. This refers, in the first place, to the microtheory of ferroelectric phenomena, but neither can the thermodynamical theory evolved by Ginzburg¹ and developed in Refs. 2-6 be considered fully complete. On the one hand, there are still questions not considered in these works and on the other, there is a need to compare the existing theories among themselves.

In Ref. 1, there are discussed two variants of a theory which is in conformance with the experimentally observed facts. According to the first version, the phase transition at 120° should be considered as a second order phase change, but close to a phase change of first order. According to the second version it should be considered as a first order change, but close to a change of second order. In Refs. 2 and 3, this phase change is considered as a first order change, while in Refs. 4-6, as a second order change.

An attempt was made⁷ to settle the question about the character of the phase transformation from the nonferroelectric phase by way of investigation of the dependence of the dielectric permeability near the Curie point on the strength of a steady electric field. The author found that the experimental data are in good agreement with the theory² and on that basis concluded that the phase change under investigation must be considered as a change of first order. As will be pointed below, however, (see Sec. 2) experimental data obtained by other authors rather favors the hypothesis that the phase transformation we are speaking of must be regarded as a phase change of second order.

If one again takes into account that even the other experimental results quoted by the various authors differ sharply among themselves (for instance, the thermal behavior of the spontaneous

polarization, the constant in the Curie-Weiss law, the jump in specific heat) and depend most strongly on the technique of preparation of the specimens and on their chemical purity, the idea suggests itself that the character of the phase change of which we speak is likewise also determined by these factors and was different in the works of the different authors. The distinction between the theories¹⁻⁶ is not only in the question of the character of the phase change under discussion. These theories differ further in that they operate with different thermodynamic functions. In Refs. 1, 4 and 5, the thermodynamic potential is considered, while in Refs. 2 and 6, the free energy is considered.

Just as in the treatment proposed by Landau⁸ for phase changes of second order, the conditions of thermodynamic equilibrium of a system are obtained by considering the conditions for a minimum of the appropriate thermodynamic function, written down for a thermodynamically nonequilibrium states. Insofar as in all the works¹⁻⁶ the behavior of a crystal is studied in a given electric field and under a given system of stresses (homogeneous), the appropriate thermodynamic function is precisely the thermodynamic potential. Utilization of the free energy, however, and application of the general formulas of the thermodynamics of quasi-statistical processes leads practically to the same results as are obtained by consideration of the thermodynamic potential of nonequilibrium states. As long as the stresses (or deformations) are not taken into account, this is obvious. Writing down nonequilibrium thermodynamic potential in the form $\Phi(P_i, T) = \Psi(P_i, T) - P_i \cdot E_i$, where $\Psi(P_i, T)$ is a polynomial in powers of P_i , and finding P_i from the condition of a minimum for Φ , we have the equations

$$\partial \Psi / \partial P_i = E_i, \quad i = 1, 2, 3,$$

which conform with the thermodynamic identities for

quasi-statistical processes, if we take Ψ to be the free energy. In the calculation of the elastic stresses an analogous situation occurs. We satisfy ourselves on this by comparing Refs. 5 and 6.* In Ref. 6 there is used an expansion of some characteristic function Φ into components of the polarization vector P_i and components of the elastic deformation tensor u_{ik} . Although the authors call this function the thermodynamic potential, it is more proper to restrict this designation to the function

$$\zeta = \Phi + \sum_{i, k} u_{ik} \sigma_{ik},$$

and to regard the function $\Phi + \mathbf{P} \cdot \mathbf{E}$ as the free energy (for quasi-statistical processes), since it complies with the conditions**

$$\partial(\Phi + \mathbf{P} \cdot \mathbf{E}) / \partial P_i = E_i; \quad (1)$$

$$\partial(\Phi + \mathbf{P} \cdot \mathbf{E}) / \partial u_{ik} = -\sigma_{ik}.$$

The authors maintain that the resolution into components u_{ik} permits taking account of the effect of electrofriction on the properties of a ferroelectric to a greater degree than the earlier applied expansion 1 of the thermodynamic potential into components σ_{ik} . We cannot agree with such a statement, however, since actually the increases in precision obtained in Ref. 6 are illusory. In order to be convinced of this, it is sufficient to transform the formulas obtained in Ref. 6.

