SOVIET PHYSICS JETP VOLUME 27, NUMBER 5 NOVEMBER 1968

DYNAMIC POLARIZATION AND LOSSES IN FERROELECTRIC SUBSTANCES

V. V. DEM'YANOV and S. P. SOLOV'EV

Submitted December 20, 1967

Zh. Eksp. Teor. Fiz. 54, 1542–1553 (May, 1968)

A model of dynamic polarization and of the losses related to it in ferroelectric substances is analyzed on the basis of certain assumptions regarding the distribution of the internal field within the domain boundary, and also regarding the oscillations of the domain volume in an external field. A solution of the domain-volume oscillation equation is obtained. The dispersion relations for the dielectric spectrum and absorption spectrum of the ferroelectric substance, which follow from the solution and from the underlying model concepts, are also derived. Formulas for the resonance frequency of the domains and for the frequency of the loss maximum, which determine the dispersion boundary of ε', are deduced; they are in satisfactory agreement with the experiments. Some regularities of the reversal of polarization of ferroelectrics are described qualitatively and quantitatively on the basis of the volume model.

1. INTRODUCTION

In spite of the large number of proposed models,[1-5] the nature of many experimentally observed regularities in the polarization of ferroelectrics and the accompanying losses in the frequency region below infrared dispersion still remains unclear. The most consistent mechanism, which accounts for a large number of experimental polarization effects, is the one borrowed from the theory of dynamic magnetization[6] and based on the formalism of the domain-wall motion (DMW).[1, 7] However, the estimates obtained in [1, 5, 7] on the basis of the mechanism of motion of plane domain wall-oscillators are insufficiently convincing (see the table below), because the equation used in these papers, of the form (η is defined below following formula (5))

$$M_{\rm eff}\, d^2X/dt^2 + R\,dX/dt + F'X = F''/\eta \tag{1}$$

did not take correct account of the influence of the polarized state in the volume of the domain on the dynamics of the transition regions. This was manifest in the fact that the coefficients $M_{\rm eff}$, R, F′, and F″ were normalized to unit surface of the domain boundary, as a result of which the dependence of the resonance frequency f_0 on the average domain dimension d was obtained in the form $f_0 \backsim 1/\sqrt{d}$. However, it is more natural physically to consider the polarization of the ferroelectric due to the DWM as a consequence of the change of the volume of the domains in the external field. In this case, when solving Eq. (1), its coefficients are normalized to the corresponding volume, leading to a dependence $f_0 \backsim 1/d$, which agrees with the theory of the linear classical oscillator and with the experimental data[8-11].

An analogous $f_0 \backsim 1/d$ dependence, which Devonshire[2] used as a basis of a qualitative explanation of the microwave dispersion of ε', was introduced by him on the basis of thermodynamic calculations that agreed with the observed fact that the sample had different susceptibilities in the "free" and "clamped" states; this difference was regarded as the property of homogeneous crystals. However, recently obtained data[11] can be interpreted only by assuming that the indicated difference is due to the natural inhomogeneity of the real "single-domain" single-crystal samples, and that the really homogeneous section of the crystal should not have the clamping property. Nonetheless, as will be shown theoretically below, the piezoactivity of single-domain formation plays an important role in the explanation of the microwave dispersion in ferroelectrics (an experimental proof is given in [11]).

The model of local minima,[3] proposed for an explanation of the processes of polarization and polarization reversal of $BaTiO_3$, is also insufficiently well founded, starting with its initial premises of local minima. This model ignores completely the role of the domain structure. It follows from it also the possibility of a jumplike reversal of polarization of a homogeneous crystal as a whole, a fact contradicting the experimental data. Furthermore, the possibility of the Ti ions jumping over inside the entire homogeneous crystal as a result of thermal fluctuations is doubtful, owing to the presence in the crystal of large internal electric fields[12-14] and of their gradients.[15]

An essential shortcoming of all the foregoing models is the absence of a general approach to the problem of polarization (weak fields) and polarization reversal (strong fields) of the ferroelectrics even within the framework of a single mechanism.

The present paper is devoted to the development of concepts of polarization and the accompanying losses on the basis of a model, with the aid of which it is possible to obtain a satisfactory explanation of many observed regularities and to understand in part their physical nature.

2. INTERNAL FIELD WITHIN THE LIMITS OF THE DOMAIN BOUNDARY AND NATURE OF THE DISPLACEMENT POLARIZATION

As is well known, the spontaneously polarized state in ferroelectrics is characterized by large internal fields ($\sim 10^8$ V/cm), acting on the ions which have been displaced from the equilibrium positions occupied by them in the crystal lattice above the Curie point. In the case of ferroelectrics of the $BaTiO_3$ type, for a homogeneous unbounded crystal, a reasonable value of the spontaneous polarization is obtained by taking into account the ordered arrangement of the dipole moments, produced by the displaced point charges, on which are superimposed pointlike dipole moments due to the polarization of the electron shells of the ions in the effective field of the given ion.[12-14]

If these considerations are applied to a ferroelectric "ionic" crystal broken up into 180° domains, assuming the latter likewise to be unbounded, then the distribution of the internal field acting on the ions of type i along the x axis perpendicular to the domain boundary can be represented in the form

$$E^i(x) = E_s{}^i(x) + E^i_{\text{ind}}, \tag{2}$$

where $E^i_s(x)$ and E^i_{ind} are the fields due to the spontaneous polarization P_s and the polarization P_{ind} induced by the external field E_0.

