Polarization response of crystals with structural and ferroelectric instabilities

E. V. Balashova and A. K. Tagantsev
I. F. Ioffe Physical Technical Institute of Russian Academy of Sciences, St. Petersburg, 194021, Russia
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A simple phenomenological model with two coupled structural and ferroelectric order parameters is under consideration. The small-signal dielectric response, dielectric response to a strong electric field (hysteresis phenomena included), and the phase diagram in the presence of the bias field are analyzed in the framework of Landau theory. It is shown that for the set of properties studied one can single out six qualitatively different types of behavior of the model. It is also shown that, in the framework of a unified phenomenological scheme, this model can describe the gradual conversion of ferroelectric to antiferroelectric behavior. The application of the model to the description of real compounds with a sequence of phase transitions is discussed.

I. INTRODUCTION

It is well known that there exist many crystals with several soft modes at different points of the Brillouin zone. This is a common situation for perovskite-type structures. For example, $SrTiO_3$ crystals possess two instabilities: a ferroelectric one with a soft mode at the Brillouin-zone center and an antiferroelectric distortion with a soft mode at the R point of the zone. Another well-known example is antiferroelectrics. That became clear after the papers by Cross[1] and Okado[2] who transformed the Kittel model[3] to a form explicitly containing two instabilities (ferroelectric and structural). However, this model is not sufficient to describe some important features of systems with ferroelectric and structural instabilities, especially in the case of a crystal with a sequence of antiferroelectric and ferroelectric phase transitions.

The behavior of systems with two order parameters has been studied in several papers (see, e.g., Refs. 4 and 5, and the references therein). In those papers, the main attention has been paid to the analysis of the phase diagram in the absence of an external electric field for a number of cases with a rather complicated structure of the free-energy expansion. However, such important properties of the system as the phase diagram in the presence of an external electric field and the behavior of the hysteresis loops was not addressed and no analysis was done of the whole set of dielectric properties of the system, in order to identify its characteristic features.

The aim of this paper is to present a detailed analysis of the simplest phenomenological model with ferroelectric and structural instabilities, the Kittel model being a special case. For this model, we theoretically investigate the dielectric response, the phase diagram in the presence of an electric field, and the behavior of the hysteresis loops. We analyze the whole set of results obtained to show that one can single out six types of behavior of the system considered, the set of aforementioned properties being qualitatively different for any two of them. The application of the model to real compounds is discussed.

II. FREE ENERGY

For our analysis of the problem we choose the simplest system, a system with two one-component order parameters: P, the polarization along the polar axis and η, a nonpolar order parameter. The free energy of the system is

$$F=\tfrac{1}{2}\alpha_1\eta^2+\tfrac{1}{4}\beta_1\eta^4+\tfrac{1}{2}\alpha_2P^2+\tfrac{1}{4}\beta_2P^4+\tfrac{1}{2}\gamma\eta^2P^2-EP\ . \quad (1)$$

Here E is the component of the macroscopic electric field along the polar axis, $\alpha_1=\lambda_1(T-T_{c1})$, $\alpha_2=\lambda_2(T-T_{c2})$. We restrict ourselves to consideration of the case where $T_{c1}>T_{c2}$, and β_1, β_2, and γ are positive, i.e.: (i) the temperature of the structural instability is higher than that of the ferroelectric instability. (Note that this relation between the transition temperatures is of importance for the phase diagram of the system, which is the main item of our analysis, so the case where $T_{c1}<T_{c2}$ needs additional consideration.) (ii) In the absence of interaction between the order parameters ($\gamma=0$), both phase transitions are second order. (iii) The sign of γ corresponds to the suppression of ferroelectric ordering in the presence of a nonpolar order parameter. One should note that the sign of γ is of primary importance for the behavior of the system. For $\gamma<0$, the system may reveal, for example, a "trigger-type"[6] phase transition.

The free-energy expansion (1) can be normalized so that only dimensionless quantities are involved:

$$a=\tfrac{1}{2}\Delta tq^2+\tfrac{1}{4}q^4+\tfrac{1}{2}(1+t)Q^2+\tfrac{1}{4}Q^4+\tfrac{1}{2}\varphi q^2Q^2-eQ\ , \quad (2)$$

where

$$\begin{aligned}
a&=F\beta_2/\lambda_2(T_{c1}-T_{c2})\ ,\\
t&=(T-T_{c1})/(T_{c1}-T_{c2})\ ,\\
q^2&=\eta^2(\beta_1\beta_2)^{1/2}/\lambda_2(T_{c1}-T_{c2})\ ,\\
Q^2&=P^2\beta_2/\lambda_2(T_{c1}-T_{c2})\ ,\\
e&=E(\beta_2)^{1/2}/\lambda_2^{3/2}(T_{c1}-T_{c2})^{3/2}\ .
\end{aligned} \quad (3)$$

It is clear from Eq. (2) that there are two independent parameters φ and Δ governing the behavior of the system:

$$\Delta=(\lambda_1/\lambda_2)(\beta_2/\beta_1)^{1/2}, \quad \varphi=\gamma/(\beta_1\beta_2)^{1/2} . \tag{4}$$