Equations (1) and (2), when developed, have the form:

$$\begin{aligned} & [\alpha + \beta_1 P_x^2 + \beta_2 (P_y^2 + P_z^2) \\ & + q_{11} u_{xx} + q_{12} (u_{yy} + u_{zz})] 2P_x \\ & + q_{44} (u_{xy} P_y + u_{xz} P_z) = E_x; \\ & [\alpha + \beta_1 P_y^2 + \beta_2 (P_z^2 + P_x^2) \\ & + q_{11} u_{yy} + q_{12} (u_{zz} + u_{xx})] 2P_y \\ & + q_{44} (u_{yz} P_z + u_{yx} P_x) = E_y; \\ & [\alpha + \beta_1 P_z^2 + \beta_2 (P_x^2 + P_y^2) + q_{11} u_{zz} \\ & + q_{12} (u_{xx} + u_{yy})] 2P_z + q_{44} (u_{zx} P_x + u_{zy} P_y) = E_z; \end{aligned} \quad (2)$$

*We note that the theories¹⁻⁶, apart from the difference in the thermodynamic functions utilized, further differ in the extent of the expansions employed and in notation. Thus, in Ref. 2, only one invariant of 6th order is utilized while in Ref. 4 all three of such invariants are taken into account.

**More often, one writes $\partial\Psi/\partial u_{ik} = +\sigma_{ik}$, but owing to the arbitrariness of the condition which establishes the positiveness of the components σ_{ik} , the manner of writing employed in Eq. (1) is also feasible.

$$c_{11} u_{xx} + c_{12} (u_{zz} + u_{yy}) + q_{11} P_x^2 \quad (3)$$

$$+ q_{12} (P_y^2 + P_z^2) = -\sigma_{xx};$$

$$c_{11} u_{yy} + c_{12} (u_{xx} + u_{zz})$$

$$+ q_{11} P_y^2 + q_{12} (P_z^2 + P_x^2) = -\sigma_{yy};$$

$$c_{11} u_{zz} + c_{12} (u_{yy} + u_{xx}) + q_{11} P_z^2$$

$$+ q_{12} (P_x^2 + P_y^2) = -\sigma_{zz};$$

$$c_{44} u_{xy} + 2q_{44} P_x P_y = -\sigma_{xy};$$

$$c_{44} u_{yz} + 2q_{44} P_y P_z = -\sigma_{yz};$$

$$c_{44} u_{zx} + 2q_{44} P_z P_x = -\sigma_{zx}.$$

Solving the system of Eqs. (3) with respect to u_{ik} and substituting the obtained expressions into Eqs. (2), we obtain a system not essentially different from (1,4)₅** in notation and in the signs of the σ_{ik} .

In order that the system Eqs. (2) agree with Eqs. (1,4)₅*** (accurately with respect to the signs of the σ_{ik} , with regard to which see footnote*) it is necessary to assume

$$\beta_1 = \beta'_1 - [q_{11}^2 s_{11} + 4q_{11} q_{12} s_{12}] \quad (4)$$

$$+ 2q_{22}^2 (s_{11} + s_{12})],$$

$$\beta_2 = \beta'_2 - \beta'_1 + (s_{11} - s_{12}) (q_{11} - q_{12})^2$$

$$- s_{44} q_{44}^2 - 2q_{44}^2 / c_{44}.$$

The coefficients denoted by β'_1 and β'_2 in Eqs. (4) are the β_1 and β_2 of Ref. 6. The other symbols have the following meaning:*

$$s_{11} = (c_{11} + c_{12}) / (c_{11} + 2c_{12}) (c_{11} - c_{12}); \quad (5)$$

$$s_{12} = c_{12} / (c_{12} - c_{11}) (c_{11} + 2c_{12});$$

$$s_{44} = 2 / c_{44};$$

**Here and further on, the subscript after an equation number refers to the reference from which the equation is taken.

***Equation (1.4) in Ref. 5 contains misprints.

*The quantities $\kappa_1, \kappa_2, \kappa_3$ which figure in Ref. 5, appear to correspond, respectively, to the quantities $\vartheta_{33}, \vartheta_{31}, \vartheta_{15}$ from Ref. 6.

$$\kappa_1 = -(2q_{12}s_{12} + q_{11}s_{11}); \quad (6)$$

$$\kappa_2 = -[(q_{11} + q_{12})s_{12} + q_{12}s_{11}];$$

$$\kappa_3 = -2q_{44}/c_{44}.$$

From the agreement of Eqs. (2) with the Eqs. (1,4) of Ref. 5 it follows that their consequences, examined in Refs. 4 and 5 from one side and in Ref. 6 from the other, must likewise also be identical. As a matter of fact, the formulas for the degree of spontaneous polarization, spontaneous deformation, longitudinal and transverse dielectric permeability, piezoelectric moduli and for the dependence of the Curie point on pressure, differ, as can be seen, only in notation**.

