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On the Theory of Phase Phenomena in Barium Titanate

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An explanation is given of "temperature hysteresis" which accompanies phase transitions. The temperature dependence of the dielectric constant in the vicinity of phase transition points has been found. Expressions are found for the coefficients involved in the thermodynamic theory; these are determined in terms of easily measured quantities. The relaxation time has been estimated.

INTRODUCTION

THE thermodynamic theory of piezoelectric phenomena in barium titnate[1-7] is built on a consideration of the thermodynamic potential (or the free energy), and on a search for those conditions under which it takes on minimum values. In this way the presence of four different phases has been established and the transition conditions from one phase to another have been made clear. Here it has been assumed that the transition from one phase to another takes place at that temperature for which the value of the thermodynamic potential becomes identical for both phases under consideration. In essence, this approach implies a neglect of metastable states, which are characterized by a relative, and not an absolute, minimum of the thermodynamic potential. It is known that in a number of cases, the relaxation time is so large that the metastable states are practically stable. Neglect of the metastable states allows us to make clear the chief features of the phenomenon, but it does not allow a satisfactory look at a number of details, including hysteresis phenomena and the piezoelectric properties close to the transition point.

In order to carry out such an analysis, we must (in addition to a consideration of the metastable states) make a definite hypothesis on the temperature dependence of the coefficients in the well-known expression of the thermodynamic potential

$$\Phi = \Phi_0 + \alpha P^2 + {}^1\!/_2\beta_1 P^4 + \beta_2 (P_x^2 P_y^2 + P_y^2 P_z^2 + P_z^2 P_x^2) + {}^1\!/_3\gamma_1 P^6 + \gamma_2 [P_x^4 (P_y^2 + P_z^2) + P_y^4 (P_z^2 + P_x^2) + P_z^4 (P_x^2 + P_y^2)] + \gamma_3 P_x^2 P_y^2 P_z^2. \qquad (1)$$

In the case of a second order phase transition, we can regard (1) as an expansion in a power series P. It is evident that not only α but also β_1, β_2, γ_1, γ_2, γ_3 are in this case functions of the temperature and pressure. In the case of a first order phase transition, it is no longer possible to regard Eq. (1) as an expansion in a series, but only as a more or less successful approximation. It is evident that in this case also, there is no basis for considering the quantities β_1, β_2, γ_1, γ_2, γ_3 as constants. Moreover, the fact of the temperature dependence of these coefficients is immediately evident from the independence of P (as observed experimentally) of temperature in the orthorhombic and rhombic phases.* While, in the literature (for example, Refs. 2,3, 8), all the enumerated coefficients are regarded as constant. In the present research, the following approximation is used: the quantities γ_1, γ_2, γ_3 are considered constant, but the quantities α $_1\beta_1$, β_2 are considered as linear functions of the temperature. This approximation permits an explanation of the order of the phase changes observed experimentally, and reduces to a series of relations which are easily tested experimentally.

Unfortunately there is a lack in the literature today of data on a sufficiently complete investigation (if only of a single specimen) which includes the temperature dependence of the polarization and the dielectric constant in both phases, on the consideration of temperature hysteresis, heat capacity, elastic modulus and piezomodulus. Such a complete investigation would permit a quantitative comparison of theory with experiment, which would be the more desirable in that the theory of other piezoelectrics with "perovskite" structure ought to be built in analogy with the theory of barium titanate.

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*Actually, in the orthorhombic phase, for example, P^2 is given by the relation[4]

$$P^2 = [2\gamma_1 + {}^3\!/_2\gamma_2]^{-1} [-\beta_1 - {}^1\!/_2\beta_2) + \sqrt{(\beta_1 + {}^1\!/_2\beta_2)^2 - 4\alpha(\gamma_1 + {}^3\!/_4\gamma_2)}\,].$$

For α increasing linearly with the temperature, and for constant P^2 increases monotonically upon a decrease in temperature, and does not remain constant. (For details, see Sec. 2).

1. CONDITIONS FOR THE STABILITY (METASTABILITY) OF THE DIFFERENT PHASES AND THEIR INTERPRETATION

As is well known, the thermodynamic potential (1) has extrema for the values P_x, P_y, P_z which correspond to I) nonpiezoelectric (cubic), II) tetragonal, III) orthorhombic, IV) rhombic phases,* where the equations that are satsfied by nonzero components, their solutions, and the conditions that the extrema be minima, have the forms:[4]

$$\text{Phase I } P_x = P_y = P_z = 0, \quad \alpha > 0. \tag{2}$$

$$\text{Phase II } \gamma_1 P^4 + \beta_1 P^2 + \alpha = 0, \quad (P = P_z \text{ or } P_x \text{ or } P_y), \tag{3}$$

$$P^2 = [-\beta_1 + \sqrt{\beta_1^2 - 4\alpha\gamma_1}]/2\gamma_1, \tag{4}$$

$$\beta_1 + 2\gamma_1 P^2 > 0. \tag{5}$$

$$\beta_2 + \gamma_2 P^2 > 0, \tag{6}$$

$$\text{Phase III } (\gamma_1 + {}^3/_4\,\gamma_2) P^4 + (\beta_1 + {}^1/_2\,\beta_2) P^2 + \alpha = 0, \tag{7}$$

$$P^2 = {}^1/_2 (\gamma_1 + {}^3/_4\,\gamma_2)^{-1} [-(\beta_1 + {}^1/_2\,\beta_2) + \sqrt{(\beta_1 + {}^1/_2\,\beta_2)^2 - 4\alpha(\gamma_1 + {}^3/_4\,\gamma_2)}]. \tag{8}$$