As is well known[12-14], when $E_0 = 0$ we have inside the domain

$$E_s{}^i = \sum_k \left(\frac{4\pi}{3} + C_{ik}\right) p_s{}^k = \xi_i P_s, \qquad \xi_i = \sum_k \zeta_k \left(\frac{4\pi}{3} + C_{ik}\right),$$

where C_{ik}—structure sums, $p^k_s/V_c = \zeta_k P_s = P^k_s$—contribution of the ions of type k to P_s, and V_c—volume of the unit cell. According to [16], the distribution of the polarization inside the domain boundary with thickness is $P_z(x) = P_s \tanh(x/\delta)$. It is obvious that an analogous functional dependence, i.e., $E^i_s(x) = E^i_s \times \tanh(x/\delta_1)$, where $\delta_1 \approx \delta$, will determine the change of the internal field within the limits of the boundary. It is easy to verify, furthermore, that when $E_0 = 0$ it is possible to separate inside the boundary a plane within which $E^i_s = 0$, and consequently, the ions located there are electrically "free" along the z axis, unlike the analogous ions inside the domains. In fact it is possible to regard as "free" all the ions in a layer of thickness δ_{eff}, within which the energy of the internal electric field is of the order of the energy of the thermal motion of the ions, and which we shall call henceforth the domain wall.

In the presence of an external field, which induces in the entire crystal an additional polarization $P_{\text{ind}} = \Sigma p^k_{\text{ind}}$, the corresponding internal field is

$$\begin{aligned} E^i_{\text{ind}} &= E_0 + \sum_k \left(\frac{4\pi}{3} + C_{ik}\right) p^k_{\text{ind}} \\ &= E_0 + \xi_i P_{\text{ind}}, \end{aligned}$$

and in the general case

$$E^i = E + \xi_i P. \tag{3}$$

Thus, the superposition of an external field along the z axis (Fig. 1), should lead to a displacement (if such displacements are not forbidden by crystalchemical factors) of the initially "free" ions inside the wall in the direction of the action of E_0 in the region of an ever increasing internal field, and in final analysis inside a favorably oriented domain, when the displacement reaches the limiting value $Z^i = Z^i_s$ obtained from structure data. During the course of this process, ions of an unfavorably oriented domain become gradually "free" and fall inside the wall, and the initial profile of the distribution of the polarization and of the local field inside the boundary shifts by an amount X parallel to itself (wall displacement) along the x axis, which is perpendicular to the field E_0. We shall henceforth relate the contribution to the susceptibility κ_{dis} and to the dynamic polarization, which we shall call the displacement polarization P_{dis}, with the relative "freedom" of the displacement of the ions inside the wall along the z axis. At the same time, the reversal of the polarization of the unit cell inside the wall, which is realized by the directional motion of the ions, will lead to the appearance of a dynamic electric conductivity of the crystal, with which we shall relate the losses in the polarization of the ferroelectrics.

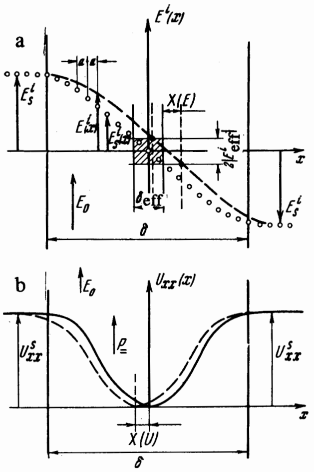

FIG. 1. Distribution of the spontaneous polarization and of the internal field (a) and of the deformation within the limits of a 180° domain boundary.

On the basis of the statistical theory of charge transport (see, for example, [17], we connect the average velocity of displacement of the ions inside the wall with the local field E^i acting on them by the relation

$$v_i = dZ^i/dt = \mu_i E^i, \tag{4}$$

where μ_i is the mobility of the ions in the wall along the z axis. If V_δ is the part of the volume V of the crystal occupied by all the walls, then the effective concentration of the quasi-free carriers

$$n_{\text{eff}} = nV_\delta/V, \quad n = V_a{}^{-1} \tag{5}$$

will determine the density of the dynamic current in the crystal $j = q_i n_{\text{eff}} v_i$ and, consequently, the losses in the ferroelectrics, connected with the polarization of the displacement. Here $V_\delta = \eta V \delta_{\text{eff}}/d$; q_i—effective charge of the quasi-free ions, and η—a coefficient that assumes values from 1 to 3, depending on the form of the domains and the number of walls per domain in the crystal.

The mobility of the quasi-free ions inside the wall, which enters in Eq. (4) can be calculated under the assumption that, owing to crystal-chemical considerations, the effective length of the "free" path of the ion cannot be larger than the spontaneous displacement Z^i_s of the charges, obtained from structure data (concerning the magnitude of the displacements see, for example, [18]). Under these conditions, assuming that $\frac{1}{2} m_i (v^i_z/dt)^2 \approx kT$ when $Z^i = Z^i_s$ we can determine the effective time of "free" path:

$$\tau_f = 2Z_s{}^i\sqrt{m_i/kT}. \tag{6}$$

This quantity, according to [17], determines the mobility of the ions inside the wall:

$$\mu_i = \frac{q_i \tau_f}{m_i} = \frac{2q_i Z_s{}^i}{\sqrt{m_i kT}}, \tag{7}$$

where m_i is the effective mass of the displaced ions.