Thus, contrary to the opinion of the authors⁶, the use of the free energy and its resolution into components u_{ik} is formally equivalent to the use of the thermodynamic potential and its resolution into components σ_{ik} . It would be in error to discern an advantage in the first of these methods in that it allows the determination of the structure of the coefficients β_1 and β_2 . In fact β_1 and β_2 must be continuous functions of temperature, while β'_1 and β'_2 can change discontinuously at points of phase transformation, in connection with the discontinuous changes of the elastic moduli s_{ik} . Herein must be found a reflection of the fact that the condition for thermodynamic equilibrium for given temperature and stresses σ_{ik} , is the minimum of the thermodynamic potential, and not that of the free energy.

Completing the comparison of Refs. 4 and 5 with Ref. 6, we note one essential difference in the conclusions. In Ref. 5 it is asserted that for a crystal with $\kappa_1 > 0$, a unidirectional compression (as well as an elongation) must raise the Curie point, while in Ref. 6 the opposite is maintained. The origin of this disagreement is as such: In Ref. 5 it was shown that the state of a crystal compressed along the z axis with polarization directed also along the z axis does not correspond to the absolute minimum of the thermodynamic potential. The absolute minimum corresponds to the direction of polarization along the x or y axis. Therefore, as ideal crystal must transform under compression into the other phase*, with which the increase in the Curie point is also associated. This effect is not considered in Ref. 6. In a real crystal, the

**The equation for d_{15} , Eq. (20)⁶ and the third of Eqs. (4.1)⁴ do not agree, apparently due to the inaccuracy of Eq. (20).

*Also tetragonal, but with a different direction of the vector P .

turning of the spontaneous polarization vector is hindered and therefore one can expect "thermal hysteresis". On cooling a previously heated and compressed crystal the transition from the nonferroelectric phase into the ferroelectric must proceed at higher temperatures than the reverse transition in the heating of a crystal compressed along an axis which coincides in direction with the vector P .

2. THE DEPENDENCE OF CERTAIN PROPERTIES OF A CRYSTAL NEAR A PHASE TRANSFORMATION POINT ON THE CHARACTER OF THAT TRANSFORMATION

The question of the properties of a crystal in the neighborhood of the phase transformation point in the presence of an electric field and, in particular, the question of the shift of the transformation point was raised and discussed in Ref. 7. This work, however, does not contain a detailed examination of the question.

In the case of a phase transformation of the first kind there occurs both a shift in the transformation point and a change in the jump of the dielectric permeability at this point. In the case of a phase transformation of the second kind, the phenomenon bears a different character. The fact is, that for a phase transformation of the second kind in the absence of a field, changes in crystal symmetry come about which are also manifested in the appearance of spontaneous polarization. The application of a field, however, promotes the appearance of polarization and consequently, also a change in symmetry at temperatures above the Curie point. That particular Curie point ceases to be more or less discrete in the presence of a field and, strictly speaking it is generally meaningless to speak of a phase transition in this case insofar as all the properties of the crystal vary smoothly with temperature*. In particular, the dielectric permeability also varies continuously, upon which its maximum point is displaced by the applied field. We examine both of these cases, considering terms of sixth degree in the expansion of Φ .

A. PHASE TRANSITION OF THE FIRST KIND

The transformation point is determined from the condition of the equality of the thermodynamic potentials in the nonferroelectric phase I and in the ferroelectric phase II. They have the form**

*This circumstance was pointed out to us by V. L. Ginzburg.

**The notation is the same as in Ref. 4.

$$\Phi_{\text{I}} = \Phi_0 + \alpha P_{\text{I}}^2 + \frac{1}{2} \beta_1 P_{\text{I}}^4 \quad (7)$$

$$+ \frac{1}{3} \gamma_1 P_{\text{I}}^6 - P_{\text{I}} E; \quad \Phi_{\text{II}} = \Phi_0$$

$$+ \alpha P_{\text{II}}^2 + \frac{1}{2} \beta_1 P_{\text{II}}^4 + \frac{1}{3} \gamma_1 P_{\text{II}}^6 - P_{\text{II}} E.$$

Setting in the first phase $P_{\text{I}} = \kappa E = E/2\alpha$ and restricting ourselves everywhere in the calculations to terms which contain E no higher than to the second power, we get

$$\Phi_{\text{I}} = \Phi_0 - E^2/4\alpha. \quad (8)$$

Comparing Eqs. (7) and (8) and taking into consideration that P_{II} satisfies the equation

$$(\gamma_1 P_{\text{II}}^4 + \beta_1 P_{\text{II}}^2 + \alpha) 2P_{\text{II}} = E, \quad (9)$$

we obtain

$$\frac{1}{6} \beta_1 P^4 + \frac{2}{3} \alpha P^2 - \frac{5}{6} P E = -E^2/4\alpha \quad (10)$$

(here and below, the index II of P is dropped).

