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FEATURES OF DIELECTRIC NONLINEARITY IN PARAELECTRICS

Analytical expressions describing the polarizability of insulators in the framework of main mechanisms of polarization have been derived and analyzed. The obtained formula can adequately describe the effects that emerge, when the electric field penetrates into a dielectric crystal. A dielectric nonlinearity occurring at the ferroelectric-paraelectric phase transition is analyzed. The results of analytical calculations confirmed the results of previous researches concerning the application of thin paraelectric films in microwave technology and as gate insulators.

Keywords: dielectric nonlinearity, paraelectricity, polarization, polarizability, ferroelectric, ferroelectric phases, phase shift.

1. Mechanisms of Dielectric Polarization

The dielectric nonlinearity, i.e. a nonlinear dependence of the dielectric permittivity on the electric field, in a vicinity of the phase transition is an important property of ferroelectric materials, which can find its application in superhigh-frequency electronics. With the development of modern technologies, in particular with the advent of nanometer-thickness films, there emerged an opportunity to take advantage of the dielectric nonlinearity, because the breakdown of such films takes place at very high electric fields.

The dielectric nonlinearity itself reflects more elementary microscopic processes that run in a crystal, where the electric field F nonlinearly depends on the polarizability of the insulator, α. It can be seen by expressing the magnitude of local electric field F in relation to the macroscopic electric field E, i.e. $F = E(\varepsilon + 2)/3$, whence the Clausius–Mossotti–Lorentz equation $\frac{\varepsilon+2}{\varepsilon-1} = \frac{\sum N_k\alpha_k}{3\varepsilon_0}$ can be derived. In this expression, N_k is the concentration of atoms of the k-th kind, and α_k is their polarizability. Hence, in order to express the dependence of the dielectric permittivity on the electric field, it is necessary to analyze more elementary mechanisms of polarization in the paraelectric phase.

When an electric field is applied to an insulator, the bound electric charges shift with respect to one another, so that the insulator becomes polarized. The external electric field induces elementary electric moments $p = qx$ in dielectric particles, where q is the shifted electric charges, and x the relative charge shift. Electric moments are produced by electrons (shifted with respect to the nuclei), ions (deviated from their equilibrium positions), and dipoles (by varying their orientation under the influence of external forces). Those particles promote the formation of a polarized state by means of various mechanisms.

The polarizability is one of the most important parameters, which characterizes the mechanisms of polarization of insulators. It determines the ability of an insulator to be polarized, and its magnitude is governed by the parameters of a polarized system, which can be described in different forms for different polarization mechanisms. The dependence of the polarizability on the parameters can be analyzed by expanding the formula for the polarizability in a series and evaluating its terms. For simplification, we will consider that there is no electric conductivity in the insulator ($\sigma = 0$) [2].

1.1. Features of elastic polarization mechanisms

If the particles in a crystal structure are connected rather rigidly and elastically with one another, the external action in the form of an electric field or another influence gives rise to very small displacements of those particles. However, since all particles in the insulator become shifted at that, even a small displace-

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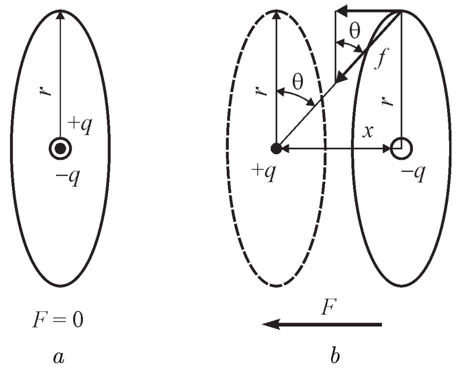


Fig. 1. Simplified model of electronic polarization [2]

ment of charges gives rise to the polarization. This mechanism of polarization is called elastic.

1.1.1. Electronic elastic polarization

In the nonpolarized state, the electron shells are located symmetrically with respect to the nuclei. Therefore, the center of negative charges coincides with the positively charged nucleus, and the electric moment is absent ($p = qx = 0$), because the displacement of charges does not take place: $x = 0$.

If an electric field is applied, the orbitals in structural particles become deformed and shifted with respect to the nuclei. Owing to the displacement of the negative charge center, an elementary polarization $p = qx > 0$ arises. Since the mass of nuclei is by 3 to 5 orders of magnitude larger than the mass of electrons, this is electrons and the electron cloud as a whole that actually undergo shifting. The main contribution to this polarization is given by electrons at the outer shells, which are weakly bound with the nucleus of an atom or ion.