$(P_x^2 = P_y^2,\ P_z = 0$ or similar solutions),

$$(2\beta_1 + \beta_2) + (4\gamma_1 + 3\gamma_2) P^2 > 0, \tag{9}$$

$$2\beta_2 + (\gamma_3 - \gamma_2) P^2 > 0, \tag{10}$$

$$\beta_2 + \gamma_2 P^2 < 0. \tag{11}$$

$$\text{Phase IV } (\gamma_1 + {}^2/_3\,\gamma_2 + {}^1/_9\,\gamma_3) P^4 + (\beta_1 + {}^2/_3\,\beta_2) P^2 + \alpha = 0, \tag{12}$$

$$P^2 = {}^1/_2 (\gamma_1 + {}^2/_3\,\gamma_2 + {}^1/_9\,\gamma_3)^{-1} \times \left[-(\beta_1 + {}^2/_3\,\beta_2) + \sqrt{(\beta_1 + {}^2/_3\,\beta_2)^2 - 4\alpha\left(\gamma_1 + {}^2/_3\,\gamma_2 + \frac{1}{9}\gamma_3\right)}\right]. \tag{13}$$

$$(P_x^2 = P_y^2 = P_z^2),$$

$$(\beta_1 + {}^2/_3\,\beta_2) + 2(\gamma_1 + {}^2/_3\,\gamma_2 + {}^1/_9\,\gamma_3) P^2 > 0, \tag{14}$$

$$3\beta_2 + \gamma_3 P^2 < 0\ ^{**} \tag{15}$$

In order to give graphic meaning to these general conditions, which characterize the minimum of Φ relative to an arbitrarily small deviation from the equilibrium position, let us consider some concrete deviations. With this aim, we set $P_z = 0$ and introduce polar coordinates in the plane P_x, P_y. Substituting $P_y = P \cos \varphi$ $P_x = P \sin \varphi$ in Eq. (1), we get

$$\Phi = \Phi_0 + \alpha P^2 + {}^1/_2\,\beta_1 P^4 + {}^1/_3\,\gamma_1 P^6 + \cos^2\varphi \sin^2\varphi P^4 (\beta_2 + \gamma_2 P^2). \tag{16}$$

The extrema (16) are found from the equations $\partial \Phi/\partial p = 0$, $\partial \varphi/\sigma \varphi = 0$, which have the solutions I) $P = 0$, II), $P \neq 0$, $\varphi = 0$, III) $P \neq 0$, $\varphi = \pi/4$, which evidently correspond to phases I, II, III. Calculating the second derivatives of Φ we find that the solutions II ($\varphi = 0$) correspond to a minimum for

$$\beta_2 + \gamma_2 P^2 > 0 \text{ и } \alpha + 3\beta_1 P^2 + 5\gamma_1 P^4 > 0,$$

and the solutions III for

$$\beta_2 + \gamma_2 P^2 < 0,\ \alpha + 3\beta_1 P^2 + 5\gamma_1 P^4 + {}^3/_2\,\beta_2 P^2 + {}^{15}/_4\,\gamma_2 P^4 > 0.$$

These conditions, by virtue of Eqs. (3) and (7), coincide with the conditions (9) and (11), which can then be interpreted as the conditions for a minimum in Φ relative to the value of the vector **P** and the angle φ

In order to interpret the inequalities (10), (14) and (15), let us consider small departures from equilibrium of another type. To be precise, we set

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*For brevity, we shall call these phases I,II,III,IV.

**Another minimum condition is given in Ref. 4 for the phase IV; however, it appears as a consequence of Eqs. (14) and (15).

$$P_x = P\cos\theta; \quad P_y = P_z = 2^{-1/2} P \sin\theta,$$

which correspond to the position of the vector P in the plane which passes through the x axis and the diagonal of the yz plane. In this case, Eq. (1) has the form

$$\Phi = \Phi_0 + \alpha P^2 + {}^1/_2\,\beta_1 P^4 + {}^1/_3\,\gamma_1 P^6 \qquad (17)$$

$$+ \beta_2 P^4 (\sin^2\theta\cos^2\theta + {}^1/_4 \sin^4\theta)$$

$$+ \gamma_2 P^6 [\cos^4\theta\sin^2\theta + {}^1/_2 \sin^4\theta\,(\cos^2\theta$$

$$+ {}^1/_2 \sin^2\theta)] + {}^1/_4\,\gamma_3 P^6 \cos^2\theta \sin^4\theta.$$

Investigation of this equation leads to the following result. The extrema of Φ occur, for II), at $\theta = 0$, for III) at $\theta=\pi/2$, and for IV) at tan $\theta=2$. These correspond to the phases II, III, IV. The necessary conditions that these extrema be minimal are the satisfaction of the conditions $\Phi_{\varphi\varphi} > 0$, $\Phi_{\varphi\varphi} > 0$. The first of these, which is applicable to solutions of II and III, as should be expected, again reduce to the equations (5) and (9), while that applicable to the solution of IV reduces to the inequality (14). The second requirement gives, for the solution of II: $\beta_2 + \varphi\varphi_2 P^2 > 0$. for the solution of III): $2\beta_2 + (\gamma_3 - \gamma_2) P^2 > 0$, and for the solution of IV): $3\beta_2 + \gamma_3 P^2 > 0$.

Summing up the results we can say that the conditions for a minimum of Φ for each of the phases II, III, IV consist of a single inequality, which expresses the minimum in the quantity P and which contains coefficients both for the isotropic and for the anisotropic terms of Φ, and of one or two inequalities which express the minimum in terms of angles and which contain only the coefficients for the anisotropic terms.

2. TEMPERATURE HYSTERESIS

If we consider that the metastable states are states of virtual equilibrium, which is evidently valid for BaTiO$_3$, the state of the crystal (in the sense of the attachment of it to a certain phase which we denote as phase A) remains unknown so long as this relative minimum of the thermodynamic potential (to which phase A corresponds) does not disappear. Only after this does the transition to another phase B take place. We denote the temperature, at which this occurs, by T_{AB}, The reverse transition from phase B to phase A takes place at the same temperature T_{BA}, at which phase B loses stability (it ceases to correspond to a minimum). The temperature T_{BA}, generally speaking, does not coincide with T_{AB}, which indicates the presence of temperature hysteresis.