Assuming $P \gg E$, the solution of Eq. (10) can be written in the form

$$P = \sqrt{-4\alpha/\beta_1} + C E + D E^2, \quad (11)$$

$$C = -\frac{5}{8} \alpha, \quad (12)$$

$$D = -(51/128 \alpha^2) \sqrt{-\beta_1/4\alpha}.$$

On the other hand, the solution of Eq. (9) can, under the same assumption, be written in the form

$$P = P_0 + A E + B E^2, \quad (13)$$

$$A = -\frac{1}{4} (\beta_1 P_0^2 + 2\alpha)^{-1}. \quad (14)$$

$$B = -A^2 (7\beta_1^2 P_0^2 + 10\alpha) / P_0 (2\beta_1 P_0^2 + 4\alpha).$$

Here P_0 is the solution to Eq. (9) for $E = 0$:

$$P_0^2 = (-\beta_1 + \sqrt{\beta_1^2 - 4\alpha\gamma_1}) / 2\gamma_1. \quad (15)$$

At the transformation point, the values of P determined from Eqs. (11) and (13) must coincide. In the calculation of the shift of the transformation point, we restrict ourselves to first order in E . Then for the determination of the amount of this shift we obtain

$$\sqrt{-4\alpha/\beta_1} + C E = P_0 + A E. \quad (16)$$

We denote α and β_1 at the transformation point for $E = 0$ by α_0 and β_{10} , and the value of P_0 at this point by P_{00} :

$$P_{00} = \sqrt{-4\alpha_0/\beta_{10}} = \sqrt{-3\beta_{10}/4\gamma_1}. \quad (17)$$

Denoting the transformation point by T_c , and the shift of the transformation point by ΔT_c , expanding α and β_1 into series in ΔT_c near α_0 and β_{10} and restricting ourselves to linear terms, we find after substitution of these expansions in Eq. (16)

$$\Delta T_c = E / P_{00} (\dot{\alpha} - 2\alpha_0 \dot{\beta}_1 / \beta_{10}), \quad (18)$$

where α and β_1 are the values of the derivatives with respect to T at the point $(T_c)_{E=0}$. Thus the sign of the shift of the transformation point is determined by the sign of the quantity $(\dot{\alpha} - 2\alpha_0 \dot{\beta}_1 / \beta_{10})$. For BaTiO_3 , as numerical estimates show (see below), the second term is considerably smaller in absolute value than the first. Consequently the transformation point is shifted in the direction of higher temperatures by the field and the magnitude of the shift is equal to

$$\Delta T_c \approx E / P_{00} \dot{\alpha}. \quad (19)$$

We now find the jump of κ at the transformation point. First of all, from Eq. (13) we find

$$\kappa = (\varepsilon - 1) / 4\pi = (\partial P / \partial E)_T = A + 2BE. \quad (20)$$

In order to find the value of κ for $T = T_c$ on the low temperature side it is necessary to expand A and B into series in ΔT_c and to substitute the value of ΔT_c from Eq. (18), whereupon it is obviously sufficient for the calculation of B to terminate with terms of zero degree, and for the calculation of A , with terms linear in ΔT_c . Performing the expansion, we find

$$A = \frac{1}{8\alpha_0} \left[1 + \Delta T_c \left(2 \frac{\dot{\alpha}}{\alpha_0} - \frac{6\dot{\beta}_1}{\beta_{10}} \right) \right]; \quad (21)$$

$$B = -\frac{9}{128 \alpha_0^2} \sqrt{-\frac{\beta_{10}}{4\alpha_0}}.$$

Substituting the value of ΔT_c in A , we find from Eq. (20)

$$\kappa_{T_c} = \frac{1}{8\alpha_0} \quad (22)$$

$$+ \frac{E}{4\alpha_0^2} \sqrt{-\frac{\beta_{10}}{4\alpha_0}} \left[\frac{5}{16} - \frac{\dot{\beta}_1 / \beta_{10}}{\alpha / \alpha_0 - 2\dot{\beta}_1 / \beta_{10}} \right].$$