The mechanism of electronic polarization has a general character and takes place in all insulators. The effective mass of shifted electrons is much smaller than that of atoms and ions, relatively to which they are shifted. Therefore, this mechanism is the least inertial one among the others. The stationary polarization is reached quickly and allows its contribution to the static dielectric permittivity $\varepsilon_{\rm st} = n^2$, where n is the low-frequency refractive index, to be determined.

For the maximum simplicity and the illustrative purpose, let us consider the mechanism of electronic polarization using the Bohr model of hydrogen atom as an example. The absolute electric charges of a proton and an electron equal $q = 1.6 \times 10^{-19}$ C, the proton mass is $m_+ = 1.67 \times 10^{-24}$ g, the electron mass $m_- = 9.11 \times 10^{-28}$ g, and the distance between the electron and the positively charged nucleus $r_e = 0.53$ Å. The strength of the electric field between the proton and the electron amounts to $E_r = 5 \times 10^{11}$ V/m.

In the absence of an external electric field, the effective center of negative charges coincides with the nucleus. In the electric field F much lower than the field E_r, the atomic electron shell shifts, the geometrical center of the negative charge shifts by the distance x from the nucleus, and an electric moment proportional to the applied field strength arises:

$$p = \alpha_e F = qx, \tag{1}$$

where α_e is the sought electronic polarizability.

The equilibrium in the proton–electron system under the action of an electric field is provided by the equality between the perturbation force and the force that tends to return the system into the nonpolar state, which is proportional to the deformation x:

$$f_{\rm per} = qF = cx. \tag{2}$$

The “elasticity” coefficient c in this model is determined from the returning force, $f_{\rm ret} = f \sin\theta$ (see Fig. 1). From Eqs. (1) and (2), it follows that $\alpha_e \frac{cx}{q} = qx$; hence,

$$\alpha_e = \frac{q^2}{c}. \tag{3}$$

Since

$$f = \frac{q^2}{4\pi\varepsilon_0 \sqrt{r^2 + x^2}}, \quad \sin\theta = \frac{x}{\sqrt{r^2 + x^2}},$$

we can obtain from Eq. (2) that

$$cx = f_{\rm ret} = \frac{q^2 x}{4\pi\varepsilon_0 (r^2 + x^2)^{3/2}}. \tag{4}$$

The field F is very low in comparison with E_r; therefore, the shift is much smaller than the distance r_e. The previous expression can be simplified to $c = \frac{q^2}{4\pi\varepsilon_0 r^3}$. This expression obtained for the coefficient of “elasticity” should be substituted into the polarizability formula (3); then, $\alpha_e = 4\pi\varepsilon_0 r^3$.

The coefficient $4\pi\varepsilon_0$ is necessary when the value of elastic polarizability is expressed in the SI system, i.e. when it has the dimension of fm^3. In order to get rid of the coefficients required in the SI system, let us introduce the relative polarizability $\alpha_{\mathrm{erel}} = r^3$. From formula (3), the polarizability can be determined as

$$\alpha'_{\mathrm{erel}}(F) = \frac{q^2}{c}. \tag{5}$$

While calculating the nonlinearity of the polarizability coefficient, one should take formula (2) into account and find an expression for the quantity c from expression (4) not neglecting x. Bearing in mind that, in the general case, the nonlinearity can be expanded in the series $\alpha'_{\mathrm{erel}} = \alpha_0 + \alpha_1 F + \alpha_2 F^2 + \alpha_3 F^3 + ...$, we expand the denominator of c in a series in the parameter x^2/r^2,

$$c \approx \frac{q^2}{r^3} \cdot \frac{1}{\left(1 + \frac{3}{2}\frac{x^4}{r^4} + \frac{1}{8}\frac{x^6}{r^6} + ...\right)}, \tag{6}$$

and substitute this expression into formula (5):

$$\alpha'_{\mathrm{erel}}(F) = r^3 \left(1 + \frac{3}{2}\frac{x^4}{r^4} + \frac{1}{8}\frac{x^6}{r^6} + ...\right). \tag{7}$$

The required coefficients are determined taking into account that only the even-order ones differ from zero, i.e. $\alpha_0 = r^3$, $\alpha_1 = 0$, $\alpha_2 = \frac{3}{2}\frac{r^7}{q^2}$, $\alpha_3 = 0$, $\alpha_4 = \frac{1}{8}\frac{r^9}{q^2}$.