3. CONTRIBUTION OF THE DISPLACEMENT POLARIZATION TO THE DYNAMIC SUSCEPTIBILITY OF FERROELECTRICS

In connection with the fact that at temperatures below the Curie point the ion potential-energy curve obtained from the thermodynamic theory[2] has two minima separated by a barrier, it is of interest to estimate the magnitude of the threshold effect predicted in this manner for the excitation of P_{dis}, as applied to the model considered here. According to this model, the possibility of overcoming the potential barrier is realized not in the entire volume, but only in transition regions between oppositely polarized sections of the crystal. To this end, we measured ε' for single-crystal and polycrystalline $BaTiO_3$ at frequencies 460 kHz and 5 MHz in weak fields from zero to 10 V/cm. The measurement was performed with a laboratory setup containing a measuring receiver of sensitivity < 1 μV, at the input of which was installed a carefully screened tank circuit made up of a high-Q inductance coil and a capacitor incorporating the sample of the investigated $BaTiO_3$.

When ε' was measured by the method of substituting a standard capacitor for the sample capacitance, in measuring fields E_0 from 10 V/cm to zero, ε' remained constant within 10–15%. In a zero measuring field, the indication was by means of the "signal" of the intrinsic noise of the tank circuit. The results of such measurements give grounds for assuming that at room temperature the thermal vibrations of the atoms (noise) of the crystal lattice of the ferroelectric provide full excitation of the displacement polarization ($Z^i = Z_s^i$).

On the basis of these data, let us calculate the effective local field E_{eff}^i (Fig. 1), the action of which on the ions inside the wall causes a complete excitation of the displacement polarization P_{dis}^i, as a result of the displacement of ions of type i along the z axis through the maximum possible amount Z_s^i. Recognizing that $\frac{1}{2} m_i (dZ^i/dt)^2 = q_i Z_s^i E_{eff}^i$ when $Z^i = Z_s^i$, we can obtain the field that determines the height of the potential barrier inside the wall:

$$E_{eff}^i = 2q_i Z_s{}^i / m_i \mu_i^2. \tag{8}$$

The action of this field is equivalent to applying to the electrodes an external field $E_{eff} = E/\kappa \xi_i$.

It is obvious that in our case

$$P_{dis}{}^i = n_{eff}\,(q_i Z^i + \alpha_i E^i) = P_s V_\delta Z^i / V Z_s{}^i, \tag{9}$$

where P_s^i is the contribution of the ions of type i to the spontaneous polarization, and α_i is their electronic polarizability. On the other hand, if the field $E = E_0 + E_{eff}$ induces in the ferroelectric the indicated polarization $P_{dis}^i(E)$, then

$$\varkappa_{dis}{}^i = \theta P_{dis}{}^i(E) / E, \tag{10}$$

where θ is the coefficient that takes into account the orientation of the c axes of the domains. Substituting in (10) the relations (5) and (9), we obtain the expression

$$\varkappa_{dis}{}^i = \theta\eta P_s{}^i \delta_{eff} Z^i / E Z_s{}^i d, \tag{11}$$

which, with allowance for (7) and (8) (for $\kappa \gg 1$) can be readily transformed to a form that is convenient for practical use ($E_0 \ll E_{eff}$)

$$\varkappa_{dis}{}^i = \frac{P_s{}^i \xi_i \theta \eta m_i \varkappa \delta_{eff} \mu_i^2}{2q_i Z_s{}^i d}. \qquad \varkappa = \varkappa_0 + \sum_i \varkappa_{dis}{}^i, \tag{12}$$

where κ is the total small-signal susceptibility of the crystal and κ_0 is the susceptibility of the multi-domain crystal without allowance for the contribution of the domain boundaries.

4. VELOCITY OF DOMAIN BOUNDARIES

Inasmuch as the motion of the domain boundaries is based on the mechanism described above, of the displacement of the ions inside the wall, Eq. (4) can be expressed in terms of the dynamic parameters of the boundary:

$$v_\delta = dX / dt = \mu_\delta E^i, \tag{13}$$

where $v_\delta = v_i X/Z^i$ is the velocity and $\mu_\delta = \mu_i X/Z^i$ is the mobility of the wall, and for estimates it is reasonable to restrict the ratio X/Z^i to the range

$$a / Z_s{}^i < X / Z^i \leqslant \delta_{eff} / Z_s{}^i \tag{14}$$

(a—lattice period). Expression (13) is important for a comparison of the conclusions of the here-developed microscopic model of polarization with the results of experimental investigations, which are usually based on a direct observation of the motion of the domain boundaries. As follows from (8), the displacement of the domain boundaries due to the directional motion of the quasifree ions inside the wall is possible only in the case when $E_{ind}^i \geq E_{eff}^i$, and therefore the field E_{eff}^i referred to the external electrodes of the crystal plays the role of the coercive field

$$E_c = 2q_i \delta_{eff}^2 / \xi_i Z_s{}^i m_i \varkappa \mu_\delta^2. \tag{15}$$

