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DISPERSION IN FERROELECTRICS

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The frequency dependence of the permittivity of a ferroelectric associated with domain wall displacements is considered. Numerical calculations have been made, and are compared with experiment for $BaTiO_3$.

THE motion of domain walls in ferromagnetics under the influence of an external magnetic field has been discussed theoretically in a number of papers.[1-3] Dispersion of the magnetic permeability associated with domain wall motion has been observed experimentally in ferrites (e.g., see [4-5]). The ideas developed for ferromagnetic materials are applied in the present paper to ferroelectrics.

We consider a free boundary separating two ferroelectric regions polarized parallel to the boundary in opposite directions, i.e., to be definite, we consider a single 180-degree boundary. It follows from energy considerations that the wall will be displaced by a uniform external electric field if it has a component parallel to the spontaneous polarization inside the domains. We take this direction as the z axis, and the direction perpendicular to the wall as the x axis. We take as the steady-state solution, i.e., the structure of the stationary wall in the absence of external field, the solution obtained by Zhirnov.[6] A feature of this solution is that the change with x coordinate of the polarization vector P is confined to the P_z component, and $P_y = 0$. If we take the external electric field E along the z axis, the only component of the polarization vector P different from zero will be, as before, P_z, which for brevity we will simply call P.

It is convenient to write the thermodynamic potential of unit volume of a ferroelectric with cubic symmetry in terms of the variables P and u_{ij} (the deformation tensor):

$$\begin{aligned}F = F_0 &+ \tfrac{1}{2}\varkappa\,(\partial P/\partial x)^2 + \alpha P^2 + \tfrac{1}{2}\beta P^4\\ &+ \tfrac{1}{2}c_1\,(u_{xx}^2 + u_{yy}^2 + u_{zz}^2)\\ &+ c_2\,(u_{xx}u_{yy} + u_{xx}u_{zz} + u_{yy}u_{zz})\\ &+ \tfrac{1}{2}c_3\,(u_{xy}^2 + u_{xz}^2 + u_{yz}^2) + q_1 u_{zz}P^2\\ &+ q_2\,(u_{xx} + u_{yy})\,P^2 - PE,\end{aligned} \tag{1}$$

where the energy of anisotropy, the elastic and electrostrictive energies, and the correlation energy associated with the nonuniformity of P are included explicitly.

We write the density of kinetic energy in the form

$$T = \frac{1}{2}\rho\left(\frac{\partial u_i}{\partial t}\right)^2 + \frac{1}{2}\frac{m}{ne^2}\left(\frac{\partial P}{\partial t}\right)^2, \tag{2}$$

where the first term is the energy of elastic oscillations (ρ is the density, and u_i is the displacement vector), and the second term is the energy of the oscillations of the ions (it is assumed[7,8] that the polarization in a ferroelectric is due to the displacement of a definite ion, $P = nez$, where z is the displacement of the ion, e is the effective charge, m is the effective mass, and n is the number of ions in unit volume).

The equations connecting P, u_i, and σ_{ij}, the deformation tensor, are now obtained, following the usual rule, from the Lagrange density $L = T - F$ by allowing variations with respect to P and u_i:

$$\begin{aligned}\frac{m}{ne^2}\frac{\partial^2 P}{\partial t^2} + \frac{m}{ne^2}\omega_r\frac{\partial P}{\partial t} = \varkappa\frac{\partial^2 P}{\partial x^2} - 2\alpha P - 2\beta P^3 - 2q_1 u_{zz}P\\ - 2q_2\,(u_{xx} + u_{yy})\,P + E,\end{aligned} \tag{3}$$

$$\rho\,\partial^2 u_i/\partial t^2 = \partial\sigma_{ij}/\partial x_j, \qquad \sigma_{ij} = \partial F/\partial u_{ij}, \tag{4}$$

where a decay term has been added to the left-hand side of equation (3); ω_r is the frequency of the ion causing the decay. In what follows we will take the field to depend harmonically on the time $E = E_0 \times e^{i\omega t}$.

