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PHENOMENOLOGICAL THEORY OF DIELECTRIC ANOMALIES IN FERROELECTRIC MATERIALS WITH SEVERAL PHASE TRANSITIONS AT TEMPERATURES CLOSE TOGETHER

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In ferroelectrics with phase transitions at temperatures close together, the different phases are considered on a single basis as the result of a distortion of a single more symmetric phase. A description of the anomalies of physical properties in such a manner requires a smaller number of constants than does the description on the basis of a separate consideration of the phase transitions in Landau's theory. Certain information about the character of the phase diagrams is also obtained. The dielectric anomalies in Rochelle salt are analyzed on the basis of the proposed theory.

IN solid bodies, there are often observed phase transitions close together in temperature. A typical example is Rochelle salt, in which two transitions occur, at temperatures $\Theta_1 = 24^\circ$C and $\Theta_2 = -18^\circ$C. A description of the anomalies of physical properties at the transitions in Rochelle salt can be obtained on the basis of the phenomenological theory of Landau, Ginzburg, and Devonshire. It is then necessary either to use two thermodynamic potentials with two sets of coefficients for each transition, or to suppose that the coefficients of one thermodynamic potential have a complicated temperature dependence.

In the present paper, a different method is suggested[1]. The three phases of Rochelle salt are considered on a single basis as the result of a distortion of a single more symmetric phase. A thermodynamic potential is described for this "superphase." Its coefficients have the usual temperature dependence; that is, only one of them changes with temperature according to a linear law, going through zero. The description of the thermodynamic anomalies in Rochelle salt in such a manner turns out to be more complete in the sense that a smaller number of constants is required than in the corresponding approaches based on separate consideration of the phase transitions or on the assumption of a special temperature dependence of the coefficients of the thermodynamic potential.

The choice of Rochelle salt as an example to illustrate the possibility of this approach is based on the fact that the anomalies in the phase transitions in Rochelle salt have been studied most completely, as compared with the many other crystals with phase transitions close together in temperature.

A fact essential for the proposed approach is that the characteristic parameter of a phase transition is a many-component quantity; that is, it corresponds to a multidimensional representation of the symmetry group of the superphase. Thanks to this, there are several unsymmetric phases. Together with transitions from the superphase to these unsymmetric phases, transitions between them can be investigated.

We shall consider the case in which the irreducible representation corresponding to a transition out of the superphase is two-dimensional; that is, the characteristic parameter of the transition is a two-component quantity η, ξ. We shall write the thermodynamic potential in the form of a series in invariants constructed from the components η and ξ:

$$\Phi = \alpha(\eta^2 + \xi^2) + \beta_1(\eta^2 + \xi^2)^2 + \beta_2(\eta\xi)^2 + \delta(\eta\xi)^4. \qquad (1)$$

This expression takes account of all the invariants of the second and fourth orders and of one of the invariants of eighth order, which turns out to be essential. It is assumed that there are no invariants of third order, because only transitions of the second kind are being considered. Invariants of sixth order are not written because they do not change the qualitative results for phase transitions of the second kind.

We shall explain how the invariants of second and fourth order in expression (1) are obtained. As is well known[2], an irreducible representation has only one invariant of second order, namely the sum of the squares of the quantities η and ξ: $\eta^2 + \xi^2$. The invariants of fourth order can be found by considering a representation according to which the quantities η^2, ξ^2, and $\eta\xi$ are transformed. This representation is reducible, since from it there can be separated the unitary representation according to which the quantity $\eta^2 + \xi^2$ is transformed. This unitary representation corresponds to the invariant of fourth order $(\eta^2 + \xi^2)^2$. The remaining two-dimensional representation is either reducible or irreducible. If it is reducible, then it divides into two one-dimensional irreducible representations, to each of which it corresponds according to a single invariant, for example $(\eta^2 - \xi^2)^2$ and $(\eta\xi)^2$. Of the three fourth-order invariants enumerated, only two are linearly independent, for example those introduced in (1). If the representation under consideration is irreducible, then to it there corresponds the single invariant $(\eta^2 - \xi^2)^2 + (\eta\xi)^2$, and it is again possible to choose as the two independent invariants those introduced in (1). The case is also possible in which the one-dimensional irreducible representations into which the reducible two-dimen-

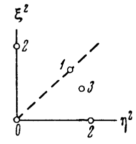


FIG. 1. Solutions (2) in the η-ξ plane.