Parameter φ determines the coupling between order parameters. To elucidate the physical meaning of Δ one should compare the free energies of the polar ($Q\neq 0$, $q=0$) and nonpolar ($Q=0$, $q\neq 0$) phases in the absence of the electric field. Minimizing the free energy (2), it is easy to find that, in these phases, the spontaneous values of the order parameters q_0 and Q_0 and the values of the free energies are

$$q_0^2=-t\Delta, \quad a_q=-\frac{1}{4}(t\Delta)^2 , \tag{5}$$

$$Q_0^2=-(1+t), \quad a_Q=-\frac{1}{4}(1+t)^2 , \tag{6}$$

respectively. As one can see, for $\Delta>1$, we have $a_q<a_Q$ for any $t<0$ (i.e., for the temperatures $T<T_{c1}$), and therefore the polar phase ($Q\neq 0$, $q=0$) cannot occur in a system without an electric field. For $\Delta<1$, the energies a_q and a_Q can be equal at some $t=t_c$,

$$t_c=-(1-\Delta)^{-1} , \tag{7}$$

and therefore, for $t<t_c$, there may exist the aforementioned polar phase. Thus, one can expect the qualitative behavior of the system to be quite different for $\Delta<1$ and $\Delta>1$.

As was mentioned above an important feature of the model is the suppression of the ferroelectric ordering in the presence of the nonpolar order parameter. In this respect, one should point out the important role of the product $\Delta\varphi$: for $\Delta\varphi>1$, the appearance of the nonpolar order parameter completely suppresses the ferroelectric instability whereas, in the opposite case, the impact of the appearance is not so strong and the critical ferroelectric phase transition is possible. These two cases manifest themselves in the qualitatively different behavior of the dielectric susceptibility at the structural phase transition (at $T=T_{c1}$ or $t=0$ in dimensionless units). Using the expression for the free energy (2) one can easily find the normalized dielectric susceptibility $X=dQ/de$ [the true susceptibility $\chi=X/\lambda_2^3(T_{c1}-T_{c2})^3$]:

$$X=dQ/de$$
$$=\frac{t\Delta+3q^2+\varphi Q^2}{[(1+t)+3Q^2+\varphi q^2](t\Delta+3q^2+\varphi Q^2)-4\varphi^2q^2Q^2} \tag{8}$$

and therefore, for $t>0$ ($T>T_{c1}$), i.e., in the high-temperature phase ($q=0$ and $Q=0$),

$$X=(1+t)^{-1} \tag{9}$$

and, for $t<0$ in the phase with $q=q_0=-t\Delta$ and $Q=0$,

$$X=[1+t(1-\Delta\varphi)]^{-1} . \tag{10}$$

As can be seen from Eq. (10), for the case of strong suppression $\Delta\varphi>1$, we have a cusplike anomaly and in the opposite case we have only a change of the slope.

Comparing the free energy (2) and the transformed expression for the Kittel-model free energy,[2] we can see that, for $\varphi=3$ and $\Delta=1$, the considered model is identical to the Kittel model.

III. THE E-T PHASE DIAGRAM OF THE MODEL AND THE BEHAVIOR OF THE HYSTERESIS LOOPS AND THE DIELECTRIC CONSTANT

In the absence of an external electric field the phase diagram of the model has been analyzed by Gufan and Larin.[5] The analysis presented below does not contradict their results.

The electric-field–temperature phase diagram and the temperature behavior of the dielectric susceptibility of our model can be substantially different for different values of the Δ and φ parameters. One can single out six regions on the Δ-φ plane (see Fig. 1) corresponding to different behaviors of the system.

Let us start from the consideration of the U, T, and S regions which relate to the case of strong suppression ($\Delta\varphi>1$; "antiferroelectric" cusplike anomaly of the dielectric constant at T_{c1}).

A. T region

In this region Δ meets the inequalities: $\varphi/(3-2\varphi)^2>\Delta\geq 1$. The Kittel model applies to this region. To determine the state of the system one should consider the extremization condition of the free energy

$$\begin{aligned} \partial a/\partial q &= t\Delta q+q^3+\varphi qQ^2=0 , \\ \partial a/\partial Q &= (1+t)Q+Q^3+\varphi Qq^2-e=0 , \end{aligned} \tag{11}$$

and the stability conditions

$$\begin{aligned} &\partial^2a/\partial q^2>0, \quad \partial^2a/\partial Q^2>0 , \\ &[(\partial^2a/\partial q^2)(\partial^2a/\partial Q^2)-(\partial^2a/\partial q\partial Q)^2]>0 . \end{aligned} \tag{12}$$

The calculation in the Appendix shows that two states of the system are possible: $q=0$ and $q\neq 0$. For $t_1<t<0$,