1.1.2. Ionic elastic polarization

If the ionic crystal does not undergo the action of an external electric field, the cations and the anions in it are located at the crystal lattice sites. This system of charges is electrically neutral and does not create an electric moment (polarization). However, in an external electric field, the cations and the anions are shifted under the influence of Coulomb forces and form a polarized lattice with the elementary electric moments $q^+ - q^-$. This is a mechanism of ionic elastic polarization in crystals, which has a great importance for the electric properties of ionic insulators [2].

Ionic elastic polarization is not a universal phenomenon, being typical of only insulators with the ionic character of bonds in molecules or the crystal lattice. The ionic elastic polarization plays a crucial role in alkaline haloid crystals of the NaCl type. This mechanism of polarization as a response to the applied field is also a main one for active insulators, such as piezo-, pyro-, and ferroelectrics. Owing to a relatively large mass of ions, the establishment time for the ionic polarization is longer than that for the electronic one. However, even in this case, we can determine the contribution of a polarization to the dielectric permittivity.

While calculating the polarizability in the case of the ionic elastic polarization, α_i, a simple model of this mechanism is used. Two ions form a molecule. At the same time, they can also belong to two sublattices – cation and anion ones – inserted into each other and thus forming a simplest ionic crystal (of the $\mathrm{Na}^+\mathrm{Cl}^-$ type). In this model, only the Coulombic attraction between ions and the repulsion forces that arise in the case where their electron shells start to overlap are made allowance for. In the framework of the model, the charge q is considered to be concentrated at the ionic center, so that r is the distance between the centers of ions.

According to the Coulomb law, the energy of attraction between ions falls down proportionally to the distance between them and equals $\frac{q^2}{4\pi\varepsilon_0 r}$. The energy of repulsion between the electron shells drastically grows only in the case where the ions strongly approach each other, which can approximately be described by the power function d/r^n, where the parameter $n = 8 \div 11$, being dependent on the properties of that or another ionic pair and the specific features of the crystal lattice.

The coefficient d can be determined from other parameters of this model. The total potential energy of the system is the difference between the attraction and repulsion energies:

$$U(r) = \frac{d}{r^n} - \frac{q^2}{4\pi\varepsilon_0 r}. \tag{8}$$

Its curve has a minimum that characterizes the equilibrium state of the ionic system. In the equilibrium state ($r = a$), the force acting on the ions vanishes: $F = \left[\frac{dU}{dr}\right]_{r=a} = 0$. Since $U'(r) = d - \frac{q^2 r^n}{4\pi r\varepsilon_0}$, $d = \frac{q^2 a^n}{4\pi a\varepsilon_0} = \frac{q^2 a^{n-1}}{4\pi\varepsilon_0}$, the expression for the energy of interaction between ions looks like

$$U'(r) = \frac{d}{r^n} = \frac{q^2 a^{n-1}}{4\pi\varepsilon_0}\frac{1}{r^n}. \tag{9}$$

When the ions are relatively shifted under the field action, there arises a force that tries to return the system to the nonperturbed state. In the equilibrium state, this force equals the force that acts on

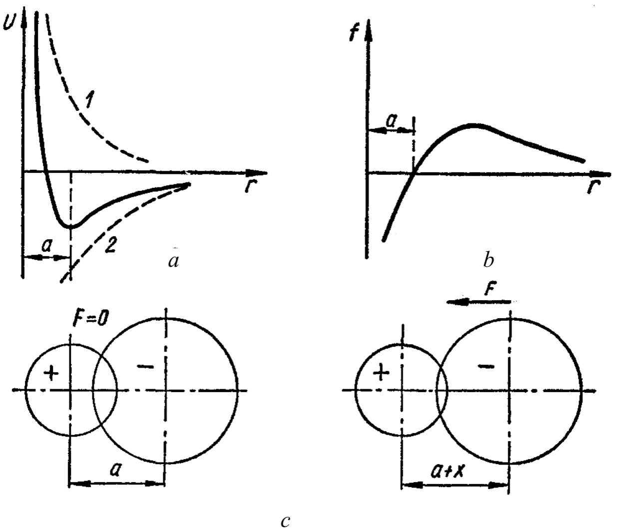


Fig. 2. Elastic ionic polarization of the simplest molecule consisting of a positive and a negative ion: (a) energy dependence on the distance between the centers of ions (the energy of repulsion between the electron shells (*1*) and the energy of Coulomb attraction (*2*)), (b) dependence of the total interaction force on the distance between the ions, (c) change of the ion-to-ion distance under the field action [2]