In this connection, great interest attaches to a derivation of a theoretical relation between the wall velocity v_δ and the external field E_0. If $E_0 \gg E_c$, then the field $E_{ind}^i \gg E_{eff}^i$ inside the wall causes a drift of the quasi-free ions within the limits $\pm Z_s^i$, and in this case it can be assumed (see (2) and Fig. 1) that $\delta_{eff}(E^i) \backsim E_{ind}^i$. Recognizing that the drift of the quasi-free ions is determined by the ion-phonon interaction between the ions and the crystal lattice, we can employ in this situation the "hot electron" approximation (see, for example [17]), which in our case can be called the "hot ion" approximation. Then, the well known relation in the form $\mu_i \backsim T_i^{-1/2} T_L^{-1}$,[17] where T_L and T_i are respectively the temperatures of the lattice and of the quasi-free ions (this approximation $(T_i E^i) \backsim (E_{ind}^i + E_{cr}^i)$; $T_L(E^i) = \text{const}$, whence $T_i > T_L$) yields $\mu_i(E^i) \backsim (E_{ind}^i)^{-1/2}$ (E_{cr}^i is defined later). As a result we get from (3), (4), (7), and (13) the relation $v_\delta(E_0) \backsim E_0^{3/2}$, which was established experimentally earlier.[18]

When $E_0 < E_c$, the internal field $E^i_{ind} < E^i_{eff}$ and cannot influence directly the drift of the quasi-free ions, which is determined under these conditions by the probability distribution $\exp(-m_i v_i^2/2kT_i)$ of the instantaneous values of their velocity. This distribution yields, when (8) and (14) are taken into account, the relation $v_\delta(E^i) \propto \exp(-\beta E^i_{eff}/E^i_{ind})$, where β is a certain coefficient, which is equivalent to the relation $v_\delta(E_0) \propto \exp(-\beta E_c/E_0)$, if we introduce the values of the macroscopic field in place of the internal field. This dependence, which was obtained[19] also on the basis of the probability distribution of the dimensions of the nuclei of domains requiring different activation energy, agrees well with the experimental data.[18]

Thus, besides defining more concretely the concept of the coercive field (the condition $E^i_{ind} \approx E^i_{eff}$), the foregoing considerations allow us, first, to understand the absence of a threshold field for the switching-over of ferroelectrics up to values $E_0 = E_{cr} \leq 0.1-1$ V/cm, which is equivalent to fields $E^i_{ind} = E^i_{cr} \leq 100-1{,}000$ V/cm for semiconductors,[17] at which the condition $T_i \approx T_L$ is established, and, second, uncover possibilities of determining the ion–phonon interaction from ferroelectric singularities.

5. TWO DISPERSION MECHANISMS

Connection between the displacement polarization and the deformations in a crystal. We consider an individual domain surrounded by similar domains with opposite polarization and having a crystallographic axis c oriented along the coordinate axis z perpendicular to the electrodes of the sample. The cross section of the domain can be regarded, without loss of generality of the conclusions, as rectangular, since such a configuration has been observed in a number of investigations.[18] In a weak external field, the volume V of a favorably oriented domain increases by ΔV as a result of the transverse displacement of its boundaries, induced by the drift of the quasi-free ions (Fig. 2a), so that the polarization of the crystal changes $P_{dis} = P_s \Delta V/V$. It follows from Fig. 2 that when $X \ll d_x$, $Y \ll d_y$, and $z = 0$, and also from the assumed isotropy of the crystal in the xy plane ($X = Y$, $d_x = d_y = d$), the relative change of the volume $\Delta V/V = \eta X/d_x$ is mathematically equivalent to an effective displacement of one domain boundary by an amount ηX, and then we have

$$\varkappa_{dis} = P_s \theta\eta X(E)\,/\,Ed. \qquad (16)$$

The phenomenologically obtained expression (16) coincides with formula (11) derived on a microscopic basis, provided we calculate in the latter the contributions κ^i_{dis} from all the ions inside the wall, and then change over from the displacements Z^i to X with the aid of the condition (14).

If the components of the crystal deformation tensor are connected in the general case with its polarization by the relations $U_{ij} = C_i P_j^m$ then, in accordance with Fig. 1a and with the conditions stipulated for the distribution $P_s(x)$ assumed by us, we can find the distribution $U_{xx}(x)$ in the form shown in Fig. 1b, i.e., $U_{xx}(x) = U^s_{xx}\,|\tanh^m(x/\delta)$, where U^s_{xx} is the spontaneous deformation of the cell along the x axis inside the domain.

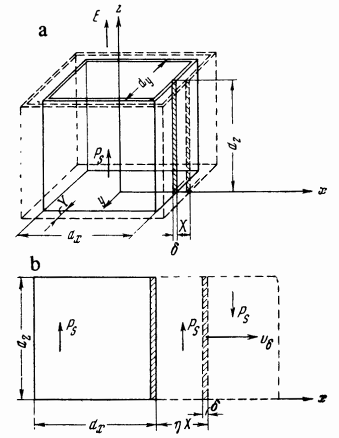

FIG. 2. Diagram showing displacement of the main boundaries (8) and equivalent one-dimensional diagram of displacement of the domain volume (b) (not to scale).