We find the value of κ on the high temperature side from

$$(\kappa)_{T_c} = \left(\frac{1}{2\alpha} \right)_{T_c} = \frac{1}{2\alpha_0} \left(1 - \frac{\alpha}{\alpha_0} \Delta T_c \right).$$

Substituting here ΔT_c from Eq. (18); we get

$$\chi_{T_c} = \frac{1}{2\alpha_0} \quad (23)$$

$$-\frac{\dot{\alpha}}{2\alpha_0^3} \sqrt{\frac{\beta_{10}}{4\alpha_0} \frac{E}{\dot{\alpha}/\alpha_0 - 2\dot{\beta}_1/\beta_{10}}}$$

From Eqs. (22) and (23) it is seen that application of an electric field somewhat reduces the jump of χ at the transformation point, which conforms in the absence of a field to the "rule of four"¹.

B. PHASE TRANSITION OF THE SECOND KIND

As was explained above, in the application of a field, the phase transition is "washed out". In this case it is meaningless to speak of the dielectric permeability at the transition point, but it is expedient to set up the problem of finding P and ϵ for temperatures in the neighborhood of the Curie point*¹⁰. Since in this temperature range one can disregard the term in P^5 in Eq. (9), the problem reduces to the finding of the solution of the equation

$$\beta_1 P^3 + \alpha P = E/2 \quad (24)$$

and to finding the susceptibility

$$\chi = (\partial P / \partial E)_T = 1/2(3\beta_1 P^2 + \alpha)^{-1}. \quad (25)$$

The solution of Eq. (24) can be easily studied by means of tables.⁹ The dependence of χ on E for $T=\text{const.}$ is seen immediately from Eq. (25):

$$(\partial \chi / \partial E)_T = -3\beta_1 P / 2(3\beta_1 P^2 + \alpha)^3 < 0. \quad (26)**$$

For a fixed temperature χ decreases with an increase in E .*** The detailed dependence $\chi(E)$ can be followed by the use of the tables, but we are confining ourselves only to the observations made.

The function $\chi(T)$ for $E=\text{const.}$ is of great interest.

The function $y(q)$, is shown in Fig. 1 where

*By the Curie point, naturally, is understood the temperature which corresponds to the phase transition for $E=0$, i.e., the temperature for which $\alpha=0$.

** The positiveness of the denominator in Eq. (26) follows from the fact that the solution of Eq. (24) satisfies minimum Φ .

*** The decrease of χ with increase in E has been noted in the literature.¹

$$y = \chi (\beta_1 E^2 / 4)^{1/3}; \quad 4\alpha^3 / \beta_1 E^2 = q,$$

are plotted by use of the tables.⁹ From the graph it is seen that y has a maximum ≈ 0.21 for $q \approx 1.2$.

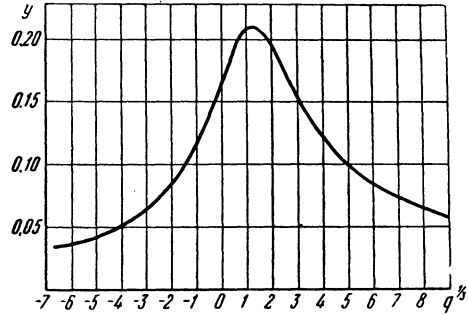


FIG. 1

We disregard the temperature dependence of β_1 . Then the relation obtained can be written in the following form:

$$\chi_{\text{max}} (\beta_1 E^2 / 4)^{1/3} \approx 0.33; \quad (27)$$

$$(\alpha)_{\chi=\chi_{\text{max}}} \approx 0.75 (\beta, E^2)^{1/3}.$$

Thus, application of a field displaces the point of maximum χ into the region of higher temperatures, whereupon this displacement is proportional to $E^{2/3}$, while the maximum value of χ is inversely proportional to $E^{2/3}$. If we denote the amount of the shift of temperature which corresponds to the maximum, by $\Delta T = T_{\text{max}} - T_c$ and assume for α a linear dependence on temperature, $\alpha = \alpha(T - T_c)$, we can get from Eq. (27)

$$\chi_{\text{max}} \Delta T = \text{const} \approx 0.25 / \dot{\alpha}. \quad (28)$$

With β_1 temperature dependent, these simple relations no longer hold. In this case however, it is not difficult to calculate the function $\chi(T)$ for $E=\text{constant}$ by means of the tables. In Fig. 2 several curves for various values of E are shown. In their construction, a linear dependence of α and β_1 on temperature was assumed*:

*The value of the constant in α is known from Ref. 10. As regards the coefficient in β_1 , using the numbers given, a satisfactory agreement of several theoretical formulas⁴ with the experimental results¹¹ was successfully obtained.