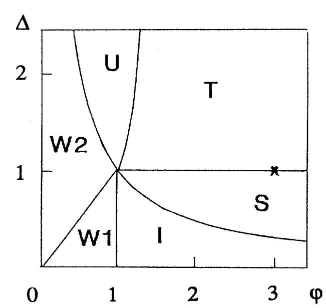

FIG. 1. The classification of the types of dielectric behavior of the model. The symbols U, T, S, I, $W1$, and $W2$ on the plane of Δ and φ parameters indicate the areas corresponding to the different types of behavior. The cross shows the values of the parameters ($\Delta=1$ and $\varphi=3$) at which the considered model is equivalent to the Kittel model.

where

$$t_1 = -\varphi/[\varphi(1-\varphi\Delta)+3\Delta(\varphi^2-1)] \ , \tag{13}$$

these states are divided by the line of the second-order phase transition, the corresponding critical field being given by the following equation:

$$e_k = (1-\Delta/\varphi)[t+\varphi/(\varphi-\Delta)](-t\Delta/\varphi)^{1/2} \ . \tag{14}$$

For $t < t_1$ the second-order phase transition transforms into a first-order one. The latter can be characterized by two critical fields e_{k1} and e_{k2} at which the states with $q=0$ and $q\neq 0$ lose their stability. The field e_{k1} is given by Eq. (14) for $t < t_1$. The field e_{k2} is

$$e_{k2} = 2(\varphi^2-1)\{[1+t(1-\varphi\Delta)]/3(\varphi^2-1)\}^{3/2} \ . \tag{15}$$

Also we have found by numerical calculations the electric field e_c (the line of the first-order phase transition itself) at which the free energies of the phases are equal. The details of the calculation can be found in the Appendix. The temperature dependence of the fields e_k, e_{k1}, e_{k2}, and e_c is shown in Fig. 2 for $\Delta=2$ and $\varphi=3$. For $\Delta=1$ and $\varphi=3$ the result of our calculation coincides with those of Okada.[2] On the basis of these data one can plot the e-t phase diagram of the model. It is shown in Fig. 3(a). Using this figure it is easy to illustrate the appearance of the double hysteresis loops in our model. For cross section A, a change in the field causes a second-order phase transition and one has a nonhysteresis polarization electric-field dependence with a change of the slope at $e=e_k$ only, whereas, for cross section B, the field causes a first-order phase transition that implies a polarization curve with double hysteresis loops. The maximal width of the loops is given by the difference $e_{k1}-e_{k2}$. However, it is well known that real hysteresis loops are always much narrower and actually the width of the

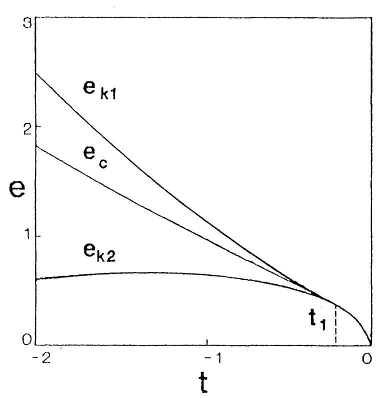

FIG. 2. The critical fields for the model in the T region vs temperature: e_{k1} is the field at which the state with $q\neq 0$ loses its stability, e_{k2} is the field at which the state with $q=0$ loses its stability, and e_c is the field at which the energies of these two states are equal. The variables e and t stand for the dimensionless electric field and temperature, respectively [see Eqs. (3)]. The temperature t_1 is given by Eq. (13).

loops is governed by nucleation processes that are not taken into account in the framework here. But it is of importance that in the common case of rather narrow hysteresis loops their position is determined by the field e_c at which the energies of the phases are equal. Thus, the temperature dependence of e_c yields the temperature dependence of the critical field for narrow double hysteresis loops.

In the considered T region, as one can conclude from Fig. 3(a), the double loops diverge with decreasing temperature, following the temperature dependence of e_c. The presence of this behavior of the loops together with the cusplike dielectric anomaly at $t=0$ [see Fig. 4(a)] is the mark of the T region. [For this region and for the U region, the temperature dependence of the dielectric constant is given by Eqs. (9) and (10).]

B. *U* region

The border between the T and U regions is the line where $t_1=-\infty$ [or $\Delta=\varphi/(3-2\varphi^2)$]. Therefore in this region the phase transition is always second order. The phase diagram is shown in Fig. 3(b). The characteristic feature of this region is the absence of any hysteresis loops and the presence of the "antiferroelectric" cusplike dielectric anomaly at $t=0$ which is similar to that for the T region [see Figs. 4(a) and 4(b)]. This similarity is caused by the common condition $\Delta\varphi > 1$ for these two regions.