If a multidomain crystal is polarized by a field $E_=$, then we can write for the susceptibility κ_{dis} in a weak measuring field $E_0 = E_0' e^{i\omega t}$ (with $E_0' \ll E_=$, $E_0' \ll E_{eff}$), without allowance for the deformations of the crystal,

$$\varkappa_{dis}(E) = \frac{P_s\theta\eta X(E)}{d(E_{eff} + E_=)}. \qquad (17)$$

At the same time, the deformations $(U_= + U_0' e^{i\omega t})$ connected with the polarization $(P_+ + P'_{ind} e^{i\omega t})$ induced by the field $(E_= + E_0')$ cause an additional displacement of the boundaries ($X(U)e^{i\omega t}$ on Fig. 1b), which coincides in phase with the displacement X(E) at frequencies much smaller than the resonant frequency of the crystal. In the case considered here, that of weak perturbations ($U_0' \ll U_=$, $U_0' \ll U'_{xx}$), we determine from the conditions

$$U_= + U_0 = C_x(P_= + P_{ind})^m, \qquad U_{xx}{}^s(x/\delta)^m = mC_x P_=^{m-1}\; P_{ind}$$

the additional displacement

$$X(U) = \frac{\delta}{P_s}[mE_=^{m-1}\;(E_= + E_{cl}\;)\varkappa^m]^{1/m},$$

substitution of which in (16) yields for $(\theta\eta \approx 1)$

$$\varkappa_{dis}(U) = \varkappa_{cl}\;\frac{\delta\sqrt{t}/d}{(1-\delta\sqrt{t}/d)} \qquad (18)$$

where $t = 2E_=/(E_= + E_{eff})$ and we put $m = 2$.[18] With the aid of (12), (17), and (18) we can calculate the susceptibility of the crystal in the "free" and "clamped" states:

$$\varkappa_{fr} = \varkappa_0 + \varkappa_{dis}(E) + \varkappa_{dis}(U), \qquad \varkappa_{cl}\;= \varkappa_0 + \varkappa_{dis}(E). \qquad (19)$$

We conclude from (18) that for physically observable domain dimensions ($d \gg \delta$) the contribution $\kappa_{dis}(U)$ induced by the deformation is found to be vanishingly small compared with $\kappa_{dis}(E)$, whereas the experimental data and thermodynamic calculation[2] lead to a ratio $\kappa_{fr}/\kappa_{cl} \approx 1-4$, which offers evidence of appreciable role of $\kappa_{dis}(U)$. However, the contribution $\kappa_{dis}(U)$ turns out to be actually appreciable if we postulate the presence of a natural inhomogeneity of the domains, and assume that they actually consist of smaller regions in which the polarization distribution is qualitatively analogous to that shown in Fig. 1. This assumption, which is favored, in particular, by certain results of [11, 20] per-

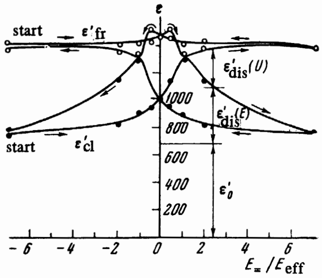

FIG. 3. Reversive ε′(E) plots for polycrystalline BaTiO$_3$: solid curves – calculated in accordance with formulas (19); points – experimental data. The value of ϵ'_0 was taken from measurements of ε′(ω) at microwave frequencies.

mits not only to explain the difference between κ_{fr} and κ_{cl} from the point of view of the role of κ_{dis}(U), but also to understand the nature of the susceptibility along the a axis of the crystal, as well as the role of these regions as nuclei for domains during the reversal of polarization processes.

A discussion of the nature of the indicated regions is beyond the scope of the present article, so that we confine ourselves to general conclusions concerning the contribution to κ_{dis}(U). Estimates show that in BaTiO$_3$ the dimension of these regions is d ~ 2δ ~ 10^{-6}–10^{-5} cm. As follows from Fig. 3, the expressions (17)–(19) describe satisfactorily the experimental relations $\kappa(E_=)$ for ceramic BaTiO$_3$ at d ≈ 2.8δ.

Thus, it seems quite probable that there exist two mechanisms causing the contribution to the displacement susceptibility and responsible for the microwave dispersion of ε′ in ferroelectrics. The first mechanism is connected with the exclusion of the contribution induced by elastic deformations in an unpolarized sample at resonant frequencies (the formula for the calculation of these frequencies is given in [11]) of domains and of polarized or single-domain crystallites. If the sample is polarized, then there appears also a resonant dispersion of κ_{dis}(U, ω) in the region of the frequencies of the free oscillations of the crystal as a whole. Estimating the characteristic frequency ω_r by means of formula (26) (see in the table below for d ~ 10^{-5}–10^{-6} cm), we get ω ~ 10^{13} sec^{-1}. Consequently, the quality factor of the oscillations of the single-domain crystallites with dimensions 10^{-3}–10 ^{5} 10^{-5} cm turns out to be Q = ω_r/ω_0 ≈ 50–10,000, and for single-domain samples with dimension ~1 mm we get Q ~ 10^6. The foregoing estimates are very important also for the understanding of the conditions that determine the Q of a ferroelectric piezoresonator.