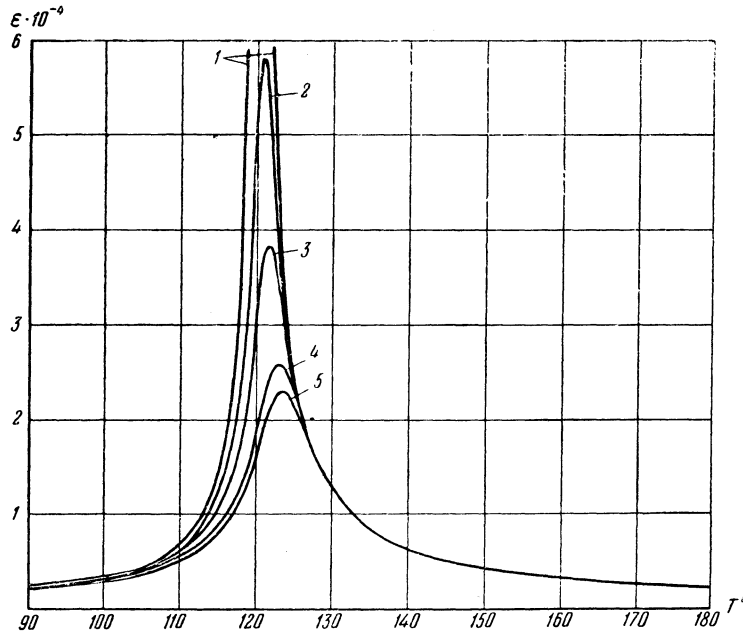


FIG. 2 1 — $E = 0$, 2 — $E = 500$, 3 — $E = 1000$, 4 — $E = 2000$,
5 — $E = 2500$ V/cm

$$\alpha = 5 \cdot 10^{-5} (t - 120);$$

$$\beta_1 = [1.4 \cdot 10^{-6} - 1.9 \cdot 10^{-7} (t - 120)] \text{ cm}^4 / \mu \text{ sec}^2.$$

The curves in Fig. 2, in their qualitative shape, are very close to the experimental curves obtained in Ref. 12. In any event, it appears very probable that these latter curves can be interpreted only regarding the phase change as a transition of the second kind. Unfortunately, a quantitative comparison is not possible since the curves of Ref. 12 were obtained for polycrystals and also since this work does not contain a sufficiently complete description of the properties of the specimens studied.

3. INDUCED PIEZOEFFECT

In the neighborhood of the Curie point, a crystal in which a phase transformation of the second kind occurs must be "friable", i.e., very compliant with respect to external influences. One can expect that one of the manifestations of this friability should be an effect where a crystal which, at a given temperature, does not have piezoelectric properties, acquires them upon application of an electric field. We shall call such an effect an induced piezoeffect. We maintain the same designation also for the more general case when a crystal, before the application of an electric field, possesses a piezo-

effect characterized by a certain matrix of piezomoduli and application of a field leads to the emergence of new piezomoduli (and to the modification of the old ones).

The phenomenon of induced piezoeffect should also be observed for a BaTiO_3 crystal near the Curie point, both above and below this point.

Let the stress component σ_{kl} , in the presence of the electric field component E_j , give rise to the appearance of the induced polarization

$$(P_i)_{\text{ind}} = C_{ijkl} \sigma_{kl} E_j.$$

We shall call the coefficients C_{ijkl} (symmetrical in the indices k, l) the induced piezomoduli. They are easy to find by use of the formulas of Ref. 5, where the components of the polarizability tensor χ_{ij} in the presence of elastic stresses σ_{kl} are calculated. In particular

$$C_{ijkl} = \partial^2 P_i / \partial E_j \partial \sigma_{kl} = \partial \chi_{ij} / \partial \sigma_{kl}.$$