the ions, but it is oppositely directed: $cx = qF$, $\alpha_i F = qx$. Taking into account that $F = cx/q$, the expression for the ionic elastic polarizability looks like $\alpha_i = q^2/c$. Therefore, in order to find the polarizability, the quasielastic constant c has to be calculated. For this purpose, we can use the dependence of the elastic energy on the deformation, $U = cx^2/2$, and obtain the expression for the variation of the ionic shift energy under the influence of an external field,

$$U_{(a+x)} - U_a = \frac{cx_2}{2}. \tag{10}$$

We now calculate the second derivatives of the right- and left-hand sides of this equation and then substitute the displacement $a + x$ rather than r into the function $U(r)$:

$$U''_{(a+x)} = \frac{q^2(n-1) - 2q^3}{4\pi(a+x)^3\varepsilon_0}. \tag{11}$$

In this formula, the term $2q^3$ in the nominator is so small that it can be neglected. Substituting the result into the formula for the polarizability, we obtain

$$\alpha_i = \frac{q^2}{c} = \frac{q^2 4\pi\,(a+x)^3\,\varepsilon_0}{q^2\,(n-1)} = \frac{4\pi\,(a+x)^3\,\varepsilon_0}{n-1}. \tag{12}$$

The nonlinearity is calculated in the same way as for the electronic polarization. The relative polarizability is introduced to get rid of the coefficients of the SI system and looks like $\alpha_{i\mathrm{rel}} = \frac{(a+x)^3}{(n-1)}$ or $\alpha_{i\mathrm{rel}} = \frac{q^2}{c}$. Since $F = cx/q$, we obtain that $c = q^2\frac{(n-1)}{(a+x)^3}$. Expanding this expression in a series, $c = \frac{q^2(n-1)}{a^3} + \frac{q^3(n-1)^2}{a^5(n+4)} + ...$, we can determine the coefficients in the series $\alpha_i(F) = \alpha + \alpha_1 F + ...$ as

$$\alpha_0 = \frac{a^3}{(n-1)}, \quad \alpha_1 = \frac{a^5(n+4)}{q\,(n-1)^2},$$

and so on.

1.1.3. Dipole elastic polarization

The elastic rotation of dipoles is possible only if an "internal polarity" exists in the crystal. It plays an important role in many active insulators. Dipoles in such a "polar" crystal lattice are bound and oriented under the action of an internal crystalline field F created by those dipoles themselves. The applied external electric field changes the orientation of each dipole and the whole polar structure. As a result, the electric moment of the insulator changes, i.e. the variation of the polarization induced by an electric field takes place. This is a simplified scenario of the dipole elastic polarization [2]

Let us consider a simple example of the elastic orientation in a polar crystal consisted of two-atomic asymmetric polar molecules, e.g., HCl. It should be noted that the elastic dipole polarization occurs only in the crystalline state, because the molecules concerned form an ordered structure with the dipoles oriented in parallel to one another only in this case. The external electric field gives rise to an elastic deviation of the dipoles from their equilibrium orientation. In polar crystals, the direction of a spontaneous polarization is characterized by the polar axis; therefore, the elastic dipole polarization can be observed in pyroelectric crystals.

In Fig. 3, we present a simple model, which helps us to calculate the polarizability given be the mechanism of dipole elastic polarization, α_d. The dipole with constant moment p is oriented by a spontaneous (internal) electric field G. Let the external electric field F acting on this dipole make the angle θ with the internal field G. The field F stimulates the dipole to rotate by a small angle x. The dipole rotation in the field F is hampered by a quasielastic backward force associated with the torsional moment emerging owing to the deviation of the dipole by an angle x. In the linear approximation, it is supposed that $F \ll G$. The polarizability within this model can be calculated assuming that the variation of the electric moment of the system in an external electric field F is proportional to the strength of this field, $p = \alpha_d F$.