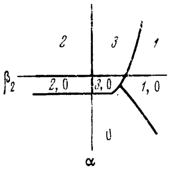
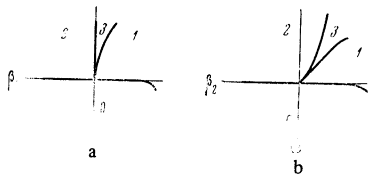


FIG. 3. Boundaries for existence of solutions (2) in the α-β_2 plane for phase transitions of the second kind ($\beta_1 < 0, \gamma_2 = 0$).



a

b

FIG. 2. Boundaries for existence and stability of the solutions (2) in the α-β_2 plane for phase transitions of the second kind ($\beta_1 > 0$): a, $\gamma_1 = \gamma_2 = 0$; b, $\gamma_1 \neq 0, \gamma_2 \neq 0$.

sional divides are equivalent. Then there appears still another invariant of fourth order, of the form $(\eta^2 - \xi^2)\eta\xi$. This case, however, will not be considered here. The results of our treatment are also not applicable to those transitions with a two-component parameter in which the original representation is only "physically" irreducible; that is, it can be divided into two complex irreducible representations. In this case, all the invariants are powers of one invariant of second order.

To the minimization condition for the thermodynamic potential (1) there correspond the following four types of solution:

$$\begin{aligned} &0: \quad \eta = 0, \ \xi = 0, \\ &1: \quad \eta = \pm\xi \neq 0, \\ &2: \quad \eta = 0, \ \xi \neq 0 \text{ when } \neq 0, \ \xi = 0, \\ &3: \quad \eta \neq 0, \ \xi \neq 0. \end{aligned} \tag{2}$$

These solutions are represented graphically by the points in Fig. 1. Phase 3, as is clear from the figure, is very asymmetric. It occurs only in the presence of the invariant of eighth order with coefficient δ in the thermodynamic potential (1). In the usual approach[3], no invariants of more than sixth order are taken into account, and therefore this phase is not obtained.

We shall now explain why, in order to obtain solution 3, it is necessary to take into account just this invariant of eighth order $\delta(\eta\xi)^4$. In the η, ξ plane, we introduce polar coordinates: $\eta = \rho \cos \varphi$, $\xi = \rho \sin \varphi$. Then the thermodynamic potential (1) takes the form

$$\Phi = \alpha\rho^2 + \beta_1\rho^4 + {}^1/_4\beta_2\rho^4 \sin^2 2\varphi + {}^1/_{16}\delta\rho^8 \sin^4 2\varphi. \tag{3}$$

From this way of writing the thermodynamic potential it is clear that although the invariant with coefficient δ is of eighth order in ρ, it is only of fourth order in $\sin 2\varphi$. Without inclusion of this invariant, one of the minimization conditions, $\partial\Phi/\partial\varphi = 0$, gives the solution $\sin 4\varphi = 0$; that is, φ must take values $\varphi = n\pi/4$, corresponding only to phases 1 and 2. A nonvanishing value of $\sin 4\varphi$, which corresponds to phase 3, can be obtained only by including an invariant of at least fourth order in $\sin 2\varphi$; that is, of eighth order in η and ξ.

From this it is also clear that inclusion of invariants of higher order will not lead to the occurrence of solutions of another type than (2). In fact, the equation for $\sin 4\varphi$ will in this case be of higher degree, but all its solutions except $\sin 4\varphi = 0$ will depend on the coefficients in the thermodynamic potential and will therefore possess the same symmetry as solution 3. This is in essence a consequence of the fact that all invariants of higher order are composed of powers of the two basic invariants $\eta^2 + \xi^2$ and $(\eta\xi)^2$.

Figure 2a shows, in the plane of the variables α and β_2, the regions of existence and stability of the four phases (2). A second-order transition from phase 0 to phase 3 can take place, as is clear from Fig. 2a, only at one point. For such a transition it is necessary that the two quantities ρ and $\sin 4\varphi$ should become different from zero together. For this it is in turn necessary that the two coefficients α and β_2 changes signs simultaneously; this determines a point in the α, β_2 plane. It is also clear that taking account of other terms in the thermodynamic potential (1) can only change the boundaries of the regions in the phase diagram. Thus, for example, Fig. 2b shows the boundaries of the regions of existence and stability of the phases for the case in which, in the expression (1), account is taken of the invariants of the sixth order:

$$\gamma_1(\eta^2 + \xi^2)^3 + \gamma_2(\eta^2 + \xi^2)(\eta\xi)^2. \tag{4}$$

Since the coefficients α and β_2 (like the other coefficients in the thermodynamic potential) are functions of the temperature T and the pressure $\mathscr{P}$, the phase diagram in the variables $\mathscr{P}$ and T will have a form topologically similar to that shown in Fig. 2a. In particular, there will exist a point at which four different phases are simultaneously adjacent. But there is here no contradiction of the Gibbs phase rule, because for transitions of the second kind the thermodynamic potentials of the different phases are not independent.