In actuality, however, the calculation of the induced piezomoduli according to the formulas of Ref. 5 still does not give correct expressions for the induced piezomoduli, since in the expansion of the thermodynamic potential used in Ref. 5, certain terms which play an essential role in the investigation of the question were not considered. On taking

them into consideration the thermodynamic potential of a crystal with cubic symmetry assumes the form:

$$\Phi = \Phi_0 + (\alpha_1 P_x^2 + \alpha_2 P_y^2 + \alpha_3 P_z^2) \quad (29)$$

$$\begin{aligned} &+ 1/2 \beta_1 P^4 + \beta_2 (P_x^2 P_y^2 + P_y^2 P_z^2 + P_z^2 P_x^2) \\ &- (P_x E_{x1} + P_y E_{y1} + E_{z1} P_z) \\ &- 2\kappa_3 (\sigma_{12} P_x P_y + \sigma_{23} P_y P_z + \sigma_{31} P_z P_x) \\ &- 2\delta_3 [\sigma_{12} (P_x E_y + P_y E_x) \\ &+ \sigma_{23} (P_y E_z + P_z E_y) + \sigma_{31} (P_z E_x + P_x E_z)] \\ &- 1/2 s_{11} (\sigma_{11}^2 + \sigma_{22}^2 + \sigma_{33}^2) \\ &- s_{12} (\sigma_{11} \sigma_{22} + \sigma_{22} \sigma_{33} + \sigma_{33} \sigma_{11}) \\ &- 1/2 s_{44} (\sigma_{12}^2 + \sigma_{23}^2 + \sigma_{31}^2), \end{aligned}$$

where the notation

$$E_{x1} = E_x + [\delta_1 \sigma_{11} + \delta_2 (\sigma_{22} + \sigma_{33})] E_x; \quad (30)$$

$$E_{y1} = E_y + [\delta_1 \sigma_{22} + \delta_2 (\sigma_{33} + \sigma_{11})] E_y;$$

$$E_{z1} = E_z + [\delta_1 \sigma_{33} + \delta_2 (\sigma_{11} + \sigma_{22})] E_z.$$

is used. Here δ_1 , δ_2 and δ_3 are the coefficients with the invariants not treated in Ref. 5. The remaining notation agrees with that used in Ref. 5.

The necessary conditions for a minimum of Φ have the form:

$$2P_x [\alpha_1 + \beta_1 P^2 + \beta_2 (P_y^2 + P_z^2)] \quad (31)$$

$$= E_{x1} + 2\kappa_3 (\sigma_{12} P_y + \sigma_{31} P_z)$$

$$+ 2\delta_3 (\sigma_{12} E_y + \sigma_{31} E_z)$$

etc. In order to determine the induced piezomoduli from this, it is convenient to calculate them one after another. Thus, for the calculation of C_{1111} we set $\sigma_{11} \neq 0$, and all the remaining components σ_{kl} equal to zero and $E_x \neq 0$, $E_y = E_z = 0$.

We examine, at first, temperatures above and not too close to the Curie point. Then it is possible to assume

$$P_x = \kappa_{11} E_x + C_{1111} E_x \sigma_{11}; \quad P_y = P_z = 0.$$

Substituting this in Eq. (31) and taking into consideration that $\kappa_{11} = 1/2 \alpha$, we find, disregarding terms of higher order

$$C_{1111} = \delta_1 / 2\alpha + \kappa_1 / 2\alpha^2. \quad (32)$$

The remaining piezomoduli are calculated in an analogous way.

The results obtained can be formulated in the form of the following rules.

1. Only those induced piezomoduli are different from zero for which all indices consist of repeated numbers. Piezomoduli, the indices of which contain some number only once, are equal to zero.

2. The nonzero induced piezomoduli are expressed by a two term formula, the first term of which is proportional to $1/\alpha$, and the second proportional to $1/\alpha^2$.

3. The coefficients with $1/\alpha$ and $1/\alpha^2$ for the moduli corresponding to elongations (compressions), are equal to $\delta_1 / 2$ and $\kappa_1 / 2$ respectively, when the elongation (compression) coincides with the direction of the electric field, and are equal to $\delta_2 / 2$ and $\kappa_2 / 2$, respectively when the elongation (compression) is perpendicular to the direction of the electric field.

4. The coefficients with $1/\alpha$ and $1/\alpha^2$ for the moduli corresponding to shear are equal to $\delta_3 / 2$ and $\kappa_3 / 4$, respectively.