The longitudinal acoustic wave along the z axis, arising when the field is switched on, decays with time. A solution can, therefore, be sought in the variables x and t. We introduce the dimensionless variable $\xi = (x - X)/\delta$, which is a measure of the distance from the instantaneous center of the wall X(t); $V = dX/dt$ is the velocity of the wall, δ

$= \sqrt{\kappa/(\beta - q_2^2/c_1)P_0^2}$ is a parameter of the wall thickness, and P_0 is the static polarization in the uniform ferroelectric. We also introduce the notation

$$\omega_p^2 = E_0 ne^2/P_0 m, \qquad \omega_q^2 = 4\beta P_0^2 ne^2/m. \tag{5}$$

We seek a solution of the system (3) and (4) in the special form

$$P(x, t) = P^c(\xi) + p(\xi)e^{i\omega t}, \qquad V = ve^{i\omega t},$$
$$u_i(x, t) = u_i^c(\xi) + u_i(\xi)e^{i\omega t}, \tag{6}$$

where the field P_0 is considered to be sufficiently small [see inequality (10) below] so that it is possible to use perturbation theory with respect to p and u_i. A solution in the form of (6) means that the wall, without changing its form ($P^c(x)$, $u_i^c(x)$ is the static solution[6] in the absence of the field E), oscillates with frequency ω and velocity V. A small distortion of the form of the wall occurs due to the superposition of the small oscillations of ions with the same frequency ω about the equilibrium position in the moving boundary. Such a type of solution is dictated by the physics of the situation, and is justified by the fact that a solution of (3) and (4) in the form given by (6) exists, and is determined uniquely.

By substituting (6) in (3) and (4) we obtain, in the linear approximation with respect to p and u_i, a system of linear equations in total differentials for p and u_x ($u_y = u_z = 0$).*
In the particular case $q_2 = 0$ (according to the data of Devonshire[8] $q_2 = 0$ for $BaTiO_3$), and on satisfying the inequalities

$$\omega^2 \lll \omega_q^2, \qquad \omega\omega_r \lll \omega_q^2 \tag{7}$$

this system of equations becomes simpler, and leads to a single equation for p:

$$\frac{d}{d\eta}\left[(1-\eta^2)\frac{d}{d\eta}\right]p + \left[6 - \frac{4}{1-\eta^2}\right]p$$
$$= -\frac{4}{1-\eta^2}\frac{\omega_p^2}{\omega_q^2}P_0 - 4i\frac{\omega}{\omega_q^2}\frac{v}{\delta}\left(1 - i\frac{\omega_r}{\omega}\right)P_0. \tag{8}$$

Here we have written $\eta = \tanh \xi$. For the inhomogeneous equation (8) to have a finite solution, the following condition must be satisfied†

$$\int_{-1}^{+1} d\eta P_2^2(\eta) F(\eta) = 0,$$

where $F(\eta)$ is the right-hand side of (8), and $P_2^2(\eta)$, the associated Legendre polynomial, is the finite solution of the corresponding homogeneous equation. From this condition is obtained the solution for the wall velocity of interest to us:

$$V = \frac{dX}{dt} = \frac{3}{2}\delta\frac{\omega_p^2}{\omega^2}\frac{1}{1 - i\omega_r/\omega}i\omega e^{i\omega t}. \tag{9}$$

We now make more precise the conditions under which expression (9) was obtained. The condition for a linear approximation in p and u_i is the satisfying of the weaker of the inequalities

$$\omega_p^2 \lll \omega^2 \quad \text{or} \quad \omega_p^2 \lll \omega_r^2. \tag{10}$$

For a fixed frequency of the external field ω, the first of these inequalities imposes a limitation on the value of the field strength E_0. The presence of significant ionic damping ($\omega < \omega_r$) allows the requirement that E_0 be small to be weakened. The satisfying of conditions (10) ensures that the distortion of the form of the moving boundary, as compared with that of the stationary boundary, is small. The velocity of wall displacement, as is seen from Eq. (9), is also small, and is proportional to the strength of the external field E_0.

Condition (7), if decay is neglected, assumes that the frequency of the external field is small in comparison with the resonance frequency of the ions in the internal field [see formula (19) below]. The wall oscillates with the frequency of the external field, and thus condition (7) means neglecting the interaction of the wall oscillations with the intrinsic oscillations of the ions in the internal field. This simplifies the problem and allows us to find without difficulty solution (9) for the wall velocity. If P_0^2 depends on the temperature T linearly, $P_0^2 \sim \Theta - T$ (second order phase transition), then, for a fixed frequency of the external field ω, condition (7) imposes a limitation on the temperature, which must not be too close to the Curie temperature Θ. The greater the ionic damping, i.e., the greater ω_r, the stronger becomes this limitation [see the second inequality of condition (7)].