C. *S* region

The border between the T and S regions is the line where $\Delta=1$. For $\Delta<1$, the energies of the phase with $q=0$ and that with $q\neq 0$ (in the absence of the field) can be equal at some $t_c<0$ [see Eq. (7)]. That qualitatively changes the form of the phase diagram and the temperature dependence of the dielectric constant. This is shown in Figs. 3(c) and 4(c). Now at $t=t_c$, in the absence of the electric field, we have a first-order phase transition into the ferroelectric state ($Q\neq 0$, $q=0$). This phase transition is a noncritical one (the ordered nonpolar state does not lose its stability at any $t<0$). It is followed, as is seen from Fig. 4(c), by an additional steplike dielectric anomaly at t_c. For $t>t_c$, the behavior of the dielectric susceptibility X is given by Eqs. (9) and (10) and, for $t<t_c$ in the ferroelectric phase ($q=0$, $Q\neq 0$), as is shown in the Appendix, the following expression for X should be used

$$X = -\tfrac{1}{2}(1+t)^{-1} \ . \tag{16}$$

To elucidate the properties of the model for the S region let us consider three cross sections (A, B, and C) of the diagram [Fig. 3(c)]. For the A cross section, we have no hysteresis loops, for the B cross section we have double hysteresis loops, and, for the C cross section we have an ordinary "ferroelectric" loop. (Note that in terms of the e-t phase diagram the crossing of a line of the first-order phase transition at a nonzero value of the electrical field corresponds to double hysteresis loops whereas the crossing of a line of that kind at a zero value of the field