In order to investigate phase transitions of the first kind, it is necessary to include in the thermodynamic potential (1) the invariants (4) of the sixth order and to set $\beta_1 < 0$. Figure 3 shows the regions of existence of the solutions (2) when account is taken of a single invariant of sixth order, the one with coefficient γ_1. As is seen from Fig. 3, Gibbs' rule for transitions of the first kind is not violated. The region of overlap of phases 0 and 3 grows with increase of $|\beta_1|$.

The considerations presented can be generalized to the case of parameters of a transition with a larger number of components, for example three: η, ξ, ζ. Now eight different types of solution are possible. In the superphase 0, $\eta = \xi = \zeta = 0$. In phases 1, 1′, and 1″, the components of the parameter are connected by two relations; for example, $\xi = \zeta = 0$; $\eta = \xi$, $\zeta = 0$; and $\eta = \xi = \zeta$, respectively. In phases 2, 2′, and 2″, a single relation is satisfied: for example, $\zeta = 0$, $\eta = \xi$; and $\eta + \xi + \zeta = 0$, respectively. In the very asymmetric phase 3, the values of the components of the parameter are arbitrary. In order to obtain all these solutions, it is necessary to consider the change not of two coefficients in the thermodynamic potential, as in the case of a two-component transition parameter, but of three. The complete phase diagram is obtained in three dimensions: these three coefficients are plotted along three axes. The form of the $\mathcal{P}-T$ phase diagrams can vary widely, since they correspond to various sections of the three-dimensional diagram. In the $\mathcal{P}-T$ phase diagrams for transitions of the second kind, phases 0 and 1, 1 and 2, and 2 and 3 touch along lines; phases 0 and 2 and phases 1 and 3 touch at isolated points. A second-order phase transition between phases 0 and 3 is in general impossible. In the general case, upon suitable change of the coefficients in the thermodynamic potential, up to seven successive phase transitions are possible; these are thus described on a single basis, starting from the general expression for the thermodynamic potential.

We return to Rochelle salt, which we shall consider as an example illustrating the possibilities of the proposed approach to the description of phase transitions close together in temperature. We emphasize at once that the space groups of the three phases of Rochelle salt may not be considered to have been reliably determined. Therefore it is impossible at present to carry out an exhaustive analysis of phase transitions in Rochelle salt, including a deduction of the thermodynamic potential on the basis of symmetry considerations. What is treated below is the simplest variant of the theory, with a two-component transition parameter. As the analysis has shown, similar results for the anomalies of physical properties of Rochelle salt are obtained also in more complicated variants of the theory.

We shall suppose that with lowering of the temperature, there occur successively in Rochelle salt transitions between phases 1 and 3 and between phases 3 and 2 (see Fig. 2) because of change of the coefficient β_2 in the thermodynamic potential (1). Phase 3 corresponds to the pyroelectric phase. The superphase 0 is not observed experimentally. In order to describe the anomalies in the dielectric properties of Rochelle salt, it is necessary to add, in the thermodynamic potential (1), terms dependent on the polarization P,

$$\varkappa P^2 - PE, \tag{5}$$

and a cross term (see[4])

$$a(\eta^2-\xi^2)\eta\xi P. \tag{6}$$

The cross term (6) is so chosen as to be zero in phases 1 and 2 and to differ from zero in phase 3. Phases 1 and 2 will thereby be nonpyroelectric and phase 3 pyroelectric. Examples will be given below of irreducible representations permitting invariants of such a form as (6).

We shall suppose that the coefficient β_2 is linearly dependent on temperature,

$$\beta_2 = \beta'(\Theta_2 - T), \tag{7}$$

and that the remaining coefficients α, β_1, δ, κ, and a are constant. On minimizing the thermodynamic potential (1), (5), (6) with respect to the variables η, ξ, and P, we obtain the following results.