For a concrete consideration of temperature hysteresis, it is first of all necessary to establish the temperature dependence of β_1 and β_2. Within the framework of the chosen approximation (β_1 and β_2 are linear functions of temperature; γ_1, γ_2 γ_3 are constants) the problem reduces to the sign and value of the derivatives $(\partial\beta_1/\partial T)_P \equiv \beta_1$ and $(\partial\beta_2/\partial T)_p \equiv \beta_2$. To find these quantities, it is convenient to make use of the fact that, as experiment shows,[9] P^2_{III} and P^2_{IV} are practically independent of temperature.* Differentiating Eqs. (7), (12) with respect to temperature, we have for $\partial P^2/\partial T = 0$:

$$(\dot{\beta}_1 + {}^1/_2\,\dot{\beta}_2)\, P^2_{III} = -\alpha, \qquad (18)$$

$$(\dot{\beta}_1 + {}^2/_3\,\dot{\beta}_2)\, P^2_{IV} = -\dot{\alpha},$$

where P^2_{III} and P^2_{IV} are the values of P in the phases III and IV, and $\alpha \equiv (\partial\alpha/\partial T)_p$. We find from Eq. (18)

$$\dot{\beta}_1 = \dot{\alpha}\,(3/P^2_{IV} - 4/P^2_{III}), \qquad (19)$$

$$\dot{\beta}_2 = 6\dot{\alpha}\,(P^2_{IV} - P^2_{III})/P^2_{III}P^2_{IV}.$$

In accord with the experimental data,[10] $P^2_{IV} > P^2_{III}$ and $P^2_{IV} - P^2_{III} << P^2_{III}$. It therefore follows that $\dot{\beta}_1 < 0$ and $\dot{\beta}_2 > 0$ and is small in comparison with $\dot{\beta}_1$. Thus β_1 falls off rapidly, while β_2 increases slowly with increase in temperature.

Furthermore, it is not difficult to establish that $\gamma_2 < 0$** Inasmuch as the regions of stability of

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*The independence of P of T in phases III and IV probably has an accidental character and cannot be observed in other piezoelectrics of the type of BaTiO$_3$. However, we can also find $\dot{\beta}_1$ and $\dot{\beta}_2$ without making use of this independence.

**As a consequence of the uncertainty of the experimental data, the opposite assumption has been made in Ref. 4.

phases II and III overlap (temperature hysteresis), conditions (6) and (11) are simultaneously satisfied in the region of overlap, for any temperature. Then, by virtue of the fact that $P^2_{II} < P^2_{III}$ [10], it is true that $\gamma_2 < 0$.

Assembling this information on the coefficients β_1, β_2, γ_2, it is easy to determine which of the conditions (5), (6) limits the region of existence of phase II on the high temperature side. This cannot be Eq. (6), since if $\gamma_2 P^2_{II} + \beta_2 (T_{21}) = 0$ held at the temperature T_{21}, then, for much lower temperatures $T < T_{21}$, it would be necessary that $\gamma_2 P^2_{II} + \beta_2 < 0$, and phase II could not exist. Consequently, the transition from phase II to phase I proceeds at the temperature T_{21} which satisfies the condition $2\gamma_1 P^4 + \beta_2 P^2 = 0$. The reverse transition from phase I to phase II proceeds at a temperature T_{12} which is determined by the condition $\alpha = 0$, since for $\alpha < 0$, $P = 0$ corresponds to maximum Φ.

Let us proceed to the transition between phases II and III. We first note that condition (9), which is, by Eq. (8), equivalent to

$$[(\beta_1 + {}^1/_2\,\beta_2)^2 - 4\alpha\,(\gamma_1 + {}^3/_4\,\gamma_2)]^{1/2} > 0,$$

is automatically satisfied if $\alpha < 0$.* Consequently, the region of stability of phase III is determined by the conditions (10), (11). Let the crystal be in phase II and let us carry out a decrease in the temperature. Initially, Eq. (6) is satisfied. With a decrease in the temperature, β_2 decreases and at temperature T_{23} [determined from $\gamma_2 P^2_{II} + \beta_2(T_{23}) = 0$] phase II loses stability. A transition to phase III occurs. Inasmuch as $P^2_{III} > P^2_{II}$, condition (11) will be satisfied at the temperature T_{23}. We now trace the reverse transition from phase III to phase II. It takes place at the temperature $T_{32} > T_{23}$, determined by the condition $\gamma_2 P^2_{III} + \beta_2 (T_{32}) = 0$. At this temperature, phase III loses its stability, since condition (6) will be satisfied.

Now let us consider transitions between phases III and IV. Here the coefficient γ_3 plays an essential role. For the interpretation of the transitions considered, we must regard γ_3 as negative (with the subordinate condition $\gamma_1 + 2/3\,\gamma_2 + 1/9\,\gamma_3 > 0$[4]).

Let the crystal be in phase III and the temperature be lowered. Further, let the condition

$$3\beta_2 + \gamma_3 P^2_{III} > 0, \tag{20}$$

hold, along with condition (11). Condition (10) then follows from (11) and (20). For a lowered temperature, β_2 decreases and at the temperature T_{34}, which satisfies the condition $3\beta_2 + \gamma_2 P^2_{III} = \beta_2 + \gamma_2 P^2_{III} < 0$ or $2\beta_2(T_{34}) + (\gamma_3 - \gamma_2) P^2_{III} = 0$, phase III loses its stability and the crystal undergoes a transition to phase IV, the stability condition for which [Eq. (15)] is of course satsified since $T_{43} < T_{34}$. The reverse transition from phase IV to phase III takes place at a temperature $T_{43} < T_{34}$, at which the quantity $3\beta_2 + \gamma_3 P^2_{IV}$ vanishes and, consequently, phase IV loses its stability. It is easy to see that the conditions for the stability of phase III are satisfied at temperature T_{43}. Condition (14) for $\alpha < 0$, $\gamma_1 + 2/3\gamma_2 + 1/9\gamma_3 > 0$ [4] is also satisfied automatically.

In the picture drawn here of the phase transitions, it is clear that the sequence of phase changes depends sensitively on the size of the coefficients; therefore we can expect that other piezoelectrics of the $BaTiO_3$ type can be found with another sequence of phases or with the absence of some of them.

Operating on the above basis, it is not difficult to calculate the width of the regions of temperature hysteresis.