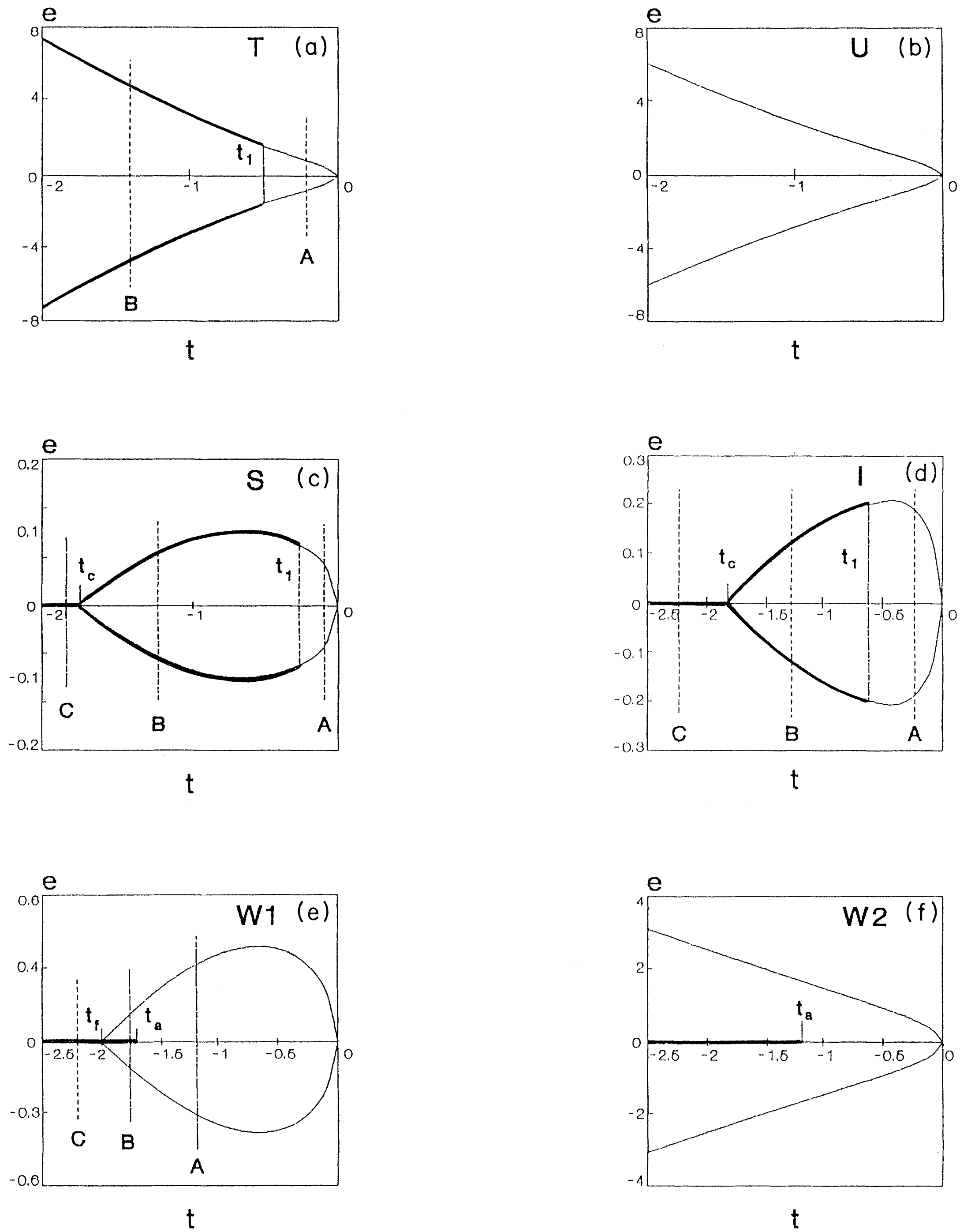

FIG. 3. The electric-field–temperature phase diagrams of the model for various types of its behavior. These types relate to the regions shown in Fig. 1. The variables e and t stand for the dimensionless electric field and temperature, respectively [see Eqs. (3)]. The temperatures t_1, t_c, t_a, and t_f are given by Eqs. (13), (7), (18), and (17), respectively. The diagrams have been calculated for the following values of the Δ and φ parameters: (a) $\Delta=3$ and $\varphi=1.5$ (T region); (b) $\Delta=2$ and $\varphi=1$ (U region); (c) $\Delta=0.4$ and $\varphi=4$ (S region); (d) $\Delta=0.45$ and $\varphi=2$ (I region); (e) $\Delta=0.45$ and $\varphi=0.9$ ($W1$ region); (f) $\Delta=0.45$ and $\varphi=0.35$ ($W2$ region). A, B, and C indicate isothermal cross sections. The thin and thick lines stand for the second- and first-order phase transitions between the state with $q\neq0$ and that with $q=0$. One thick line in a cross section (at $e=0$) mean a single hysteresis loop. Two thick lines in a cross section mean double hysteresis loops with critical fields given by the ordinates of the crossing points. Two thin lines in a cross section mean a change of the slope on the polarization electric-field dependence. The corresponding critical fields are given by the ordinates of the crossing points.

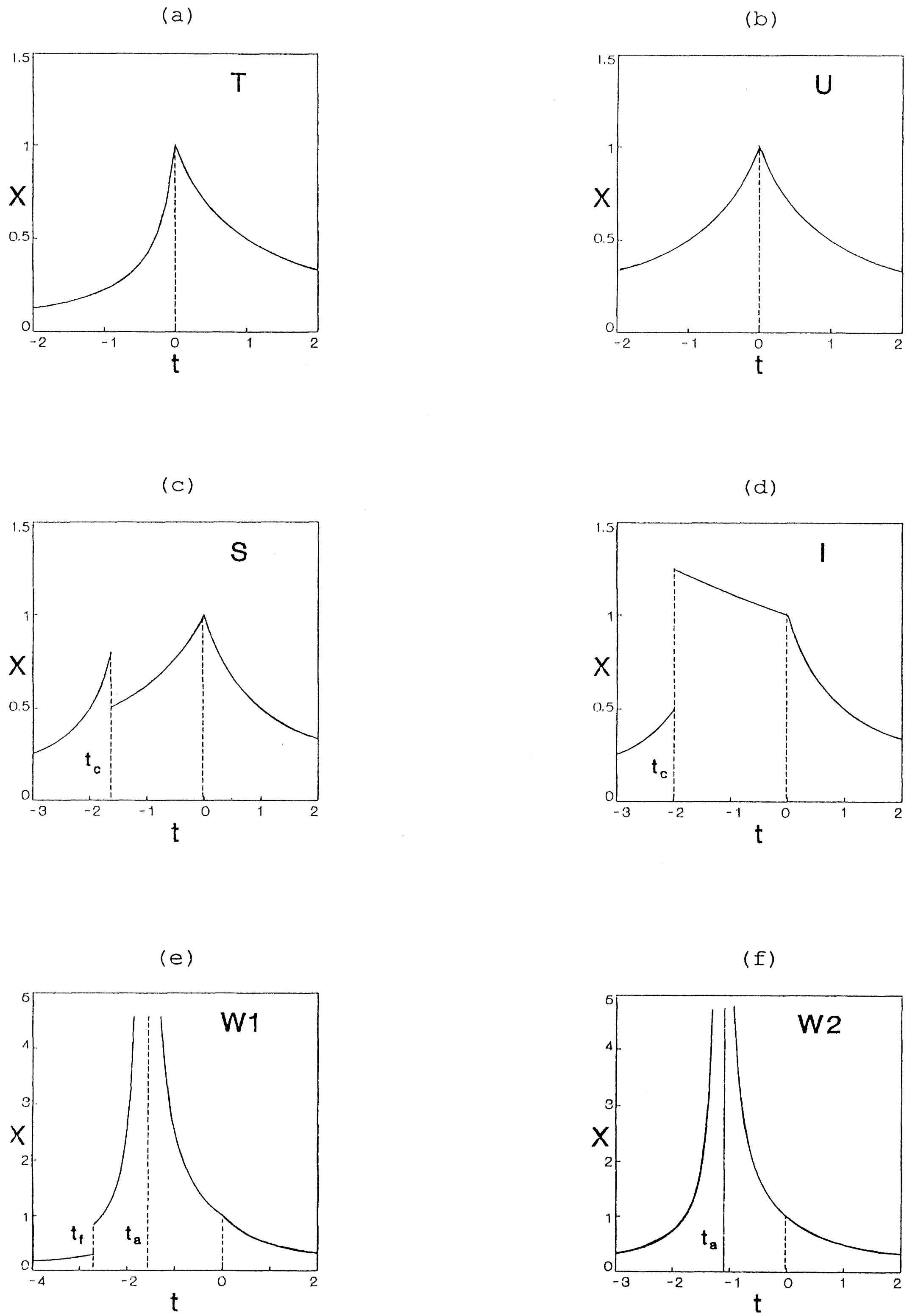

FIG. 4. The temperature dependence of the dielectric susceptibility of the model for various types of its behavior. The notations are identical to those in Fig. 3. The values of the Δ and φ parameters used for the calculations of the dependences are indicated in the caption for Fig. 3.

corresponds to a single hysteresis loop.) The difference in the behavior of double loops for the T and S regions is that in the latter case the loops converge with decreasing temperature, transforming into a single hysteresis loop at t_c. The presence of the converging double loops together with the cusplike dielectric anomaly at $t=0$ is an indication of the S region.

