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ANOMALIES IN DIELECTRIC PROPERTIES IN PHASE TRANSITIONS

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Anomalies in static dielectric properties are studied on the basis of the Landau phenomenological theory of phase transitions for the case when polarization is not a phase transition parameter. Examples with one or two transition parameters are considered. In the case of two parameters ferroelectric transitions are also possible in addition to transitions which are not accompanied by the appearance of spontaneous polarization. The anomalies in such transitions differ essentially from the usual ferroelectric anomalies described by the Ginzburg-Devonshire theory. It is shown that dielectric anomalies can turn out to be quite pronounced even in nonferroelectric transitions. The theory is compared with the experimental data for ammonium fluoroberyllate.

1. It is well known that phase transitions can be accompanied by anomalies in dielectric properties. These anomalies are particularly great in the case of ferroelectric transitions.[1] In the papers of Ginzburg[2], and later of Devonshire[3], the dielectric properties of ferroelectrics were successfully explained on the basis of the general theory of phase transitions due to Landau[4]. A characteristic parameter in the Ginzburg-Devonshire theory is the polarization. Such a choice is quite natural since it is polarization in particular that appears in a ferroelectric phase transition. However, it is by no means necessary that the quantity appearing in the transition should be at the same time a parameter of the transition. For example, in barium titanate spontaneous dislocation deformation also arises, but it is not a parameter of the transition, whereas the polarization is. Indeed, if one polarizes the cubic phase of barium titanate then one obtains a structure with the symmetry of the low-temperature phase; but if the cubic phase is subjected to a dislocation deformation then such a structure does not arise. One can say that spontaneous deformation appears in barium titanate as a result of spontaneous polarization, and is essentially a secondary effect. Similarly the appearance of spontaneous polarization may be a secondary effect of some other more complex restructuring of the lattice described by other parameters.

In such ferroelectric transitions (they were first pointed out by Indenbom[5]) polarization is not a characteristic parameter of the transition. For example, if a ferroelectric transition occurs involving a change in the number of atoms in an elementary cell (i.e., involving the appearance of a superstructure), then the magnitude of the polarization cannot be a parameter of the transition, since it is not possible to produce a superstructure by polarizing the symmetric phase. An example of a substance in which a ferroelectric transition occurs involving the doubling of the number of atoms in an elementary cell is ammonium fluoroberyllate. Possibly there exist also other ferroelectrics in which polarization is not a transition parameter. It is appropriate to recall here that the properties and particularly the structure of the majority of ferroelectrics known at present have not as yet been extensively investigated. But such investigations are being carried out now, and, apparently, it is quite timely to discuss the anomalies in dielectric properties accompanying ferroelectric transitions of which polarization is not the parameter and which, consequently, are not described by the Ginzburg-Devonshire theory. Such an investigation will be carried out in the present paper on the basis of Landau's phenomenological theory.

Dielectric anomalies (even though they are not as strong as those in ferroelectrics) are also observed in nonferroelectric phase transitions when no spontaneous polarization arises. Usually for the explanation of such anomalies model representations of one kind or another are utilized. However, the models utilized are, as a rule, far removed from real cases, and attempts to make them more precise greatly complicate the theory. It is, therefore, useful to consider dielectric anomalies accompanying nonferroelectric transitions on the basis of Landau's phenomenological theory, and this will also be done in our paper.

Thus, in the present paper we investigate on the basis of Landau's theory dielectric anomalies accompanying transitions for which polarization is not a characteristic parameter. In doing this we simultaneously investigate both ferroelectric and nonferroelectric transitions. Landau's theory of phase transitions gives a correct description of the qualitative nature of the majority of the anomalies discussed below, and only occasionally does the need appear to take additionally into account corrections to this theory associated with the fluctuations in the characteristic parameter of the transition (cf., for example,[6]).