Region $T_{21} - T_{12} \equiv (\Delta T)_{21}$. It is easily seen that in the case of a second order phase transition, hysteresis is absent, as would be expected.* In the case of a first order transition,

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*Condition (9), as was pointed out in Ref. 4, only determines the choice of the sign in front of the square root in the solution of (7). So far as the sign of $(\gamma_1 + 3/4\,\gamma_2)$ is concerned, this quantity is positive.[4]

*Phase II loses its stability at a temperature T_{21} determined from $2\gamma, P^4 + \beta_1 P^2 = 0$ or, by virtue of Eq. (3), from $\beta_1 P^2_{II} + 2\alpha = 0$. Since, for a second order phase transition, P tends to zero at the ransition point, the latter condition means that $\alpha(T_{21}) = 0$, i.e., that $T_{21} = T_{12}$.

$$\alpha(T_{12}) = 0, \quad 2\gamma_1 P_{\mathrm{II}}^2 + \beta_1(T_{21}) = 0. \tag{21}$$

By taking Eq. (4) into account, the latter equation can be written in the form

$$\alpha(T_{21}) = [\beta_1(T_{21})]^2 / 4\gamma_1. \tag{22}$$

Substituting $(\Delta T)_{21}$ α for α (T_{21}), we get

$$(\Delta T)_{21} = [\beta_1(T_{21})]^2 / 4\gamma_1\alpha. \tag{23}$$

Region $T_{32} - T_{23} \equiv (\Delta T)_{32}$. The temperatures T_{23} and T_{32} are determined by the equations

$$\gamma_2 P_{\mathrm{II}}^2(T_{23}) + \beta_2(T_{23}) = 0, \tag{24}$$

$$\gamma_2 P_{\mathrm{III}}^2(T_{32}) + \beta_2(T_{32}) = 0.$$

Replacing β_2 (T_{32}) by β_2 $(T_{23}) + \beta_2$ $(\Delta T)_{32}$, we findfrom these equations,

$$(\Delta T)_{32} = (\gamma_2/\dot\beta_2)[P_{\mathrm{II}}^2(T_{23}) - P_{\mathrm{III}}^2(T_{32})]. \tag{25}$$

Region $T_{43} - T_{34} \equiv (\Delta T)_{43}$. Here the temperatures T_{34} and T_{43} are determined by the equations

$$2\beta_2(T_{34}) + (\gamma_3 - \gamma_2) P_{\mathrm{III}}^2 = 0,. \tag{26}$$

$$\beta_2(T_{43}) + \gamma_3 P_{\mathrm{IV}}^2 = 0.$$

Setting β_2 $(T_{43}) = \beta_2$ $(T_{34}) + (\Delta T)_{43}$ β_2, we find

$$(\Delta T)_{43} = [\gamma_3(P_{\mathrm{III}}^2 - 2P_{\mathrm{IV}}^2) - \gamma_2 P_{\mathrm{III}}^2]/2\dot\beta_2. \tag{27}$$

To conclude this Section, we note that Eqs. (23), (25), (27) are approximately true even if the dependence of the coefficients β_1 and β_2 on the temperature is more complicated than is assumed in this work.

3. BEHAVIOR OF THE DIELECTRIC CONSTANT NEAR THE POINTS OF PHASE TRANSITIONS

Having Eqs. (21), (24), (26) for the temperatures of the phase transitions, nnd making use of the general expressions for the dielectric constant in each of the phases [that were obtained in Ref. 4], we can make explicit the temperature dependence of the dielectric constant near the transition points.

Boundaries of phases I, II. Here we need to distinguish between the cases of phase transitions of the first and second kind. In the latter case the well known "pair law" holds.[1] We pause only on the first order phase transition. Near T_{12}, for $T > T_{12}$, we have

$$\varepsilon = 2\pi/\alpha = c_{12}/(T - T_{12}), \text{ где } c_{12} = 2\pi/\dot\alpha. \tag{28}$$

If the crystal is in phase II near $(T < T_{21})$ we have

$$\varepsilon_{\parallel} = -\pi / (\beta_1 P^2 + 2\alpha) = \pi / (2\gamma_1 P^4 + \beta_1 P^2); \tag{29}$$

$$\varepsilon_{\perp} = 2\pi / (\beta_2 P^2 + \gamma_2 P^4),$$

where T_{21} satisfies Eq. (21). From Eqs. (4) and (21) it follows that

$$[\beta_1(T_{21})]^2 = 4\gamma_1\alpha(T_{21}), \quad P^2(T_{21}) = -\beta_1 / 2\gamma_1.$$

Making use of these expressions, and limiting ourselves to terms of lowest order, we obtain the small quantity

$$2\gamma_1 P^4 + \beta_1 P^2 = -(\beta_1 / 2\gamma_1)[-2\dot\beta_1\beta_1(T_{21}) \tag{30}$$

$$+ 4\alpha\gamma_1]^{1/2}(T - T_{21})^{1/2}.$$

From Eqs. (29)–(30) we get

$$\varepsilon_{\parallel} = c_{21} / (T_{21} - T)^{1/2}, \text{ where } c_{21} \tag{31}$$

$$= -[2\pi\gamma_1 / \beta_1(4\dot\alpha\gamma_1 - 2\beta_1\dot\beta_1)]_{T=T_{21}}.$$

$\epsilon_\perp$ has no singularity at $T = T_{21}$.

Boundaries of phases II and III. The temperature T_{23} is determined from Eq. (24). It is evident trom (29) that $\epsilon_{\|}$ has no singularity at this temperature, whereas $\epsilon_\perp$ obeys the Curie-Weiss law. Actually, expanding the denominator of Eq. (29) in powers of $T-T_{23}$ and considering that P^2 changes slowly in the neighborhood of T_{23} (so that we can neglect the terms dP^2/dT), we get*

$$\varepsilon_\perp \approx c_{23}/(T - T_{23}), \qquad (32)$$

$$c_{23} = (-2\pi\gamma_2/\beta_2\dot{\beta}_2)_{T=T_{23}}.$$

The temperature T_{32} is obtained foom Eq. (24). In phase III, if we choose the coordinate axes so that $P_x = 0$, $P_y^2 = P_z^2$, the following components are different from zero:

$$\varepsilon_{ik}: \varepsilon_{xx}, \ \varepsilon_{yy} = \varepsilon_{zz} \ \text{И} \ \varepsilon_{yz} = \varepsilon_{zy}.$$

They are expressed by the equations (3), (7) from the work of Ref. 4. It is immediately clear from these equations that the component ϵ_{xx} has no singularity at the temperature T_{32}, while the remaining non-zero components obey the Curie-Weiss law. Because of insufficient space, we shall not deduce the expressions for the corresponding constants, and limit ourselves only to a consideration of the principal values of the tensor ϵ_{ik}. These will be the components ε'_{xx}, ε'_{yy}, ε'_{zz}, where the axes z', x', y' are directed respectively along the vector P, the original x-axis and the direction perpendicular to the first two.