Now let us consider the case of weak interaction between the order parameters ($\varphi\Delta<1$) where the dielectric anomaly at $t=0$ is a change of slope. The behavior of the model in this case differs substantially from that in the case of the strong interaction. The influence of the nonpolar order parameter now is not so strong and the phase transition into the polar state appears to be of critical type (of second order or of first order close to second order).

D. *I* region

For this region ($\varphi\Delta<1$ and $\varphi>1$), the e-t phase diagram shown in Fig. 3(d) and the behavior of the hysteresis loops are qualitatively the same as those in the S region. But the temperature interval $t_c<t<t_1$ now is narrower than in the previous case, tending to zero when φ goes to 1. The main difference between the S and I regions is that, for the I region, the ferroelectric phase transition (at t_c) is of first order close to second order. This fact is responsible for the crucial change in the temperature dependence of the dielectric susceptibility [cf. Figs. 4(d) and 4(c)] given by Eqs. (9), (10), and (16). Actually, in the I region, our model describes the usual ferroelectric phase transition with a strong dielectric anomaly, a single hysteresis loop below the transition, and double hysteresis loops above it, as one should expect for a first-order ferroelectric phase transition. In this region, the structural instability at $t=0$ manifests itself only in the change of slope in the temperature dependence of the dielectric constant.

E. *W*1 region

On moving from the S region to the $W1$ region ($1>\varphi>\Delta$) the first-order phase transition from a nonpolar state ($q_0\neq 0$ and $Q_0=0$) to a polar state ($q_0=0$ and $Q_0\neq 0$) at $t=t_c$ converts into two second-order phase transitions: the first from the state ($q_0\neq 0$ and $Q_0=0$) to the state ($q_0\neq 0$ and $Q_0\neq 0$) and the second from the state ($q_0\neq 0$ and $Q_0\neq 0$) to the state ($q_0=0$ and $Q_0\neq 0$). Thus, in the absence of an electric field the transition from nonpolar to polar phases occurs through an intermediate mixed phase existing in the temperature interval $t_f<t<t_a$, where

$$t_f=(\Delta/\varphi-1)^{-1} \tag{17}$$

and

$$t_a=(\Delta\varphi-1)^{-1} . \tag{18}$$

For the $W1$ region, the e-t phase diagram and the temperature dependence of the dielectric constant are shown in Figs. 3(e) and 4(e).

For the high-temperature and ordered nonpolar phases, i.e., for $t>t_a$, and for the polar phase ($t<t_f$) the behavior of the dielectric constant is given by Eqs. (9), (10), and (16). The temperature dependence of the dielectric constant in the mixed phase, as is shown in the Appendix, obeys the following expression:

$$X=-\tfrac{1}{2}[1+t(1-\Delta\varphi)]^{-1} . \tag{19}$$

To elucidate the properties of the model for the $W1$ region let us consider three cross sections (A, B, and C) of the diagram [Fig. 3(e)].

For cross section A, a change in field causes a second-order phase transition and there is a nonhysteresis polarization electric-field dependence with a change of slope at $e=e_k$. For cross section B, the variation of the field apart from the aforementioned transition also causes a first-order phase transition at $e=0$ between states with opposite signs of the spontaneous polarization of the intermediate ferroelectric phase. This phase transition being induced by the electric field implies a single ferroelectric hysteresis loop. For temperatures close to but below the temperature of the transition to the intermediate phase t_a, one can expect the coercive field for the loop e_f to be smaller than e_k. For these temperatures the polarization electric-field dependence should have two features: a single hysteresis loop and a change of slope for a greater value of the field. At the "low-temperature end" of the intermediate phase, i.e., close to t_f, one can expect the inverse relation between the coercive and critical fields $e_f\gg e_k$. That should manifest itself in the distorted shape of the hysteresis loop. That is due to the superimposing of the change of the slope and the single hysteresis loop. For the C cross section we have an ordinary single "ferroelectric" loop.

The most interesting feature of the behavior of the model in the $W1$ region is the second-order phase transition between two polar phases at $t=t_f$ accompanied by a discontinuity in the dielectric susceptibility. This discontinuity can be easily understood, on the analogy of the discontinuities in the longitudinal sound velocity at a second-order phase transition. This discontinuity is due to the "electrostriction"-type term in the free-energy expansion. We mean the term proportional to

$$u\eta^2 , \tag{20}$$

where u is the strain and η is the order parameter of the transition. In the case of the second-order phase transition between two polar phases, the discontinuity in the dielectric susceptibility can be obtained on the same lines using the term in the free-energy expansion proportional to

$$P_0P\eta^2 . \tag{21}$$

We would like to draw your attention to the fact that this term is allowed in the high-symmetry phase for the phase transition considered.