2. We restrict ourselves to a study of anomalies in static dielectric properties. The nature of such anomalies is determined by the dependence of the thermodynamic potential on the parameters of the transition and on the polarization vector P_i. We consider first the case when the transition is characterized by a single parameter η. The physical meaning of this quantity is different for different transitions. For example, for the $\alpha \rightleftarrows \beta$ transition in quartz the parameter η characterizes the magnitude of a definite displacement of several sublattices (such a displacement is not accompanied by the appearance of polarization). For subsequent dis-

cussion only the transformation properties of the parameter are essential. According to Landau's theory these properties are uniquely determined if we know the symmetry of the crystal in the high- and the low-temperature phases. In the thermodynamic potential which is representated in the form of a series in terms of the variables η and P_i, terms are contained which include η and P_i simultaneously (we shall in future refer to them as cross terms). Cross terms could, generally speaking, have the form ηP_i, $\eta^2 P_i$, $\eta P_i P_j$, $\eta^2 P_i P_j$, etc. However, none of the terms of the thermodynamic potential should be altered by any of the transformations belonging to the symmetry group of the symmetric phase of the material. Therefore, taking into account the definite symmetry of a given crystal and the transformation properties of the variables η and P_i themselves, restricts in an essential manner in each specific case the possible choice of cross terms.

Thus, terms of the type ηP_i are admissible only in the case when η transforms like P_i. But then the parameter η can be interpreted as polarization, and the whole discussion reduces to the Ginzburg-Devonshire case. Terms of the type $\eta^2 P_i$ are admissible only in the case when the symmetric phase of the material corresponds to one of the pyroelectric classes, i.e., the material is polarized spontaneously already in the symmetric phase. Terms of the type $\eta P_i P_j$ are admissible only when the parameter η has certain definite transformation properties, viz., it is necessary that the parameter η transform like $P_i P_j$. Terms of the type $\eta^2 P_i P_j$ appear in the thermodynamic potential in all cases since η^2 is an invariant, and one can always construct an invariant combination from quantities of the type $P_i P_j$: for example, in a uniaxial crystal the cross terms have the form $a\eta^2(P_x^2 + P_y^2)$ and $b\eta^2 P_z^2$, in a cubic crystal the coefficients a and b are equal. There is no point in discussing cross terms of higher order in η and P_i.

We discuss in greater detail the case when the cross terms in the thermodynamic potential have the form $\eta^2 P_i P_j$. If the symmetry of the crystal is such that terms of the type $P_x P_y$ are absent, then we can restrict ourselves to one of the components of the polarization vector. Denoting it by P we represent the thermodynamic potential Φ in the form

$$\Phi = \Phi_0 + \frac{\alpha}{2}\eta^2 + \frac{\beta}{4}\eta^4 + \frac{\gamma}{6}\eta^6 + \frac{\varkappa}{2}P^2 + \frac{a}{2}\eta^2 P^2 - PE. \qquad (1)$$

From the very existence of a phase transition it follows that the coefficient α changes sign at a certain temperature. We assume, as is usually done, that in the neighborhood of the transition point $\alpha = \alpha'(T - \Theta)$. The temperature dependence of the other coefficients of the thermodynamic potential (1) is not determined by the existence of a phase transition. We shall therefore, as is usually done, treat them as constant in the neighborhood of the transition point. For $\beta > 0$ a transition of the second kind occurs in the system, for $\beta < 0$ a transition of the first kind occurs. Conditions for a minimum in Φ yield equations for determining the equilibrium values of η and P:

$$\begin{aligned} \partial\Phi / \partial\eta &= \eta(\alpha + \beta\eta^2 + \gamma\eta^4 + aP^2) = 0, \\ \partial\Phi / \partial P &= (\varkappa + a\eta^2)P - E = 0. \end{aligned} \qquad (2)$$

As follows from these equations, there exist no stable solutions with a spontaneous polarization ($P \neq 0$ with $E = 0$). Consequently, the transition is not a ferroelectric one.