The components ϵ'_{xx}, ϵ'_{yy}, ϵ'_{zz} have the form:[4]

$$\varepsilon'_{xx} = 8\pi/[2\beta_2 P^2 + (\gamma_3 - \gamma_2)P^4]; \qquad (33)$$

$$\varepsilon'_{yy} = -2\pi/(\beta_2 P^2 + \gamma_2 P^4);$$

$$\varepsilon'_{zz} = -2\pi/(4\alpha + (2\beta_1 + \beta_2)P^2).$$

It is evident from these formulas that the longitudinal component ϵ'_{zz} and the one of the transverse components (ϵ'_{xx}), which corresponds to the direction of the crystallographic axis of a fourth order cubic crystal, have no singularities at the transition point. Conversely, the transverse component ϵ'_{yy}, which corresponds to the direction of the diagonal of the cubic crystal, obeys the Curie-Weiss law.

Repeating the calculations used in deriving Eq. (32), we obtain for T close to T_{32} ($T < T_{32}$),

$$\varepsilon_{yy} = c_{32}/(T_{32} - T); \qquad (34)$$

$$c_{32} = (-2\pi\gamma_2/\beta_2\dot{\beta}_2)_{T=T_{32}}.$$

Boundaries of regions III and IV. The temperatures T_{34} and T_{43} are determined by Eqs. (26). Let the crystal be in phase III and T close to T_{34} ($T < T_{34}$). As is evident from Eq. (2.7),[4] the components $\epsilon_{yy} = \epsilon_{zz}$ and $\epsilon_{yz} = \epsilon_{zy}$ have no singularities at thepoint T_{32}. However, the component $\epsilon_{xy} = \epsilon'_{xx}$ follows the Curie-Weiss law. Close to T_{34}, the denminator of the first of Eqs. (33) can be written in the form $2\dot{\beta}_2 P^2_{\text{III}}(T - T_{34})$, and consequently,

$$\varepsilon_{xx} = \varepsilon'_{xx} = c_{34}/(T - T_{34}); \qquad (35)$$

$$c_{34} = 4\pi/\dot{\beta}_2 P^2_{\text{III}} = -4\pi(\gamma_3 - \gamma_2)/2\beta_2\dot{\beta}_2.$$

The remaining components ϵ'_{yy} and ϵ'_{zz} have no singularities for $T = T_{34}$. Thus, even in the case of a transition to the second phase, one of the transverse dielectric constants tends to infinity, but not that one which has a singularity at the point T_{32}.

Now let the crystal be in phase IV, close to the point T_{43} ($T < T_{43}$). As is evident from Eq. (3.8) of Ref. 4, all the components ϵ_{ik} in this case ($\epsilon_{xx} = \epsilon_{yy} = \epsilon_{zz}$ and $\epsilon_{xy} = \epsilon_{yz} = \epsilon_{zx}$) satisfy the Curie-Weiss law. Not computing the corresponding constants, we return to the principal values. They are expressed by the equations*

$$\varepsilon'_{zz} = -3\pi/[6\alpha + (3\beta_1 + 2\beta_2)P^2]; \qquad (36)$$

$$\varepsilon'_{xx} = \varepsilon'_{yy} = -3\pi/(\beta_2 + {}^1/_3\gamma_3 P^2)P^2.$$

It follows from these equations that the longitudinal component ϵ'_{zz} has no singularity for

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*In order to obtain the more accurate expression for c_{23}, we must consider that

$$dP^2/dT = -(\beta_1 P^2 + \alpha)/(2\gamma_1 P^2 + \beta_1),$$

which is obtained upon differentiation of Eq. (3) with respect to the temperature.

*As the z'-axis, we chose the direction of the vector P, and for x', y', any mutually perpencicular directions that are also perpendicular to P.

$T = T_{43}$, but the transverse components ϵ'_{xx} $\epsilon'_{yy} = \epsilon_{\perp}$ obey the Curie-Weiss law:

$$\varepsilon_{\perp} = c_{43} / (T_{43} - T);$$

$$c_{43} = 3\pi / \dot{\beta}_2 P/_{\mathrm{IV}}^{2} = -\pi\gamma_3 / \dot{\beta}_2\beta_2. \tag{37}$$

Are the temperature dependences obtained here validated by experiment? Unfortunately, it is difficult to give a complete answer to this question in the absence of accurate measurements.

4. EXPRESSION OF THE CONSTANTS IN TERMS OF EASILY MEASURABLE QUANTITIES

The problem of the experimental determination of the constants on which the theory is constructed is undoubtedly of practical interest. In Ref. 4 formulas were proposed for the calculation of the theoretical coefficients. However, in the first place, these formulas contain quantities whose accurate measurement is very difficult, and, in the second place, which is more important, these formulas were introduced without consideration of metastable states. It is appropriate therefore to turn our attention to the problem of the coefficients.

The quantities which we need to find are, first, the constants γ_1, γ_2, γ_3. Further, as a consequence of the assumed linear dependence for each of the quantities α, β_1, β_2, it suffices to point out one value for some temperature and the value of the derivative at that temperature.