We now consider temperatures below the Curie point. The calculation of the induced piezomoduli is carried out analogously to the case where $T > T_c$. The difference is merely in that the general piezomoduli d_{ikl} are now not equal to

zero and a spontaneous polarization P_0 exists. With nonzero components E_j and σ_{kl} and the

choice of the direction of spontaneous polarization along the z axis, there should be substituted in Eq. (31):

$$P_x = \kappa_{1j} E_j + d_{1kl} \sigma_{kl} + C_{1jkl} E_j \sigma_{kl} \quad (33)$$

and analogous expressions for P_y and P_z . The results of the calculation reduce to the following:

1) as in the case for $T > T_c$, all of the induced piezomoduli whose indices contain even a single nonrepeated number are equal to zero. 2) Replacement of the index 1 by 2, and vice versa, in the first and second pair of indices does not change the

value of the modulus. The essentially different, nonzero, induced piezomoduli are equal to

$$C_{3333} = -\delta_1/4\alpha - \kappa_1/4\alpha^2; \tag{34}$$

$$C_{3311} = -\delta_2/4\alpha - \kappa_2/4\alpha^2;$$

$$C_{1133} = -\delta_2\beta_1/2\beta_2\alpha$$

$$+ (\beta_1^2/2\beta_2^2\alpha^2) [\kappa_2 - \kappa_1(\beta_1 + \beta_2)/\beta_1];$$

$$2C_{1313} = -\delta_3\beta_1/\beta_2\alpha - \kappa_3(2\beta_1 + \beta_2)\beta_1/4\beta_2^2\alpha^2;$$

$$C_{1111} = -\delta_1\beta_1/2\beta_2\alpha$$

$$+ (\beta_1/2\beta_2^2\alpha^2) [\kappa_1\beta_1 - \kappa_2(\beta_1 + \beta_2)];$$

$$C_{1122} = -(\beta_1/2\alpha\beta_2)(\delta_2 + \kappa_2/\alpha);$$

$$2C_{2121} = -\delta_3\beta_1/\beta_2\alpha + \kappa_3\beta_1^2/2\beta_2^2\alpha^2;$$

$$2C_{3131} = -\delta_3/2\alpha - \kappa_3(\beta_2 + 2\beta_1)\beta_1/4\alpha^2\beta_2^2.$$

In conclusion we note that there must also exist an effect inverse to the induced piezoeffect. From the thermodynamic formula*

$$d\Phi = -P_i dE_i - u_{kl} d\sigma_{kl} \tag{35}$$

there follows the well-known relation

$$\partial P_i / \partial \sigma_{kl} = \partial u_{kl} / \partial E_i. \tag{36}$$

It contains in itself, along with the inverse piezoeffect also the inverse induced piezoeffect. Substituting in Eq. (36)

$$(P_i)_{ind} = \kappa_{ij}E_j + d_{ikl}\sigma_{kl} + C_{ijkl}E_j\sigma_{kl}, \tag{37}$$

we find

$$u_{kl} = (u_{kl})_0 + d_{ikl}E_i + C_{ijkl}E_iE_j. \tag{38}$$

Thus the effect inverse to the induced piezoeffect is electrostriction and the coefficients C_{ijkl} are the coefficients of electrostriction.⁶

For deformations of elongation (compression) there correspond $k=1$; but then, also $i=j$ (otherwise $C_{ijkl} = 0$). Consequently, such deformations depend quadratically on the component of field intensity. To shear deformations there correspond $k \neq 1$; but then, $i=k$ and $j=1$. Consequently, shear deformations arise only in the presence of two components. In the general case when the directions of the vectors P_0 and E make an arbitrary angle, both extension (compression) and shear occur.

¹V. L. Ginzburg, J. Exptl. Theoret. Phys. (U.S.S.R.) 15, 739 (1945); 19, 36 (1949).

²A. F. Devonshire, Phil. Mag. 40, 1040 (1949).

³A. F. Devonshire, Phil. Mag. 42, 1065 (1951).

⁴M. Ia. Shirobokov and L. P. Kholodenko, J. Exptl. Theoret. Phys. (U.S.S.R.) 21, 1239 (1951).

⁵L. P. Kholodenko and M. Ia. Shirobokov, J. Exptl. Theoret. Phys. (U.S.S.R.) 21, 1250 (1951).

⁶G. A. Smolenskii and R. E. Pasinkov, J. Exptl. Theoret. Phys. (U.S.S.R.) 24, 69 (1953).

⁷W. Känzig and N. Naikoff, Helv. Phys. Acta 24, 343 (1951).

⁸L. Landau and E. Lifshitz: *Statistical Physics*, GTTI, Moscow, 1951.

⁹B. M. Shumiagskii: *Tables for the Solution of Cubic Equations*, GTTI, Moscow, 1950.

¹⁰S. Roberts, Phys. Rev., 75, 989 (1949).

¹¹W. J. Merz, Phys. Rev., 75, 687 (1949).

¹²Siniakov, Stafeichuk and Sinogubova J. Exptl. Theoret. Phys. (U.S.S.R.) 21, 1396 (1951).

*Here, we keep in mind the equilibrium thermodynamic potential.