We consider first a first-order phase transition. In the case $a > 0$ the dependence of P on E, as is shown by an analysis of the system of equations (2), has the form of a double hysteresis loop in the nonsymmetric phase. The existence of a double hysteresis loop in the case of a nonferroelectric transition is usually associated with the appearance of a so-called antiferroelectric state[1]. We note that in the case of such transitions an appreciable anomaly is observed in the temperature dependence of the dielectric permittivity,—usually a maximum at the transition point. From the solutions of the system of equations (2) it follows that the dielectric susceptibility $\chi = dP/dE$ in the nonsymmetric phase increases with increasing temperature and at the transition point undergoes a discontinuity upwards. If one also assumes that the coefficient κ in (1) increases with temperature, and, moreover, in such a manner that $d\kappa/dT < da\eta^2/dT$, then at the transition point χ will have a maximum. In the case $a < 0$ the nature of the dielectric anomalies will be different: a double hysteresis loop must now be observed in the symmetric phase, while χ must decrease with increasing temperature undergoing a discontinuity downwards at transition point.

We note that the double hysteresis loops discussed above have the property that as we go further away from the temperature of the phase transition they are displaced in the direction of ever increasing electric fields, in accordance with the relation $E \sim \kappa\sqrt{|\alpha|/|a|}$. The value of a can be approximately estimated on the basis of the following considerations. As can be seen from Eq. (2), an electric field shifts the transition temperature. It is clear in this case that fields which induce a polarization of the order of the atomic polarization $P_{at} \sim E_{at} \sim e/d^2$ displace the transition temperature by an amount of the order of magnitude of the temperature itself. From here it follows that $\alpha'\Theta \sim aE_{at}^2$. Consequently, fields at which double hysteresis loops appear will be given by $E \sim \kappa\sqrt{|T - \Theta|/\Theta}E_{at}$. Thus, apparently, one can in fact observe double loops only for substances which have in the neighborhood of the transition temperature a small value of κ, i.e., a large value of χ. It is in just such substances that double hysteresis loops are observed[1].

In the case of a phase transition of the second kind there will be no double hysteresis loops, χ is continuous at the transition point, and a discontinuity occurs in $d\chi/dT$ and in the coefficient of E^3 in the expression for P(E).

Anomalies of the type discussed above are characteristic of quite a wide class of phase transitions determined only by the transformation properties of a single transition parameter, but not by its specific physical nature. Usually, however, definite dielectric anomalies (for example, double hysteresis loops) are associated with a definite "electric structure" of a substance (antipolar or antiferroelectric state)[1]. It was in just this manner that dielectric anomalies were explained in Kittel's paper[7] where the concept of antiferroelectrics was introduced. Breaking up the crystal into two sublattices with polarizations P_1 and P_2, Kittel represents the thermodynamic potential in the form of a series in powers of P_1 and P_2:

$$\Phi = f(P_1^2 + P_2^2) + gP_1P_2 + h(P_1^4 + P_2^4) + j(P_1^6 + P_2^6) \tag{3}$$

and assumes that f depends linearly on the temperature. If we now introduce new variables $P = P_1 + P_2$ and $\eta = P_1 - P_2$, then (3) reduces to the form

$$\Phi = \frac{1}{2}\left(f - \frac{g}{2}\right)\eta^2 + \frac{h}{8}\eta^4 + \frac{j}{32}\eta^6 + \frac{1}{2}\left(f + \frac{g}{2}\right)P^2 + \frac{3h}{4}\eta^2P^2, \tag{4}$$