We now calculate the energy W of the boundary layer per square centimeter of surface:

$$W = \int_{-\infty}^{\infty} dx(T + F) - \int_{-\infty}^{\infty} dx(T + F)_{\text{uniform}}, \tag{11}$$

where the integral of the energy density of the uniformly polarized ferroelectric has been subtracted. To do this it is necessary to use solutions (6). We substitute them into (11) and expand

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*The latter is derived from the boundary conditions $u_{ij}(x) = 0$ deep in the domains ($x = \pm\infty$). Such boundary conditions are valid at sufficiently high frequencies: $c/l \ll \omega$, where c is the velocity of sound, l is the dimension of the crystal. If the reverse inequality is true, in particular when $\omega = 0$, the boundary conditions will be different: $\sigma_{ij}(x) = 0$ at $x = \pm\infty$.

†This condition becomes obvious if the solution of the inhomogeneous second-order linear equation is written in the general form, and it is remembered that the second linearly independent solution of the homogeneous equation (8) is infinite.

the integrands in series, whilst observing conditions (7), (10) and $q_2 = 0$. After integrating we obtain

$$W = W_0 + \tfrac{1}{2} MV^2 - FX + \ldots. \tag{12}$$

The first term of this expression

$$W_0 = \tfrac{4}{3} P_0^2 \varkappa / \delta \tag{13}$$

is the energy per unit surface area of the stationary wall.* The second term, proportional to the square of the velocity, is the kinetic energy of the wall. It is natural to call the coefficient M the effective mass of the wall, where

$$M = 4W_0/\delta^2 \omega_q^2 = mW_0/ne^2\varkappa. \tag{14}$$

The third term, proportional to the displacement, is the potential energy of the wall in the external field.† The coefficient F is the pressure exerted by the field on the wall, $F = -2P_0E$.

According to (12) the equation of motion of the boundary will be

$$MdV/dt + M\omega_r V = F, \tag{15}$$

where a decay term proportional to the wall velocity has been added. Its solution, as would be expected, is expression (9). It would, of course, have been possible to write down (15) (accurate to within an arbitrary constant multiplier) starting from the solution (9) obtained previously, without resorting to a calculation of the wall energy (12). However, the calculations presented confirm once more the correctness of the result obtained (9), and enable the physical meaning to be made more precise, and the coefficients M and F to be written down explicitly.

So far the domain wall has been considered to be free (if we neglect the ionic damping). This will apparently be the case in an ideal crystal. However, when inclusions and deformations are present in the crystal, the boundary can have equilibrium positions which are energetically more favorable, and can also encounter in its motion additional resistance. If it is supposed that the wall is elastically coupled in an equilibrium position, then (15) must be generalized as follows:‡

$$Md^2X/dt^2 + M(\omega_r + \omega_r')\,dX/dt + M\omega_0^2 X = F, \tag{16}$$

where $M\omega_r'$ is the additional frictional coefficient, and $M\omega_0^2$ is the elastic coupling constant. Both these coefficients must depend greatly on the structure of the material.

The polarization of the crystal changes, when the boundary is displaced a distance X, by the amount $\Delta P = -2P_0X/l$ (under conditions such that the small distortion in the form of the wall can be neglected), where l is the dimension of the crystal. If the specimen is subdivided into many domains, then l should be understood to be the mean domain width. Solving (16), we obtain an expression for the electric susceptibility χ of the ferroelectric due to the domain wall displacement:

$$\chi(\omega) = \frac{\Delta P}{E} = \frac{\chi_0 \omega_0^2}{\omega_0^2 - \omega^2 + i(\omega_r + \omega_r')\,\omega}, \tag{17}$$

where χ_0 is the susceptibility at the frequency $\omega = 0$:

$$\chi_0 = 4P_0^2 / lM\omega_0^2. \tag{18}$$

The resonance frequency ω_0 is related to χ_0 by (18).