The characteristic feature of the $W1$ region is the presence of the intermediate polar phase separated from the neighboring phases by second-order phase transitions: one of them is accompanied by a singularity of the dielectric constant and the other by a discontinuity [see Fig. 4(d)]. The presence of the intermediate phase also reveals itself in the distortion and variation of the hysteresis loop shape in the vicinity of the transition between the two polar phases.

F. $W2$ region

On moving from the $W1$ to the $W2$ region ($\varphi < \Delta < 1/\varphi$) the mixed phase that appeared in the $W1$ region becomes stable at any temperature below t_a. Actually in this region we have an ordinary ferroelectric with a second-order phase transition at t_a (cf., region I describing a ferroelectric with a first-order phase transition). For the $W2$ region, the e-t phase diagram and the temperature dependence of the dielectric constant are shown in Figs. 3(f) and 4(f), respectively.

Concluding this section we note that the defined borders between regions in the Δ-φ plane do not correspond to any steplike variation of the physical properties of the material but rather they indicate the lines on crossing which the behavior of the system changes from one type to another.

IV. CONCLUSIONS

We have analyzed the properties of the simplest model with ferroelectric and structural (nonpolar) instabilities. We have shown that the properties are governed by two parameters Δ,φ only. The model can describe many quite different types of dielectric behavior depending on the relation between the parameters.

The classification of the different types of dielectric behavior of the model is presented in Table I with the notation of the regions corresponding to Fig. 1. Roughly, the model produces two types of dielectric behavior: (i) the "ferroelectric" (I, $W1$, and $W2$ regions) type when the main dielectric anomaly corresponds to the ferroelectric phase transition; (ii) the "antiferroelectric" (U, T, and S regions) type when the interaction between the order parameters "shifts" the main dielectric anomaly from the ferroelectric phase transition to the structural one (at T_{c1}). A more detailed classification is based on simultaneous analysis of the small-signal and the "strong-signal" dielectric response, i.e., the hysteresis loops. The model can describe a gradual transition from the antiferroelectric to the ferroelectric behavior. For example, it is possible to trace how the "antiferroelectric" double hysteresis loops convert into the double hysteresis loops which appear above the usual ferroelectric first-order phase transition. This conversion corresponds to the path $T \rightarrow S \rightarrow I$ on the Δ-φ diagram (Fig. 1). The most interesting region is the S region which can be considered as intermediate between the "classic" antiferroelectric behavior (T region) and the ferroelectric behavior. The systems in this region manifest the sequence of an antiferroelectric and a noncritical first-order ferroelectric phase transition, the latter being accompanied by a weak dielectric anomaly. Also, these systems manifest double "antiferroelectric" hysteresis loops converging on cooling and finally converting into a single "ferroelectric" hysteresis loop.

A polarization response of this type has been observed in several compounds. The clearest examples are deuterated betaine arsenate[7] and Pb_2CoWO_6.[8] We have analyzed the dielectric properties of deuterated betaine arsenate and shown that the model provides us with a comprehensive description of them: the weak and strong signal response, the electric-field–temperature phase diagram, and the phase diagram (temperature–degree-of-deuteration); the compound with 85% of deuteration corresponds to the model with $\Delta = 0.7$, $\varphi = 15$ (the S region). This analysis will be presented elsewhere.[9]

TABLE I. The properties of the model for various types of its behavior. Columns: (1) Type of behavior according to the regions on the Δ-φ plane (see Fig. 1). (2) The shape of the dielectric anomaly at the structural phase transition; "cusp" implies a variation of the $\varepsilon(T)$ dependence at T_{c1} (i.e., $t=0$) from decreasing to increasing, "change of slope" implies a change of slope of the increasing dependence $\varepsilon(T)$ at T_{c1}. (3) The presence and the type of double hysteresis loops; "$-$" implies no loops, "diverge" implies diverging on cooling double hysteresis loops, "converge" implies converging loops. (4) The presence of a ferroelectric hysteresis loop; "$-$" and "$+$" imply the absence and the presence of the loop, respectively. (5) The sequence of the phase of the model on cooling in the absence of the electric field; I, the paraelectric phase ($q=0, Q=0$); II, the nonpolar phase ($q \neq 0, Q=0$); III, the polar phase ($q=0, Q \neq 0$); IV, the mixed phase ($q \neq 0, Q \neq 0$).

Region	$\varepsilon(T_{c1})$	Antiferroelectric hysteresis loops	Ferroelectric hysteresis loops	The sequence of the phase
U	Cusp		$-$	I,II
T	Cusp	Diverge	$-$	I,II
S	Cusp	Converge	$+$	I,II,III
I	Change of slope	Converge	$+$	I,II,III
W_1	Change of slope		$+$	I,II,IV,III
W_2	Change of slope		$+$	I,II,IV