where terms involving higher powers of P have been discarded. A comparison of expressions (4) and (1) for the thermodynamic potential shows that under the condition $\alpha = f - g/2$, $\beta = h/2$, $\gamma = 3j/16$, $\kappa = f + g/2$, $a = 3h/4$ they coincide. Thus, Kittel's results can be obtained from the phenomenological discussion presented above. However, the thermodynamic potential (3) is introduced on the basis of a highly simplified model, which can turn out to be far removed from the actual situation in the crystal. Attempts to make this model more precise by the introduction of a larger number of sublattices and of three components of the polarization vector complicate the theory greatly. At the same time the phenomenological discussion, in spite of all its simplicity, is free of any model representations. In particular, it shows that Kittel's results have a more general nature than his initial assumptions. In this connection we recall that, in general, it makes no sense to speak of the "electric structure" of a substance apart from its crystalline structure[8] (in contrast to magnetic structure). And in the case of the phenomenological discussion the concept of an antiferroelectric state turns out to be superfluous in general.

3. We consider now the case when the phase transition is characterized by two transition parameters η and ξ. In the thermodynamic potential there will always be contained cross terms of the type $(\eta^2 + \xi^2)P_iP_j$. They are analogous to the terms η^2P^2 in expression (1), and the anomalies due to these terms will be similar to those that we have already discussed. However, it is essential that lower order cross terms will in this case, in contrast to the case of a single parameter transition, be of considerably greater interest. Indeed, terms linear in P_i, i.e., ηP_i or $(\eta^2 - \xi^2)P_i$ are now allowable not only in crystals of the pyroelectric classes, but also in all crystals under the condition that either $\eta\xi$ or $\eta^2 - \xi^2$ transforms like P_i[5]. We restrict ourselves to a discussion of only the cross term $\eta\xi P$, where P is one of the components of the polarization vector. The case $(\eta^2 - \xi^2)P$ gives very similar results. We represent the thermodynamic potential Φ in the form

$$\Phi = \frac{\alpha}{2}(\eta^2 + \xi^2) + \frac{\beta_1}{4}(\eta^2 + \xi^2)^2 + \frac{\beta_2}{2}(\eta\xi)^2 + \frac{\gamma_1}{6}(\eta^2 + \xi^2)^3 \tag{5}$$
$$+ \frac{\gamma_2}{2}(\eta^2 + \xi^2)(\eta\xi)^2 + \frac{\varkappa}{2}P^2 + a\eta\xi P - PE.$$

Cross terms of higher order have been discarded. Just as in the case of a one parameter transition we assume that only one coefficient α in (5) depends on the temperature in accordance with $\alpha = \alpha'(T - \Theta)$, while the other coefficients are constant. Equilibrium values of η, ξ, and P are determined from the condition that Φ should be a minimum with respect to all these variables. It turns out that the following three types of stable solutions are possible:

$$\eta = \xi = 0, \quad aP = \varepsilon; \tag{6}$$

$$\eta^2 = \frac{-\beta + \sqrt{\beta^2 - 4\gamma(\alpha \pm \varepsilon)}}{2\gamma}, \quad \xi = \pm\eta, \quad aP = \varepsilon \mp \delta\eta^2; \tag{7}$$

$$\eta^2 + \xi^2 = \frac{-\beta_1 + \sqrt{\beta_1^2 - 4\gamma_1\alpha}}{2\gamma_1}, \quad \eta\xi = -\frac{1}{\Delta}\varepsilon, \quad aP = \left(1 + \frac{\delta}{\Delta}\right)\varepsilon. \tag{8}$$

Here and in subsequent discussion we utilize the notation

$$\varepsilon = \frac{a}{\varkappa}E, \quad \delta = \frac{a^2}{\varkappa}, \quad \beta = 2\beta_1 + \beta_2 - \delta, \quad \Delta = \beta_2 - \delta, \quad \gamma = 4\gamma_1 + 3\gamma_2. \tag{9}$$

The solutions (8) for η and ξ are shown for the sake of brevity in implicit form. They are obtained on the assumption $\gamma_2 = 0$. For $\gamma_2 \neq 0$ in order to determine $\eta^2 + \xi^2$ or $\eta\xi$ it will be necessary to solve algebraic equations of the fourth degree, and the analysis of the results becomes essentially more complicated.