The projection of the dipole electric moment on the direction of the field F changes owing to the dipole rotation from the angle θ, when $F = 0$, to the angle $\theta - x$, when $F > 0$:

$$p = p_0 \cos(\theta - x) - p_0 \cos\theta =$$

$$= p_0 \left(\sin x \ \sin\theta - 2\sin^2 \frac{x}{2} \cos\theta\right). \qquad (13)$$

Since $F \ll G$ at low fields, the angular displacement x is also small, and the term with $\sin^2(x/2)$ can be neglected, so that $p = p_0 \sin x \sin\theta$. The value of $\sin x$ can be found from the equilibrium condition $p_0 F \sin(\theta - x) = p_0 G \sin\theta$. At $F \ll G$, we have that $\cos x \approx 1$ and $\sin x \ll 1$. Then

$$\sin(\theta - x) = \sin\theta \cos x - \cos\theta \sin x \approx \sin\theta,$$

and

$$\sin x = \frac{F}{G} \sin\theta \ll 1. \qquad (14)$$

The expression for the energy of a quasielastic bond in the field G looks like

$$U = -pG \cos x. \qquad (15)$$

Taking into account that $F \ll G$ and $\cos x \approx 1$, we obtain $G = U/p$. Substituting this expression together with expression (14) into the expression for the torsion moment, we obtain a formula for the moment induced by the dipole rotation,

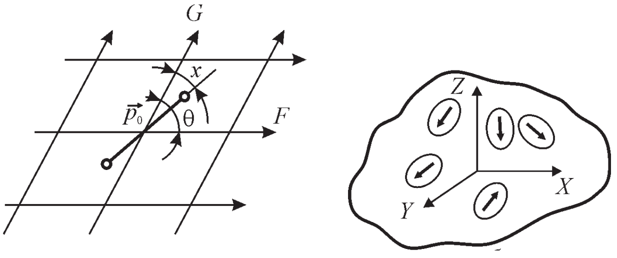
$$pF \sin\theta = p_0 G \sin\theta = U \sin\theta,$$

giving rise to the expression for p,

$$p = \frac{p_0^2 \sin^2\theta}{U_0} F. \qquad (16)$$

Formula (16) is used to find the polarizability

$$\alpha_d = \frac{p_0^2 \sin^2\theta}{U_0}. \qquad (17)$$



a *b*

Fig. 3. Model of elastic dipole polarization: (*a*) schematic diagram of the dipole rotation in an electric field F, (*b*) polarizability averaging in a polycrystalline polar insulator [2]

The nonlinearity of the dipole polarizability is determined as was done in two previous cases, namely, by expanding p in a power series in F,

$$p = \frac{p_0^2 \sin^2\theta}{U_0} F - \frac{3}{2} \frac{p_0^3 \sin^2\theta \cos\theta}{U_0^2 F} + ...,$$

so that

$$\alpha_0 = \frac{p_0^2 \sin^2\theta}{U_0}, \quad \alpha_1 = -\frac{3}{2} \frac{p_0^3 \sin^2\theta \cos\theta}{U_0^2},$$

and so on.

1.2. Mechanisms of relaxation (thermal) polarization

Besides the elastic polarization, electrons, ions, and dipoles can also participate in the relaxation one. If the particles are weakly bound in insulator's structure, their thermal motion in the crystal volume can strongly affect the polarization processes. Remaining localized in a microvolume, those particles can perform thermally induced jumps under the influence of the thermal motion and move by a distance of the atomic size order [2].

1.2.1. Thermal dipole polarization

In the absence of an external electric field ($E = 0$), the dipoles are oriented chaotically, and the electric moment of a unit volume equals zero. But if $E > 0$, some dipoles become oriented along the field in the course of their thermal chaotic motion, and a new equilibrium state, the polarized one, emerges. This equilibrium is thermodynamic: owing to thermal motions (oscillations, rotations), the dipoles are oriented

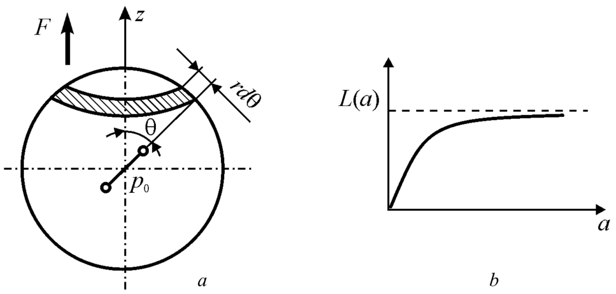


Fig. 4. Thermal dipole polarization: (*a*) schematic illustration to the calculation of the dipole moment, (*b*) schematic plot of the Langevin function [2]