Finding of α . Inasmuch as one value of α is known from $\alpha(T_{12}) = 0$, we need only to find This quantity has repeatedly been found from the temperature dependence of ϵ in phase I:

$$\dot{\alpha} = 2\pi / \varepsilon (T - T_{12}). \tag{38}$$

Finding of γ_1, $\beta_1(T_{21})$, $\dot{\beta}_1$. Here we need to distinguish the cases of phase transitions of first and second order. Let the transition between the phases I and II be of second order. Then we can find $\beta_{.1}(T_{21})$ from the initial slope of the curve $P(T)$ in phase II. From $P^2 = -\alpha/\beta$,[1] near $T = T_{12}$, it follows that

$$\dot{\beta}_1 = -\dot{\alpha} / (dP^2/dT)_{T=T_{21}}. \tag{39}$$

The value of $\dot{\beta}_1$ was found in Sec. 2. The value of γ_1 can be found from Eq. (3):

$$\gamma_1 = -\alpha(T)P^{-4} - \beta_1(T_{21})P^{-2} - \dot{\beta}_1 P^{-2}(T - T_{21}), \tag{40}$$

where T is an arbitrary temperature $T_{21} < T < T_{23}$, and P is the corresponding polarization.

In the case of a first order phase transition, Eq. (39) does not occur. To find the desired quantities, we have

$$[\beta_1(T_{21})]^2 = 4\gamma_1\alpha(T_{21}), \quad (P^2)_{T_{21}} = -\beta_1(T_{21})/2\gamma_1; \quad \alpha(T_{21}) = (\Delta T)_{21}\dot{\alpha}.$$

From these equations, we find that

$$\beta_1(T_{21}) = -2\frac{(\Delta T)_{21}\dot{\alpha}}{(P^2)_{T_{21}}}; \quad \gamma_1 = \frac{(\Delta T)_{21}\dot{\alpha}}{(P^4)_{T_{21}}}. \tag{41}$$

Finding of $\beta_2(T_{32})$ and γ_2. Solving the second of Eqs. (24) and (7), we obtain

$$\gamma_2 = -4[\alpha(T_{32})/P_{\mathrm{III}}^4 + \beta_1(T_{32})/P_{\mathrm{III}}^2 + \gamma_1]; \tag{42}$$

$$\beta_2(T_{32}) = 4P_{\mathrm{III}}^2[\alpha(T_{32})/P_{\mathrm{III}}^4 + \beta_1(T_{32})/P_{\mathrm{III}}^2 + \gamma_1],$$

$$\alpha(T_{32}) = \dot{\alpha}(T_{32} - T_{12});$$

$$\beta_1(T_{32}) = \beta_1 T_{21}) + \dot{\beta}_1(T_{32} - T_{31}).$$

Finding of $\dot{\beta}_2$. The qunntity β_2 was found in Sec. 2. For a control, and in the vanishing of the small distances $P_{\mathrm{IV}}^2 - P_{\mathrm{III}}^2$ entering in Eq. (19), we can find $\dot{\beta}_2(T_{23})$ from the first Eq. (24) and compute $\dot{\beta}_2$ from

$$\beta_2(T_{32}) - \beta(T_{23}) = \dot{\beta}_2(T_{32} - T_{23}). \tag{43}$$

Finding of γ_3. We have, from Eq. (26),

$$\gamma_3 = -P_{\mathrm{IV}}^{-2}\beta_2(T_{43}) = -P_{\mathrm{IV}}^{-2}[\beta_2(T_{32}) + \dot{\beta}_2(T_{43} - T_{32})]. \tag{44}$$

In addition to the expressions obtained for the coefficients $\alpha, \beta_1, \beta_2, \gamma_1, \gamma_2, \gamma_3$, it is evidently possible to put together many others to which, in the case of sufficiency of the approximation assumed, we can give approximate values.

5. LATENT HEAT. HEAT CAPACITY. ADIABATIC DIELECTRIC CONSTANT

Based on the derived temperature dependence of the coefficients, it is not difficult to write down the expressions for the latent heat and the heat capacity. If we limit ourselves to phase transitions between the first and second phases, we have for the latent heat

$$\lambda_{12} = T(S - S_0) = -T[\dot{\alpha}P^2 + {}^1/_2\dot{\beta}_1P^4] \qquad (45)$$

[here it is taken into account that for thermodynamic equilibrium, $(\partial\Phi/\partial p) = 0$]. In the case of a second order phase transition, $\lambda_{12} = 0$.

The first order transition from phase I to phase II occurs at a temperature T_{12}, we should therefore substitute $P_{\mathrm{II}}^2(T_{12}) = -\beta_1(T_{12})/\gamma_1$ in Eq. (45). For the reverse transition from phase II to phase I, Eq. (45) must be written in the form $\lambda_{21} = = T_{21}(\dot{\alpha}P^2 + 1/2\,\dot{\beta}_1P^4)$, where now $P^2 = P_{\mathrm{II}}^2 \times (T_{21}) = -\beta_1(T_{21})/2\gamma_1$.

For determining the heat capacity, we have

$$(C_p)_{\mathrm{II}} - (C_p)_{\mathrm{I}} = -T\left[\left(\frac{\partial S}{\partial T}\right)_{\mathrm{II}} - \left(\frac{\partial S}{\partial T}\right)_{\mathrm{I}}\right] \qquad (46)$$

$$- \quad = -T(\dot{\alpha} + \dot{\beta}P^2)\frac{dP^2}{dT},$$

where, in accord with Eq. (4), P^2 is expressed by the formula

$$\frac{dP^2}{dT} = \frac{1}{2\gamma_1}\left[-\dot{\beta}_1 + \frac{\beta_1\dot{\beta}_1 - 2\dot{\alpha}\gamma_1}{\sqrt{\beta_1^2 - 4\alpha\gamma_1}}\right]. \qquad (47)$$

In the case of a second order phase transition, the transition point is determined from $\alpha = 0$, where $\beta_1 > 0$, and the square root entering into Eq. (47) must be set equal to $+\beta_1$ at the transition point. We then obtain the usual expression

$$(C_p)_{\mathrm{II}} - (C_p)_{\mathrm{I}} = T_{12}\dot{\alpha}^2/\beta_1. \qquad (48)$$

from Eqs. (46), (47).