In the case of second-order phase transitions of the second kind, when it is possible, generally speaking, to neglect in (5) terms of the sixth order, i.e., to set $\gamma_1 = \gamma_2 = 0$, the form of the solutions of (7) and (8), becomes greatly simplified and they respectively assume the form

$$\eta^2 = -\frac{\alpha \pm \varepsilon}{\beta}, \quad \xi = \pm\eta, \quad aP = \varepsilon \mp \delta\eta^2; \tag{7'}$$

$$\eta^2 + \xi^2 = -\frac{\alpha}{\beta_1}, \quad \eta\xi = -\frac{\varepsilon}{\Delta},$$
$$\eta^2 = \frac{1}{2\beta_1}\left[-\alpha \pm \sqrt{\alpha^2 - \left(\frac{2\beta_1}{\Delta}\varepsilon\right)^2}\right], \tag{8'}$$
$$\xi^2 = \frac{1}{2\beta_1}\left[-\alpha \mp \sqrt{\alpha^2 - \left(\frac{2\beta_1}{\Delta}\varepsilon\right)^2}\right], \quad aP = \left(1 + \frac{\delta}{\Delta}\right)\varepsilon.$$

From an analysis of the second derivatives of the thermodynamic potential (5) it follows that in the high temperature phase solutions (6) are stable, while in the low temperature phase with E = 0 solutions (7) are stable if $\Delta < 0$, and solutions (8) are stable if $\Delta > 0$. Since spontaneous polarization occurs only for solutions (7), then, consequently, for $\Delta < 0$ the transition is ferroelectric, while for $\Delta > 0$ it is nonferroelectric.

We first consider the ferroelectric transition ($\Delta < 0$). It will be of second order if $\beta > 0$, and of first if $\beta < 0$. Figure 1 shows the temperature dependence of η, ξ, P, and χ for a second-order transition ($\beta > 0$). Dotted curves for the dielectric susceptibility $\chi = dP/dE$ have been obtained taking into account the fluctuation corrections calculated in the same manner as in[6]. From

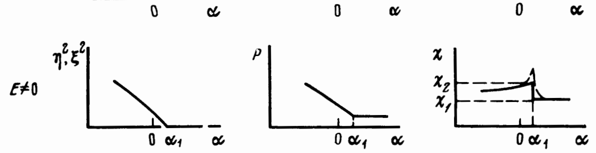

FIG. 1. Temperature dependences for a ferroelectric phase transition of the second kind ($\Delta > 0$, $\beta > 0$) from solution (6) (high-temperature phase) to solutions (7) (low-temperature phase). $\alpha = \alpha'(T - \Theta)$, $\alpha_1 = |\epsilon|$; $\chi_1 = 1/\kappa$, $\chi_2 = (1 + \delta/\beta)/\kappa$.

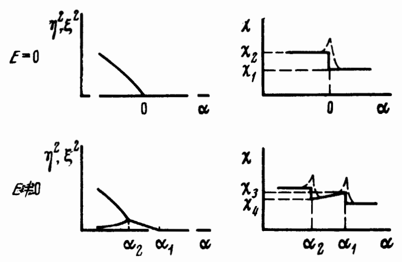

FIG. 2. Temperature dependences for a nonferroelectric second-order phase transition ($\Delta > 0, \beta_1 > 0$) from solution (6) (high-temperature phase) to solutions (8) (low-temperature phase). $\alpha = \alpha'(T-\Theta)$, $\alpha_1 = |\epsilon|, \alpha_2 = -2\beta_1|\epsilon|/\Delta; \chi_1 = 1/\kappa, \chi_2 = (1+\delta/\Delta)/\kappa, \chi_3 = (1+\delta/\beta)/\kappa$, $\chi_4 = [1+\delta/(\beta+2\gamma|\epsilon|/\Delta)]/\kappa$.