The spontaneous polarization P_s in the pyrophase 3 $(\Theta_2 < T < \Theta_1)$ changes with temperature in accordance with the law

$$P_s = \frac{\beta' a}{2\tilde{\delta}\varkappa}\sqrt{(T-\Theta_2)(\Theta_1-T)}. \tag{8}$$

Here and hereafter we use the notation

$$\tilde{\delta} \equiv \delta + a^2/\varkappa. \tag{9}$$

The difference $\Theta_1 - \Theta_2$ between the transition temperatures is given in terms of the coefficients in the thermodynamic potential by

$$\Theta_1 - \Theta_2 = \alpha^2\tilde{\delta}/8\beta_1^2\beta'. \tag{10}$$

The dielectric susceptibility χ in the nonpyroelectric phases 1 and 2 near the transition points Θ_1 and Θ_2 changes in accordance with Curie's law:

$$\chi = \frac{C_1}{T-\Theta_1} \quad C_1 = C_2\left[1+\frac{\beta'(\Theta_1-\Theta_2)}{2\beta_1}\right]$$
$$\chi = \frac{C_2}{\Theta_2 - T}, \quad C_2 = \frac{a^2(\Theta_1-\Theta_2)}{4\tilde{\delta}\varkappa^2}. \tag{11}$$

In the pyrophase 3, the value of χ depends on temperature in the following manner:

$$\chi = \frac{\Theta_1 - T}{\Theta_1-\Theta_2}\frac{C_2/2}{T-\Theta_2} + \frac{T-\Theta_2}{\Theta_1-\Theta_2}\frac{C_1/2}{\Theta_1-T} + \frac{1}{2\varkappa} - \frac{C_2}{\Theta_1-\Theta_2}. \tag{12}$$

From this expression it is seen that in the pyrophase close to the transition point, χ varies in accordance with Curie's law, the Curie constant being twice as small as C_1 or C_2 respectively.

We shall also give expressions for the coefficient B in the relation $E = AP + BP^3$. In the pyrophase 3, this coefficient depends on temperature in the following manner:

$$B^{-1} = 2\chi P_s^2. \tag{13}$$

At the transition points Θ_1 and Θ_2 it is continuous and is equal respectively to

$$B_1^{-1} = C_1C_2\beta'^2/\tilde{\delta}, \quad B_2^{-1} = C_2^2\beta'^2/\tilde{\delta}. \tag{14}$$

From the expressions (8), (11), and (14) follow, as is easily seen, the relations

$$C_1B_1 = C_2B_2 = (dP_s^2/dT)^{-1}_{T=\Theta_1,\,\Theta_2}. \tag{15}$$

The temperature dependencies (8), (11), and (12) for P_S and χ agree well with experimental data[5-7]. We notice that the $P_S(T)$ curve is symmetric, whereas the $\chi(T)$ curve is asymmetric. The Curie constant C_1, in accordance with (11), is larger than C_2 (the experimental values[6] are $C_1 = 178°$, $C_2 = 94°$). This, in particular, served as a basis for the choice of phases 1 and 2 as the high- and low-temperature phases.

According to (11), the Curie constant C_2 and the difference $\Theta_1 - \Theta_2$ between the transition temperatures are proportional to each other and consequently should vary identically with pressure; this agrees well with experimental data[5,6].

From the thermodynamic potential (1), (5), (6) one can also obtain the anomalies of other properties of Rochelle salt, for example the specific heat. Figure 4 shows the variation of specific heat C with temperature. The specific heat of the superphase 0 is chosen as zero. At the transition temperatures Θ_1 and Θ_2, the specific heat undergoes jumps of respective amounts

$$\Delta C_{T=\Theta_1} = \beta'^2\Theta_1/2\tilde{\delta}_2[1+\beta'(\Theta_1-\Theta_2)/4\beta_1], \quad \Delta C_{T=\Theta_2} = \beta'^2\Theta_2/2\tilde{\delta}_2. \tag{16}$$

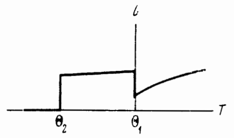


FIG. 4. Dependence of the specific heat C of Rochelle salt on temperature T.

In phase 1 the specific heat increases markedly over a temperature interval $\sim \Theta_1 - \Theta_2$. The experimental data on the specific heat of Rochelle salt, unfortunately, are very inconsistent.