In the case of a first order transition, $\beta_1 < 0$ and the heat capacities at the two transition points T_{12} and T_{21} are equal. For $T = T_{12}$, the square root entering inoo Eq. (53) is equal to $-\beta_1$ and

$$(C_p)_{\mathrm{II}} - (C_p)_{\mathrm{I}} = -\frac{T_{12}}{\beta_1(T_{12})}\left(\dot{\alpha} - \dot{\beta}_1\frac{\beta_1 T_{12})}{\gamma_1}\right)^2. \qquad (49).$$

For $T = T_{21}$, dP^2/dT, and consequently $(C_p)_{\mathrm{II}}$ also, go to infinity. Near R_{21}, for $T < T_{21}$, we get from Eqs. (30), (46), (47),

$$(C_p)_{\mathrm{II}} - (C_p)_{\mathrm{I}} \to T_{21}(4\dot{\alpha}\gamma_1 \qquad (50)$$

$$- 2\beta_1\dot{\beta}_1)^{3/2}/8\gamma_1^2(T_{21} - T)^{1/2}.$$

We now turn to the calculation of the adiabatic dielectric constant. It is essential for the following reason. The measurements of the initial dielectric constant are usually carried out on a variable current of sonic frequency. Inasmuch as thermal exchange at these frequencies is practically negligible, we can consider that the measured values of ϵ are closer to the adiabatic than to the isothermal dielectric constants.

The connection between the adiabatic and the isothermal dielectric constants is given by the expression

$$\varepsilon_S = (C_P/C_E)\,\varepsilon_T, \qquad (51)$$

where C_p is the heat capacity at constant polarization, and C_E is the heat capacity at constant field. Applying Eq. (51) to the case of a transition between phases I and II, and using Eq. (46) [where now we write $(C_p)_{\mathrm{II}} = C_E$; $(C_P)_{\mathrm{I}} = C_P$], we can obtain the following equations:
for a second order phase transition,

$$\varepsilon_S = \varepsilon_T C_P/(C_P + T_{12}\dot{\alpha}^2/\beta_1(T_{12})); \qquad (52)$$

for a first order phase transition, close to T_{12},

$$\varepsilon_S = \varepsilon_T C_P/[C_P \qquad (53)$$

$$- (T_{12}/\beta_1(T_{12}))(\dot{\alpha} - \dot{\beta}_1\beta_1(T_{12})/\gamma_1)^2].$$

Near the point T_{21},

$$\varepsilon_S = -8\varepsilon_T C_p \gamma_1^2 (T_{21} - T)^{1/2} / T_{21} \times (4\dot{\alpha}\gamma_1 - 2\beta_1\dot{\beta}_1)^{3/2}_{T=T_{21}}. \tag{54}$$

Substituting ϵ_T [from Eq. (31)] in Eq. (54) we find

$$\varepsilon_S = (16 C_p \gamma_1^3 / T_{21}\beta_1 (T_{21})) \times (4\dot{\alpha}\gamma_1 - 2\beta_1\dot{\beta}_1)^{-2}_{T=T_{21}}. \tag{55}$$

Thus ϵ_S, in contrast to ϵ_T, has no singularities at the point T_{21}.

In view of the fact that P is almost independent of temperature near the points of transition between phases II and III, and III and IV, the difference between ϵ_S and ϵ_T here is not large.

6. ESTIMATE OF THE RELAXATION TIME

In the theory outlined above, it was assumed that the transition from one phase to another occurs only when the first phase loses stability.

Such an assumption amounts to a neglect of fluctuations. The system can be found for a suitably long time in the metastable state and, consequently, the relaxation time will be infinite.

In order to correct the validity of such a consideration, it is necessary to estimate the relaxation time τ. We limit ourselves to an estimate of for the transition from phase I to phase II. The thermodynamic potential for this case can be written in the form

$$\Phi = \Phi_0 + \alpha P^2 + {}^1/_2\, \beta_1 P^4 + {}^1/_3\, \gamma_1 P^6. \tag{56}$$

The dependence of $\Phi(P)$ for $0 < \alpha < 3\beta_1^2/16\gamma_1$ has the form* sketched in the Figure, where P_2 and P_1 are the values of P corresponding to the minimum and maximum, equal to

$$P_2^2 = (-\beta_1^2 + \sqrt{\beta_1^2 - 4\alpha\gamma_1}) / 2\gamma_1;$$

$$P_1^2 = (-\beta_1 - \sqrt{\beta_1^2 - 4\alpha\gamma_1}) / 2\gamma_1,$$

where, close to $\alpha = 0$,

$$P_1^2 \approx -\alpha / \beta_1.$$

Let the crystal be found in phase I ($P = 0$) and let the temperature decrease. In this case the height of the barrier separating the minimum corresponding to the values $P = 0$ and $P = P_2$ decreases. Neglecting fluctuations, we should expect that the transition from phase I to phase II takes place at that temperature T_{12} for which this barrier disappears, i.e., when

$$\Phi(0) - \Phi(P_1) = 0. \tag{58}$$

Then, substituting P_1 from Eq. (57), and solving the the resultant equation for α, we find $\alpha(T_{12}) = 0$ in accord with Sec. 2.

Taking into consideration the fluctuations, it should be observed that the phase transition I →II takes place for $\alpha > 0$ also, but satisfies the condition

$$\alpha < 3\beta_1^2/16\gamma_1,$$

where the relaxation time τ depends on α. For an estimate of $\tau(\alpha)$, we assume that the phase transition in each specimen is guaranteed upon the formation of a nucleus of phase II in a small macroscopic volume $\Delta\nu$. For the probability of formation of such a nucleus, we must consider the probability of the origin in the volume $\Delta\nu$ of a polarization which exceeds the "barrier" value P_1. The latter proabbility is equal to [11]

$$q = C \int_{P_1}^{\infty} \exp\{-[\Phi(P) - \Phi(0)]\,\Delta v / kT\}\, dP. \tag{59}$$

In view of the fact that large fluctuations do not make significant contribution to the integral in (59), we can limit ourselves to the square term in $\Phi(P)$, and determine C from the normalization condition

$$C \int_0^{\infty} e^{-\alpha P^2 \Delta v / kT}\, dP = 1. \tag{60}$$

We further assume that the fluctuations are recorded at the moments $\Delta t, 2\Delta t, 3\Delta t, \ldots,$ where Δt is so chosen that, on the one hand, it is small

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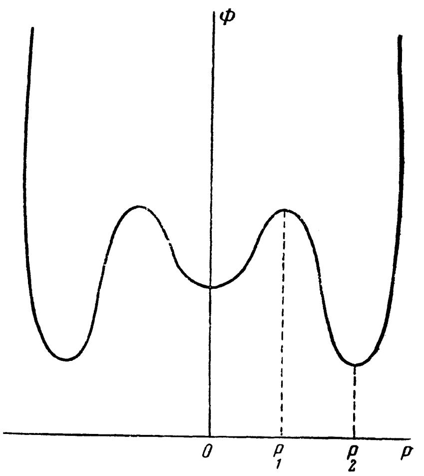
*For $0 < \alpha < \dfrac{3\beta_1^2}{16\gamma_1}$, phase I is metastable.[7]

enough that in a time Δt there takes place only a small number of fluctuations, and, on the other hand, large enough that the recorded fluctuations can be regarded as statistically independent.