Dynamics of domain boundaries. Besides the influence of elastic deformations, it is necessary to take into account another mechanism connected with the high mobility and polarizability of the domain boundaries, the contribution from which is excluded at the resonant frequencies of low-Q domains (see the estimates below). It is possible to understand the influence of that part of the crystal volume which is occupied by the walls on the inertia of the polarization processes only from the point of view of the connection with the entire volume of the ferroelectric. This connection is established when account is taken of the long-range order (the ordered state inside the volume of the domains), which determines the elastic forces that maintain the quasi-free ions in the equilibrium state (in the final analysis, their resonant frequency), and consequently, determine the main laws governing the dynamics of the domain boundaries.

We shall describe the motion of the quasi-free ions inside the wall by the usual equation

$$m_{\text{eff}}\, d^2Z^i / dt^2 + r dZ^i / dt + f'Z^i = f'' \qquad (20)$$

The coefficients of which are normalized to unit volume of the crystal. In this equation, the effective mass is $m_{eff} = m_i/V_c$.

The reduced force f″ can be calculated from the condition that each quasi-free ion in the wall is acted upon by an internal field E^i_{ind}, induced by the external field E_0, where the force $f_z = q_i E^i_{ind}$, which causes a change of the polarization in the crystal. Inasmuch as in the effective volume of the wall there are ~$d^2\delta_{eff}n$ ions, we get

$$f'' = Q_{\text{eff}} E^i_{\text{ind}}, \qquad (21)$$

where $Q_{eff} \approx \delta_{eff}P^i_s/Z^i_s d$ is the effective charge of the quasi-free carriers per unit volume.

The elastic force is determined from Eq. (20) for the static case under the assumption that the induced displacement of the ions Z^i is known, say from (11), on the basis of other known parameters of the crystal. In such a representation, we obtain from the equation $f'Z^i = f''$, with allowance for (3) and (21),

$$f' = (P_s{}^i)^2 \xi_i \theta \eta \delta^2_{\text{eff}}\, \varkappa / [(Z_s{}^i)^2 d^2 \varkappa_{\text{dis}}{}^i]. \qquad (22)$$

The dissipative factor r, which determines the character of the dielectric spectrum due to the motion of the quasi-free ions, can be calculated from Eq. (20) under the assumption that r does not depend on the elastic forces f′. In this case we can assume when $\omega \ll \omega_0$ that $m_{eff}d^2Z^i/dt^2 = 0$, so that from the equation rdZ^i/dt

Theoretical and experimental values of the damping frequency, width of the absorption spectrum, and displacement susceptibility for BaTiO$_3$

d, cm	f_r, Hz, from formula (26)	f^*_{max}, Hz, experiment [11]	$\Delta f = f_0^2/f_r$, Hz		Contribution of $\kappa_{dis} \approx 9\kappa^{Ti}_{dis}$	
			Calculation**	Experiment [5]	Calculation from (12)**	Experiment [°]
10^{-6}	10^{12}—$5\cdot10^{12}$	—	—	—	500—2000	
10^{-5}	10^{11}—$5\cdot10^{11}$	$>1,5\cdot10^{10}$	$\sim10^{10}$	$>5\cdot10^{9}$	50—200	~ 50
10^{-4}	10^{10}—$5\cdot10^{10}$	$\sim10^{10}$	$\sim10^{9}$	$\sim10^{9}$	5—20	2÷10
10^{-3}	10^{9}—$5\cdot10^{9}$	$\sim5\cdot10^{9}$	$\sim10^{8}$		0,5—2	
10^{-2}	10^{8}—$5\cdot10^{8}$		—		0,05—0,2	

*Frequency corresponding to the maximum of tan δ (f_{max} ~ $2f_0$).

**Calculation under the assumption that the entire crystal consists of oscillators of identical size.

***Estimates based on the depth of the microwave dispersion (see [11]).

= f″ we obtain, with allowance for (3), (4), and (21),

$$r = \delta_{\text{eff}} P_s{}^i / Z_s{}^i d\mu_i. \tag{23}$$

The solution of (20) is well known and makes it possible to write the dispersion relation for the dielectric constant of the ferroelectric, up to frequencies of infrared dispersion, in the form

$$\varepsilon(\omega) = \sum_j \left\{ \varepsilon_0' + \varepsilon_{\text{dis}}{}^j N(d_j)[1 - \omega^2/\omega_{0j}{}^2 + i\omega/\omega_{rj}]^{-1} \right\}, \tag{24}$$

where $\varepsilon_0' = \varepsilon_c$ is the value of ε along the c axis (if the 90° boundaries vary together with the 180° boundaries, then $\varepsilon_0 = \varepsilon_{ac}$); $N(d_j)$ is a certain function describing the distribution of the domain dimensions d_j;

$$\omega_{0j} = \left(\frac{f'}{m_{\text{eff}}} \right)^{1/2} = \frac{P_s{}^i \delta_{\text{eff}}}{d_j Z_s{}^i} \cdot \left(\frac{\varkappa \theta \eta \xi_i}{\varkappa_{\text{dis}}{}^i m_{\text{eff}}} \right)^{1/2} \tag{25}$$

is the resonant frequency of the domain;

$$\omega_{rj} = f' / r = P_s{}^i \xi_i \theta \eta \varkappa \mu_\delta / d_j \varkappa_{\text{dis}}{}^i \tag{26}$$

is the damping frequency, which makes it possible to estimate the losses with the aid of the expression for the absorption of spectrum in the form

$$\operatorname{tg} \delta(\omega) = \sum_j \frac{\omega}{\omega_{rj}} \left\{ \frac{\varepsilon_0'}{\varepsilon_{\text{dis}}{}^j N(d_j)} \left[\left(1 - \frac{\omega^2}{\omega_{0j}{}^2} \right)^2 + \frac{\omega^2}{\omega_{rj}{}^2} \right] + 1 - \frac{\omega^2}{\omega_{0j}{}^2} \right\}^{-1}. \tag{27}$$