APPENDIX

In the absence of a bias field the states of the system are determined by Eqs. (11) and (12). Four states are possible. For these states, the values of the dimensionless order parameters q_0 and Q_0, the stability condition for the state, and the normalized dielectric susceptibility X [obtained with the help of Eq. (8)] are, respectively, (i) the paraelectric state, $q=0$, $Q=0$,

$$t > 0 ,$$

$$X = (1+t)^{-1} , \tag{A1}$$

(ii) the nonpolar state, $q \neq 0$, $Q=0$,

$$q_0^2 = -t\Delta , \tag{A2}$$

$$-2\Delta(\varphi\Delta-1)t(t_a-t) > 0 , \tag{A3}$$

$$X = [1+t(1-\Delta\varphi)]^{-1} , \tag{A4}$$

where $t_a = (\varphi\Delta-1)^{-1}$, (iii) the polar state, $q=0$, $Q \neq 0$,

$$Q_0^2=-(1+t)\ , \qquad (A5)$$

$$-2(\Delta-\varphi)(1+t)(t-t_f)>0\ , \qquad (A6)$$

$$X=-\tfrac{1}{2}(1+t)^{-1}\ , \qquad (A7)$$

where $t_f=(\Delta/\varphi-1)^{-1}$, (iv) the mixed state, $q\neq0$, $Q\neq0$,

$$q_0=-[t\Delta-\varphi(1+t)]/(1-\varphi^2)\ ,$$

$$Q_0=-[(1+t)-\varphi t\Delta]/(1-\varphi^2)\ , \qquad (A8)$$

$$\varphi(\Delta-\varphi)(\varphi\Delta-1)(t-t_f)(t_a-t)>0\ , \qquad (A9)$$

$$X=-\tfrac{1}{2}[1+t(1-\Delta\varphi)]^{-1}\ . \qquad (A10)$$

In the presence of the bias field e one can distinguish only two states: with $q\neq0$ and the other with $q=0$.

(1) For $q\neq0$, the state equations obtained from Eq. (11) have the following form:

$$\begin{aligned} q^2&=-t\Delta-\varphi Q^2 \\ e&=Q[1+t(1-\varphi\Delta)]+(1-\varphi^2)Q^2\ . \end{aligned} \qquad (A11)$$

(2) For $q=0$, the state equation is

$$e=(1+t)Q+Q^3\ . \qquad (A12)$$

It is convenient to present the stability conditions (12) in the form

$$\partial^2a/\partial Q^2>0,\quad \partial^2a/\partial q^2>0,\quad de/dQ>0\ . \qquad (A13)$$

Using (A11)–(A13), one finds the explicit forms for these conditions.

(1) The state with $q\neq0$:

$$Q^2<-t\Delta/\varphi\ , \qquad (A14)$$

$$Q^2<[1+t(1-\varphi\Delta)]/3(\varphi^2-1)\ . \qquad (A15)$$

(2) The state with $q=0$:

$$Q^2>-t\Delta/\varphi\ , \qquad (A16)$$

$$Q^2>-(1+t)/3\ . \qquad (A17)$$

If the stability of the states is determined by inequalities (A14) and (A16) then the phase transition between the states is continuous. It is true if

$$[1+t(1-\varphi\Delta)]/3(\varphi^2-1)>-t\Delta/\varphi\ . \qquad (A18)$$

This inequality together with Eq. (33) yields the critical field for a continuous phase transition:

$$e_k=[1-(\Delta/\varphi)][t+\varphi/(\varphi-\Delta)](-t\Delta/\varphi)^{1/2}\ . \qquad (A19)$$

When the inequality (A18) is not met the transition is of first order. That implies the criterium for the first-order phase transition:

$$t<t_1=-\varphi/[\varphi(1-\varphi\Delta)+3\Delta(\varphi^2-1)]\ . \qquad (A20)$$

The critical fields e_{k1} and e_{k2} at which the states (with $q\neq0$ and with $q=0$, respectively) lose their stability, can be found from Eqs. (A15) and (A11) and Eqs. (A16) and (A12). They are

$$e_{k1}=(1-\Delta/\varphi)[t+\varphi/(\varphi-\Delta)](-t\Delta/\varphi)^{1/2}\ , \qquad (A21)$$

$$e_{k2}=2(\varphi^2-1)\left[\frac{1+t(1-\varphi\Delta)}{3(\varphi^2-1)}\right]^{3/2}\ . \qquad (A22)$$

To determine the electric field e_c where the energy of two states with $q\neq0$ and $q=0$ are equal, it is necessary to solve the following system consisting of two equations of the state and two expressions for the free energies for the two phases

$$\begin{aligned} a&=-\tfrac{1}{4}(t\Delta)^2-\tfrac{1}{2}Q_a^2[1-t(\varphi\Delta-1)]+\tfrac{3}{4}Q^4(\varphi^2-1)\ , \\ e&=Q_a[1-t(\varphi\Delta-1)]+Q_a^3(1-\varphi^2)\ , \\ a&=-\tfrac{1}{2}(1+t)Q_f^2-\tfrac{3}{4}Q_f^4\ , \\ e&=(1+t)Q_f+Q_f^3\ , \end{aligned} \qquad (A23)$$

where Q_a and Q_f are the equilibrium values of order parameter Q in the phase with $q\neq0$, and in that with $q=0$, respectively.

In the case of the first-order phase transition this system has a solution with $Q_f\neq Q_a$, this solution determines the critical field e_c. The $e_c(t)$ dependence has been found by numerical calculations.

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