Fig. 1 and relations (6), (7), or (7′) it can be seen that the transition under consideration differs from the usual ferroelectric transition by the following special features. The spontaneous polarization depends on the temperature not as $\sqrt{|T-\Theta|}$, but linearly: $\sim (T-\Theta)$. This circumstance has already been noted in[5]. Further the phase transition is not smeared out in an electric field, as in the usual case, but retains its sharpness shifting in the direction of greater temperatures ($\alpha_1 = |\epsilon|$). The temperature anomaly in χ is much weaker than in the usual case where χ calculated without fluctuation corrections varies according to the Curie law. In this case χ varies with temperature in the same manner as, for example, heat capacity or compressibility, i.e., apparently as $-\ln|T-\Theta|$. However, for transitions close to the critical point of second-order phase transitions[4], i.e., for small values of the coefficient β, the magnitude of χ in the nonsymmetric phase even without taking fluctuations into account will depend strongly on the temperature (cf., Fig. 1). We note that P for $E = 0$ has two equivalent solutions (7) which differ only by sign. Therefore the crystal can be broken up into domains, and the dependence of P on E for $T < \Theta$ will have the form of a hysteresis loop.

In the case of a first-order transition ($\Delta < 0$, $\beta < 0$), the results given above can be generalized in a natural manner. Spontaneous polarization appears at the transition point in a discontinuous manner, and also the so-called temperature hysteresis appears associated with the existence of metastable states within a certain temperature range. In the symmetric phase the dependence of P on E has the shape of a double hysteresis loop. In contrast to the usual case the double loop does not disappear as the temperature is increased, but is shifted towards larger values of E. The dependence of P on E at different temperatures is here schematically the same as in Fig. 4 (cf., below).

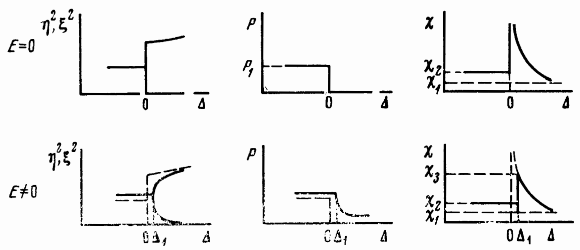

FIG. 3. Temperature dependences for a first-order ferroelectric phase transition ($\alpha < 0$) from solutions (8) (high-temperature phase) to solutions (7) (low-temperature phase). $\Delta = \Delta'(T-\Theta)$; if $\beta > 0$, then $\Delta_1 = 2\beta|\epsilon|/|\alpha|$; $aP_1 = \delta|\alpha|/\beta$; $\chi_1 = 1/\kappa, \chi_2 = (1+\delta/\beta)/\kappa, \chi_3 = (1+\delta|\alpha|/2\beta_1|\epsilon|)/\kappa$.

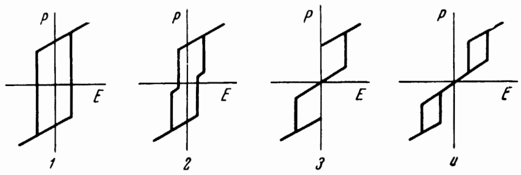

FIG. 4. Qualitative nature of the dependences P(E) for different temperatures for the first-order ferroelectric phase transition shown in Fig. 3, taking into account the coefficient γ_2. $\Delta = \Delta'(T-\Theta)$; 1, 2–$\Delta<0$, 3–$\Delta=0$, 4 – $\Delta>0$.

Thus, the ferroelectric phase transitions discussed above have a number of special features which differentiate them from the usual ferroelectric transitions. This is essentially associated with the fact that the appearance of a spontaneous polarization P is here a secondary effect due to the reconstruction of the lattice. The reconstruction itself is determined by some other parameters η, ξ. The magnitude of the spontaneous polarization in such ferroelectrics, naturally, turns out to be small compared with usual ferroelectrics, where $P \sim \sqrt{|T-\Theta|/\Theta}$. Also here $P \sim \eta^2$ while $\eta \sim \sqrt{|T-\Theta|/\Theta}$.