6. QUANTITATIVE ESTIMATES FOR BaTiO$_3$

If we take into account the small electronic polarizability of the Ti ions, as a result of which we can regard them as point charges,[15] and also the presence of crystal-chemical possibilities of their displacement in the crystal lattice of BaTiO$_3$, then, for the sake of simplicity, we can regard as quasi-free only the Ti ions and assume, as discussed earlier, that they are "ferroelectrically active" with respect to the displacements of other ions. We shall use for BaTiO$_3$ constants obtained experimentally or calculated on the basis of experimental data:[18] $m_{\text{Ti}} = 8 \times 10^{-23}$ g, $n = (4 \times 10^{-8})^{-3}$ cm^{-3}, $U_{xx}'^{S} = 2 \times 10^{-3}$, $q_{\text{Ti}} = (1-4)e$. For the case when $Z_s^{\text{Ti}} = 0.14$ Å ($Z_s^0 = 0$), a calculation similar to that given in [21] yields $P_s^{\text{Ti}} = 0.3\ T_s = 2.6 \times 10^4$ cgs esu; $\xi_{\text{Ti}} \approx 20$.

From a comparison of the value of μ_i calculated by formula (7) with the value $\mu_\delta = \mu_i \delta_{\text{eff}} / Z_s^i$ calculated from known data on the $v_\delta(E_0)$ dependence (see [18]) for the case $E_0 \geq E_c$, we can obtain

$$\delta_{\text{eff}} = v_\delta Z_s{}^i \Big/ \left[\mu_i E_0 \xi_i \varkappa \left(\frac{E_{\text{cr}}}{E_{\text{cr}} + E_0} \right)^{1/2} \right].$$

The corresponding estimates give $\mu_{\text{Ti}} = (0.5-1) \times 10^{-2}$ cm^2/V-sec, $\delta_{\text{eff}} = (0.5-1) \times 10^{-7}$ cm, where we have assumed $E_0 = 2$ kV/cm, $E_{\text{cr}} = 0.3$ V/cm, and $v_\delta = 100$ cm/sec. From the condition $\partial E_s^i(x)/\partial x = E_{\text{eff}}^i / \delta_{\text{eff}}$, which admits of a successive inversion of the spontaneous moments of the unit cells in the moving boundary, we obtain from the formula $\delta = E_s^i a m_i \mu_i^2 / 2 q_i Z_s^i$, for BaTiO$_3$, $\delta = 10^{-6}-10^{-5}$ cm. Substituting further in (15) the values of the free susceptibility $\kappa_{\text{fr}} \approx 300$ and the susceptibility along the c axis $\kappa_c \approx 15$, we calculate correspondingly the coercive field $E_c = 0.4-2.5$ kV/cm and the field of the single-domain crystal $E_{\text{sd}} = 8-50$ kV/cm, and for the ceramic—the value $E_c = 1-8$ kV/cm at $\kappa_{\text{fr}} \approx 100-150$.

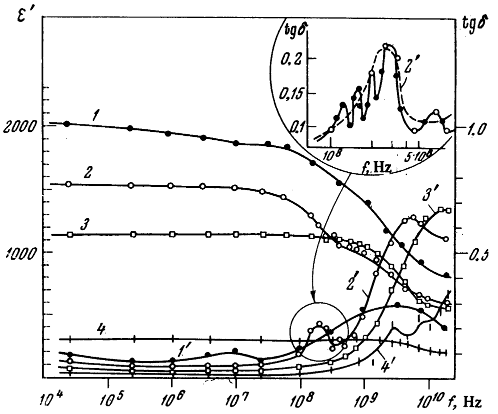

FIG. 4. Frequency dependences of ϵ' (curves 1 – 4) and of tan δ (curves 1′ – 4′) of single-crystal and polycrystalline BaTiO$_3$: 1, 1′ – multidomain single crystal; 2, 2′ – polycrystals with crystal grain dimension $d_k = 20 - 200\ \mu$; 3, 3′ – $d_k \leqslant 10\ \mu$; 4, 4 – $d_k < 1\ \mu$. The fine structure of the tan δ (ω), which offers evidence of a resonant nature of the dielectric spectrum of BaTiO$_3$, is shown separately.