We note that in the immediate vicinity of the transition points, the temperature dependences of P_S and χ found above are similar to the dependences that are obtained by the usual approach to ferroelectric phase transitions. This is because the transitions between phases 1 and 3 and between phases 2 and 3 can be treated on the basis of the Landau-Ginzburg-Devonshire theory, by considering phase 1 or 2 symmetric and using the polarization as transition parameter. It is then necessary, however, to use two expressions for the thermodynamic potential, with two independent sets of coefficients. In such an approach, therefore, a larger number of constants is used, and, furthermore, the temperature dependences in the interval between Θ_1 and Θ_2 are not described. Still another method has been proposed for describing anomalies in Rochelle salt. In it, a single thermodynamic potential is used, and it is supposed that the coefficient of P^2 changes nonmonotonically with temperature, vanishing at Θ_1 and Θ_2. However, assumption of the simplest temperature dependence for this coefficient turns out to be insufficient for description of the observed anomalies. And assumption of a more complicated dependence of several coefficients in the thermodynamic potential renders such an approach empty.

In the approach presented in this paper, the phase transitions in Rochelle salt are described on a single basis, and a linear temperature dependence is assumed for only a single coefficient in the thermodynamic potential. The anomalies of the dielectric properties at the transition points then turn out to be related to each other. In other words, there are definite relations, for example (15), between the coefficients in the two thermodynamic potentials of the separate descriptions of the phase transitions. Furthermore, the temperature dependences of physical quantities are determined for the whole interval between Θ_1 and Θ_2. Some of the dependences are significantly different from those obtained in the usual approach on the basis of the Landau-Ginzburg-Devonshire theory (see, for example, Fig. 4).

We note that the approach under consideration is of definite interest from the point of view of microscopic theories of Rochelle salt. In the existing microscopic theories[5] it is assumed that the transition between phases 3 and 1 is a transition of the order-disorder type. From the point of view of the present approach, however, only phase 0 can be unordered, whereas phases 1, 2, and 3 are all ordered, with different kinds of order.

The correspondences between theoretical and experimental data on the anomalies of the dielectric properties are insufficient for a final judgment regarding the correctness of the proposed approach to a description of the phase transitions in Rochelle salt. It is necessary to carry out an analysis on the basis of group theory and to find a superphase such that its symmetry group shall have irreducible representations corresponding to phase transitions from the superphase to all three phases of Rochelle salt. As has already been mentioned, the space symmetry groups of Rochelle salt have not yet been reliably established. There are indications that, contrary to the usual opinion, the low-temperature phase is not isostructural with the high-temperature[5]. Furthermore, the elementary cell in Rochelle salt is, according to some experimental data[8], more complicated than is commonly supposed. Therefore we shall consider only one example of a possible superphase. We shall start with the premise that according to its symmetry, the superphase belongs to the class D_4. Apparently this is the least symmetric of the possible classes for the superphase of Rochelle salt. Among the representations of the space groups of class D_4 there are several that correspond to a thermodynamic potential of the necessary form (1), (5), and (6). All of these representations give point groups that are observed in Rochelle salt: C_2 for phase 3 and D_2 for phases 1 and 2. The space groups for different representations are obtained differently. One of the representations gives for phases 1, 3, and 2 space groups D_2^3, C_2^2, and D_2^5 respectively. The space groups of phases 1 and 3 agree with those determined experimentally in Rochelle salt. The space groups of phases 1 and 2 differ from each other. Such a difference is inevitable in the approach considered. It does not depend on the choice of the superphase and is essentially due to the fact that phases 1 and 2 correspond to different types of solution.

Phase transitions close together in temperature are observed not only in Rochelle salt but also in many other materials. An analysis of the anomalies of physical properties in such materials can be carried out on a single basis just as was done above for Rochelle salt.

Of indubitable interest is the investigation of $\mathcal{P} - T$ phase diagrams of materials with phase transitions close together in temperature. In particular, one can hope to detect a characteristic point on the phase diagram, at which four phases are contiguous for second-order transitions. The form of the phase diagram near this point follows from the expression for the thermodynamic potential and is therefore related in a definite way to the nature of the anomalies in physical properties. It is seen from Fig. 2 that the boundaries of phases 1, 2, and 3 have a common tangent at the characteristic point. It is to be expected that the smaller the difference is between the transition temperatures, the closer the system will be to the characteristic point. In Rochelle salt this point should lie in a region of large negative pressures.

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