We now make some numerical estimates for $BaTiO_3$ and compare the formula obtained, (17), with the experimentally observed[9] variation of the dielectric constant ϵ of polycrystalline $BaTiO_3$ on the frequency of the external field $\omega/2\pi$. In order of magnitude, the effective mass of the ion is $m = 10^{-22}$ g (the reduced mass of Ba and the TiO_3 group is 9.4×10^{-23}g, [10] or the mass of Ti is 8×10^{-23}g). The effective charge is $e = 4 \times 4.8 \times 10^{-10}$ (twice the charge of Ba and TiO_3, or four times the charge of Ti). The number of ions per cc is $n = (4 \times 10^{-8})^{-3}\ \text{cm}^{-3}$. Thus, we have $ne^2/m = 6 \times 10^{26}\ \text{sec}^{-2}$. The experimental value of P_0 is 4.8×10^4; according to Devonshire's data,[8] we have $\beta = 7 \times 10^{-12}$. Thus, $\omega_q/2\pi = 1.2 \times 10^{12}\ \text{sec}^{-1}$ [see Eq. (5)]. Taking for κ the value $3 \times 10^{-16}\ \text{cm}^2$ (see [10]), we obtain $\delta = 1.3 \times 10^{-7}$ cm. The energy of unit area of the wall is, according to (13), $W_0 = 8\ \text{erg/cm}^2$. The effective mass of the wall is, according to (14), $M = 0.4 \times 10^{-10}\ \text{g/cm}^2$. Taking the experimental value[9] of the susceptibility at the frequency $\omega = 0$ as $\chi_0 = 1300/4\pi$ ($\epsilon = \epsilon_\infty + 4\pi\chi$), and taking the domain thickness as $l = 10^{-3}$ cm, we obtain for the resonance frequency ω_0 from formula (18) the value $\omega_0/2\pi = 0.8 \times 10^{10}\ \text{sec}^{-1}$, which agrees in order of magnitude with the experimental value[9] of $3 \times 10^{10}\ \text{sec}^{-1}$.

Since there are two damping mechanisms, it can be expected that the sum of the damping frequencies $\omega_r + \omega_r'$ will be much greater than the

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*There are misprints in the analogous expressions in Zhirnov's paper:[6] in all formulae for σ a multiplier ½ must be added.

†When calculating the energy of a wall in a ferromagnetic a similar term was erroneously omitted in [5] as well as in[3] (this did not, however, affect the result). The integral of the type $\int_{-\infty}^{+\infty} dxP^c(x)$ is, in fact, different from zero, and is proportional to the displacement of the boundary X.

‡It would be more logical to include the imperfection of the crystal in the original expression (1) for the thermodynamic potential and hence obtain Eq. (16).

resonance frequency ω_0 (ω_r has been experimentally determined for Rochelle salt,[11] and gives $\omega_r/\omega_q^2 = 2.6 \times 10^{-8}/(\Theta - T)$ sec^{-1}). In this case the dispersion (17) will show, not a resonant, but a relaxation behavior, which is observed in experiment.[9]

It is still necessary to verify that conditions (7) and (10) for the applicability of formula (17) are satisfied. If we take $E_0 \leq 1$ v/cm, then $\omega_p/2\pi = 10^9$ sec^{-1}. The value of ω_q has been obtained above. By comparing these values with the resonance frequency ω_0, we see that in the dispersion region the frequency ω in fact satisfies inequalities (7) and (10).

The treatment given and the numerical calculations show that the experimentally observed dispersion in $BaTiO_3$ can be considered as due to processes of domain wall displacement (this idea was first advanced by Kittel[12]).

Apart from the dispersion considered, there exists in ferroelectrics another dispersion region at a higher frequency, associated with the intrinsic oscillations of the ions [the resonance frequency ω_q, (5)].[7,10] In distinction from the first, the second dispersion region should also be observed in a homogeneous (single-domain) ferroeletric. Solving the system of linearized equations in the case of the homogeneous ferroelectric, we obtain for the susceptibility

$$\chi = \chi_\infty \omega_q^2/(\omega_q^2 - \omega^2 + i\omega_r\omega), \qquad (19)$$

where $\chi_\infty = \frac{1}{4}\beta P_0^2$. In distinction from formula (10) of [10], Eq. (19) was derived taking into account the elastic energy and the electrostrictive energy. The applicability of formula (19) for all frequencies is limited by the single inequality $\omega_p^2 \ll \omega_0^2$, i.e., $E_0 \ll 4\beta P_0^3$. Taking into account that in a phase transition of the second kind we have $P_0^2 \sim \Theta - T$, this inequality imposes at a fixed field strength E_0 a limitation on the temperature T, which must not be too close to the Curie temperature Θ (for more detail on this question see [10]).

In conclusion, it should be noted that the entire treatment is valid if there is a second order (but not a first order) phase transition in the ferroelectric.

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30