In spite of the paradoxical character of the estimate of δ, the model considered here explains also how an ordering, characterized by an electric-interaction energy $E_s^i q_i Z_s^i \gg kT_C$, can be generated "jumpwise" at the Curie temperature T_C. Inasmuch as $E_{\text{eff}}^i Z_s^i q_i \approx kT_C$ only within a broad boundary, it is natural to assume that the occurrence of ordering is connected with the creation at $T > T_C$ of regions with a compensated electric moment. At $T \approx T_C$ there apparently grow from these regions two domains, separated by a "fresh" 180° boundary. Our calculation of the stable width of the 180° boundary (based on the minimum of its energy) yields $\delta_{\min} \approx (1.5-2)a$ (see also [18]), which should denote the presence of a tendency towards "aging" of the boundary; this tendency has a direct bearing on the aging of ferroelectrics, during the course of which $\delta \to \delta_{\min}$, we get $\delta_{\text{eff}} \leq a$, the quasi-free ions cease to be free, and the boundaries lose their mobility. As the physical mechanism that decreases the width of the produced domain boundary, we can consider the finite probability of in-phase displacement of all its peripheral ions under the influence of low-frequency oscillations of the crystal lattice (see also [5, 19]).

Estimates of the average frequency $f_0 = \omega_0/2\pi$ of the dispersion of ε' in accordance with a formula analogous to (25) for BaTiO$_3$ together with similar calculations in

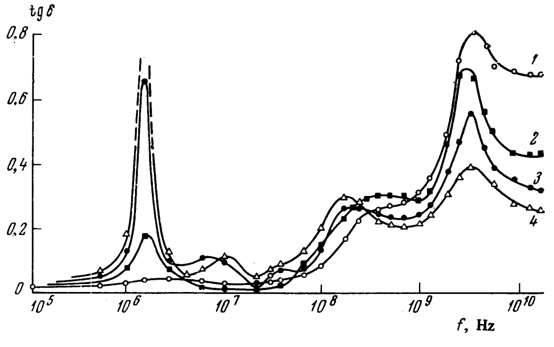

FIG. 5. Frequency dependence of tan δ of large-grain polycrystalline BaTiO$_3$ at $E_= = 0$ (1), $E_= = 4$ kV/cm (2), $E_= = 8$ kV/cm (3), and $E_= = 16$ kV/cm (4).

accordance with the formulas,[1,7] are given in [11]. The tables present estimates of the damping frequencies $f_r = \omega_r/2\pi$ in accordance with formula (26), which indicates the resonant character of the oscillations of the domains with Q equal to 3–10, as is also confirmed experimentally—see Fig. 4, curve 2′. The presence of two sections of dispersion of ε' on the curves 2 and 2′, one of which (in the region 10^9–10^{10} Hz) does not shift when a constant field is applied, is apparently connected with the dispersion due to the contribution of the crystallites $\kappa_{\text{dis}}(U)$, and the other section at frequencies $\le 10^9$ shifts upon application of a constant field towards lower frequencies, and is apparently connected with the DWM (see Fig. 5 and [11]).

---

[1] C. Kittel, Phys. Rev. **83**, 458 (1951).

[2] A. F. Devonshire, Phil. Mag. **40**, 1040 (1949); **42**, 1065 (1951).

[3] W. P. Mason and B. T. Matthias, Phys. Rev. **74**, 1622 (1948).

[4] Yu. M. Poplavko, Izv. AN SSSR ser. fiz. **29**, 2020 (1965).

[5] R. E. Nettleton, J. Phys. Soc. Japan **21**, 1633 (1966).

[6] W. Doring, Z. Naturforsch. **3a**, 373 (1948).

[7] D. G. Sannikov, Zh. Eksp. Teor. Fiz. 41, 133 (1961) [Sov. Phys.-JETP **14**, 98 (1962)].

[8] J. G. Powles and W. Jackson, Proc. IEE **96**, 383 (1949).

[9] S. Ikegami, J. Phys. Soc. Japan **18**, 1203 (1963).

[10] V. V. Dem'yanov and S. P. Solov'ev, Izv. AN SSSR ser. fiz. **31**, 1874 (1967).

[11] V. V. Dem'yanov and S. P. Solov'ev, Zh. Eksp. Teor. Fiz. **53**, 1858 (1967) [Sov. Phys.-JETP **26**, 1058 (1968)].

[12] G. I. Skanavi, Fizika diėlektrikov [Physics of Dielectrics], Gostekhizdat, 1948.

[13] J. C. Slater, Phys. Rev. **78**, 748 (1950).

[14] Yu. N. Venentsev, V. N. Lyubimov, S. P. Solov'ev, and G. S. Zhdanov, Izv. AN SSSR ser. fiz. **26**, 630 (1964).

[15] V. N. Lyubimov, Yu. N. Venevtsev, and E. Yu. Koiranskaya, Kristallografiya **7**, 949 (1962) [Sov. Phys.-Crystallogr. **7**, 768 (1963)].

[16] V. A. Zhirnov, Zh. Eksp. Teor. Fiz. **35**, 1175 (1958) [Sov. Phys.-JETP **8**, 822 (1959)].

[17] P. R. Aigrain, Electronic Processes in Solids, MIT Press, 1960.

[18] F. Jona and G. Shirane, Ferroelectric Crystals, Pergamon, 1962.

[19] R. C. Miller and G. Weinrich, Phys. Rev. **117**, 1460 (1960).

[20] D. R. Callaby, J. Appl. Phys. **38**, 431 (1967).

[21] Yu. N. Venevtsev, G. S. Zhdanov, S. P. Solov'ev, and Yu. A. Zubov, Kristallografiya **3**, 473 (1958) [Sov. Phys.-Crystallogr. **3**, 471 (1958)].

Translated by J. G. Adashko
178