The ferroelectrics under discussion must also possess peculiarities in domain structure and in the dynamics of domain boundaries. We call attention only to the fact that for such ferroelectrics transition to a single-domain state is possible, in principle, even for an unshorted sample. We explain this in greater detail. We consider first a usual ferroelectric. For the sake of simplicity we assume that it has a single axis of spontaneous polarization and is cut in the form of a plate perpendicular to this axis. If the crystal is shorted, then, as is well known, a transition is possible into a homogeneously polarized (single domain) state at a temperature corresponding to the vanishing of the coefficient α in the term $\frac{1}{2}\alpha P^2$ in the thermodynamic potential. If the crystal is not shorted then a transition to the single domain state is impossible. Indeed, in this case, when spontaneous polarization arises an electrical field E appears and one must add to the thermodynamic potential the term $-\frac{1}{2}PE$. In the case of homogeneous polarization the field in the plate is equal to $-4\pi P$ and, thus, the coefficient of P^2 will be not α, but $\alpha + 4\pi$. This coefficient does not vanish, and a transition to the single domain state does not occur. As is well known, a transition to the multidomain state occurs. We now proceed to discuss our case. Here the term $-\frac{1}{2}PE$ will lead to a change by 4π of the coefficient κ in the term $\frac{1}{2}\kappa P^2$ in (5). But the phase transition is determined by the vanishing of the coefficient α. Thus, also in an unshorted crystal a single domain state is possible (although it is energetically somewhat less favorable than a multidomain state). Such a weakening of the tendency towards the formation of domains can lead to a change in the processes associated with the formation and alteration of the domain structure. In particular, it might turn out that there exists a coercive field which is not present in the usual ferroelectrics.

We now consider a nonferroelectric phase transition

($\Delta > 0$). It will be of second order if $\beta_1 > 0$, and of first if $\beta_1 < 0$. The stable solutions determined from an analysis of the second derivatives of the thermodynamic potential (5) are shown for the case of a second-order transition ($\beta_1 > 0$) in Fig. 2. We call attention to the fact that although the transition is not accompanied by the appearance of a spontaneous polarization, nevertheless χ experiences the same anomaly as in the preceding case. Moreover, the electric field exerts an essential influence on the transition. Specifically, two transitions arise—first from solution (6) to solution (7), and then from solution (7) to solution (8). The temperature range in which solution (7) is realized increases linearly with increasing E ($\alpha_1 - \alpha_2 = \beta|\epsilon|/\Delta$). As should be expected, no hysteresis loops arise.

In the case of a first-order transition ($\beta_1 < 0$) at the transition point η^2 or ξ^2 originates in a discontinuous manner and temperature hysteresis appears. In the low-temperature phase, just as in the case of the second order transition, no hysteresis loops are observed. In the presence of a field solution (7), as in the case of a second-order transition, wedges in between solutions (6) and (8), but now, starting with a certain finite value of E (for example, for $\beta < 0$ starting with $\epsilon \approx \beta_1^2/\gamma$). If $\beta < 0$, then in the high temperature phase double hysteresis loops appear for fields $\epsilon \approx |\beta_1|\Delta/\gamma$. If $\beta > 0$, then no double loops appear.

As follows from the discussion given above in the case of two transition parameters two types of solutions (7), (8) are possible corresponding to different nonsymmetric phases of the substance. Correspondingly two types of phase transitions are possible from the symmetric phase into one of the nonsymmetric phases. Which of these two transitions will be realized depends on the sign of the coefficient Δ in (9). Naturally on the basis of the thermodynamic potential (5) one can also discuss phase transitions from one nonsymmetric phase into the other one. This will be a first-order transition, since the symmetry group of one phase is not a subgroup of the symmetry of the other phase (but they are both subgroups of the symmetry of the symmetric phase of the substance). Well known examples of transitions between nonsymmetric phases of a substance are transitions in barium titanate from the tetragonal phase into the rhombic phase and from the rhombic phase into the rhombohedral phase.