We introduce the probability p that in the time interval Δt, in the volume $\Delta\nu$, there does not take place a fluctuation exceeding the "barrier" value P_1. We can regard the quantity q in Eq. (59) as a fraction of the interval Δt during which the system is in microstates corresponding to $P > P_1$ (in the volume $\Delta\nu$), and $(1-q)$ as the fraction of this interval which corresponds to $P < P_1$. Therefore, we can take for the probability $p=1-q$. Then we can estimate the mean relaxation time in the following way:

$$\bar{\tau} \sim pq\Delta t + 2p^2q\Delta t + 3p^3q\Delta t + \dots \tag{61}$$

Actually, pq is the probability that the value P_1 is achieved at the instant t lying between Δt and $2\,\Delta t$; p^2q is the probability that it occurs at a time lying between $2\,\Delta t$ and $3\,\Delta t$, etc. Summing the right side of Eq. (61),* we get

$$\bar{\tau} \sim q\Delta tp/(1-p)^2 = \Delta tp/(1-p). \tag{62}$$

In order to establish the dependence of τ on the parameters of the system, let us find p from Eqs. (59), (60):

$$p = \sqrt{2/\pi}\int_0^{x_1} e^{-x^2/2}\,dx, \tag{63}$$

$$x_1 = \alpha\sqrt{-2\Delta v/\beta_1 kT}$$

$$= (T - T_{12})\,\dot{\alpha}\sqrt{-2\Delta v/\beta_1 kT},$$

For an estimate of x_1, we take $\Delta\nu \sim 10^{-4}$ and take the values

$$\alpha \approx 4\cdot 10^{-5}, \qquad \beta_1 \approx 3\cdot 10^{-13}$$

from Ref. 8 (all quantities in the cgs. system). Then we get

$$x_1 \sim 10^6(T - T_{12}).$$

We can simplify Eq. (63) for large values of x_1 by making use of the asymptotic value of the integral in it[12]

$$p \approx 1 - \sqrt{2/\pi}\, e^{-x_1^2/2}/x_1. \tag{64}$$

From Eqs. (62) and (64), we get

$$\bar{\tau}(\alpha) \sim x_1 e^{x_1^2/2}\,\Delta t. \tag{65}$$

There remains in Eq. (65) the undetermined quantity Δt, equal (in order of magnitude) to the mean time interval between two successive fluctuations. An estimate of Δt without a detailed knowledge of the fluctuation mechanism is very difficult. Fortunately, the strucuure of Eq. (65) is such that any accurate estimate of Δt is unnecessary in practice. Inasmuch as the fluctuations of the quantity P are determined by the thermal motion of the atoms of the crystal, we can estimate the minimum value of Δt by assuming

$$\Delta t \sim a/c \sim 10^{-8}/10^5 \sim 10^{-13} \text{ sec.}$$

We further set $T - T_{12} = 10^{-3}$ degrees, which corresponds to $x_1 \sim 10^5$. We then get from Eq.. (65) $\ln\bar{\tau} \sim 10^5$. It is clear that the order of magnitude of τ would not be changed for any other

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*For this we must write Eq. (61) in the form

$$\tau = q\Delta t(p + p^2 + \dots) + q\Delta t(p^2 + p^3 + \dots) + \dots,$$

sum the series in parantheses and the series obtained from a summation of the paranthetical expressions.

assumptions on the value of Δt .

Thus, even at a temperature very close to T_{12} (from the viewpoint of experimental possibilities), the relaxation time can be considered as practically infinitely large, which supports the basic assumption made in the research.

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The Method of Envelopes for Investigating Free Oscillations in Accelerators*

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We present a derivation of the equation for free oscillations in accelerators with an arbitrary magnetic field having a plane of symmetry. To solve the basic problems of the theory of free oscillations, which arise in the design of accelerators, an envelope method has been developed in which the study of individual orbits is replaced by consideration of the envelope of the trajectory of the particles over a large number of revolutions. The application of the method is illustrated for accelerators with a sector magnet and for strong-focusing accelerators.

1. INTRODUCTION

IN cyclic accelerators, the displacement of a particle from some average position is called a free oscillation. This average position of the particle is usually called the instantaneous orbit. The term "free" means that these oscillations are not directly connected with the process of acceleration. We can therefore consider the free oscillations in a constant magnetic field and for constant energy of the particle.

The fact that the free oscillations are independent of the acceleration process was demonstrated in the very first papers on the theory of cyclic accelerators. It was shown that with increasing magnetic field H (for a given configuration) the oscillation amplitude is damped like $H^{-1/4}$

The separation of the particle motion into a motion along the instantaneous orbit and free oscillations can be done uniquely in the absence of resonances. At resonance, the frequency of the free oscillations is integrally related to the frequency of revolution, so that the particle orbit is always closed. In this case the trajectory of the particle over a large number of revolutions does not fill an area, but merely traces out a line. (The plane area filled out by the orbit will be the subject of our investigation .) For practical purposes, because of the presence of all sorts of perturbations in the magnetic field, the acceleration process cannot proceed at resonance, since the amplitude of the free oscillations increases sharply. We shall exclude the resonance case from our further considerations

Free oscillations develop during the process of injection of particles, and also from scattering of particles by the residual gas in the accelerator cham-

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*The present paper is based on work[1–5] completed during the period 1950–1953.

*Deceased.