Just as it was necessary to assume that the coefficient α changes its sign for the transition from the symmetric phase into one of the nonsymmetric phases, for the transition between nonsymmetric phases it is necessary to assume that the coefficient Δ passes through zero. Near the transition point one can assume that $\Delta = \Delta'(T - \Theta)$, while the remaining coefficients (including $\alpha < 0$) do not depend on the temperature. Such a phase transition from solution (7), which is stable for $\Delta < 0$, to solution (8), which is stable for $\Delta > 0$, is accompanied by anomalies in dielectric properties shown in Fig. 3. We call attention to the fact that although this is a transition of the first kind there is no temperature hysteresis and no double hysteresis loops in the symmetric phase.

4. An example of a substance in which a ferroelectric phase transition is observed, but for which polarization can not be a transition parameter is, as has been noted earlier, ammonium fluoroberyllate. It is natural to attempt to compare the observations for ammonium fluoroberyllate[9] with the theoretical conclusions obtained above. We note first of all that, as should have been expected, experimental data for ammonium fluoroberyllate do not fit within the framework of the Ginzburg-Devonshire theory[9]. We compare the experimental curves of[9] with the curves of Figs. 2 and 3, since it is just in these diagrams that anomalies accompanying ferroelectric transitions are shown. In Fig. 2 the dependence of χ on T in the high-temperature phase is very weak and is due to fluctuations, while the experimental dependence obeys the Curie-Weiss law, i.e., it is strong. Consequently, it remains only to compare experiment with Fig. 3. Here we observe quite good agreement for the curves P(T) and χ(T) for different E. However, the theory does not give double hysteresis loops in the high-temperature phase which are observed experimentally. This lack of agreement is removed if we take into account the coefficient γ_2 in solutions (8).

Indeed, the absence of double loops is essentially a consequence of the absence of temperature hysteresis. As the example of barium titanate shows, temperature hysteresis in transitions between nonsymmetric phases appears only when we take into account several coefficients γ of the sixth power of P in the thermodynamic potential[10]. It is therefore natural to take into account the coefficient γ^2 which was neglected earlier in solutions (8). As analysis shows, taking this into account leads to the appearance of temperature hysteresis for $E \neq 0$ and of double hysteresis loops in the high-temperature phase. The qualitative nature of the double loops, and also of transition loops from double to single ones is illustrated in Fig. 4. Now the agreement with experiment becomes quite complete.

However, we note that the proposed explanation of the anomalies in ammonium fluoroberyllate is not yet indisputable. For a final decision it is necessary to know more reliably the structure of the high- and low-temperature phases, since the nature of this structure determines both the form of the thermodynamic potential and the choice of solutions corresponding to a particular phase. One cannot regard the structure of ammonium fluoroberyllate as being reliably established, particularly in the neighborhood of the phase transition point. Therefore, it is apparently not useful for the time being to carry out a quantitative comparison of theory with experiment, particularly since this is associated with quite awkward calculations.

Ammonium fluoroberyllate is not the only example in which anomalies are observed which differ from those that follow from the Ginzburg-Devonshire theory (cf.[1]). However, even the dielectric properties of these substances, let alone their structure, have been, as a rule, investigated very incompletely, and this does not allow us to carry out a comparison of the corresponding experiments with theory.

We emphasize in conclusion that the discussion given above does not exhaust all possible cases of transitions (for example, three transition parameters etc.). But it demonstrates to a sufficient degree those peculiarities of dielectric anomalies which are characteristic of transitions when polarization is not a transition parameter. More complete systematic investigations of different phase transitions are now only beginning, and one can hope that the theory under discussion will turn out to be useful for the interpretation of experimental data which will appear as the result of such investigations.

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