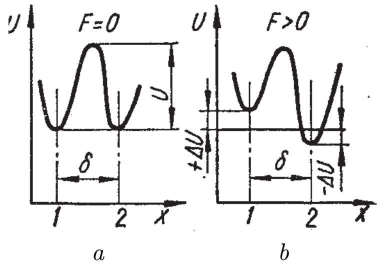


Fig. 5. Illustration to the calculation of the polarizability in the framework of the thermal ionic polarization model [2]

along the field direction, but thermally induced oscillations interfere with the orientation of all dipoles; therefore, only some part of dipoles turn out oriented. The higher the electric field strength, the larger the fraction of dipoles in the unit volume that becomes oriented along the field, and the higher is the dipole thermal polarizability α_{dt}. The electric moment averaged per one molecule is proportional to the electric field strength F provided that this field is not too high: $p = \alpha_{dt}F$. While calculating the polarizability α_{dt} in the framework of the dipole mechanism of thermal polarization, statistical models have to be considered, because only some dipoles (defective electrons or ions) change, in effect, their orientation (or become redistributed over the volume of solid insulator).

In this model, the reorientation of a statistical ensemble of dipoles is considered. The probability of the orientation depends on the temperature and the electric field strength; the values averaged over the ensemble are determined at that. In a specific model, for simplification, the spherical volume of an insulator is considered, which contains N dipoles. The dipoles have their own characteristic electric moment p, and they are reoriented independently of one another (the free rotation) under the influence of the chaotic thermal motion.

The applied electric field F should change the chaotic orientation of the dipoles, so that they become partially oriented along the field direction, giving rise to the polarization $P = N\langle p\rangle = N\alpha_{dt}F$, where

$$\langle p\rangle = \frac{Jdp}{JdN}$$

is the average moment of a polar molecule, dN is the number of dipoles directed at the angle θ with respect to the axis z (they are considered to be oriented into a certain ring ranging from θ to $\theta + d\theta$), and dp is the electric moment created by those dipoles. To verify the calculation technique, let us find the average polar dipole moment without the field, $F = 0$. In this case, dN is proportional to the ring area,

$$dN = 2\pi R^2 \sin\theta d\theta = C\sin\theta d\theta,$$

so that

$$dp = p_0\cos\theta dN = Cp_0\cos\theta\sin\theta d\theta.$$

Therefore,

$$\langle p\rangle = \frac{Jdp}{JdN} = \frac{JC\sin\theta d\theta\cos\theta p_0}{JC\mathrm{sin}\theta d\theta}. \tag{18}$$

Averaging over θ within the interval $0 \leqslant \theta \leqslant \pi$, we obtain that $\langle p\rangle = 0$. Hence, in the absence of a field, the polarization does not arise.

If the external electric field is switched-on ($F > 0$), $U = -pF\cos\theta$. According to the Boltzmann distribution law, the probability that the dipole moment is oriented "into a ring" (within the angular interval from θ to $\theta + d\theta$) is proportional to $\exp\left(-\frac{p_0F}{kT}\cos\theta\right) = \exp\left(\frac{U}{kT}\right)$. Then, the formulas for dN and dp look like

$$dN = Ce^{\frac{p_0F}{kT}\cos\theta}\sin\theta d\theta,$$

$$dp = Ce^{\frac{p_0F}{kT}\cos\theta}p_0\cos\theta\sin\theta d\theta,$$

so that

$$\frac{\langle p\rangle}{p_0} = \coth\left(\frac{p_0F}{kT}\right) - \frac{1}{\left(\frac{p_0F}{kT}\right)}. \tag{19}$$

Using the notation $a = (pF)/(kT)$, Eq. (19) is rewritten as $\frac{\langle p\rangle}{p_0} = \coth a - \frac{1}{a}$. This expression is the Langevin function $L(a)$. To calculate the nonlinearity, we should expand it in a series $L(a) = a/3 - a^3/45 - \dots$. Then

$$\alpha_{dt} = \frac{(\langle p\rangle /p_0)}{F} = \frac{p_0^2}{3kT} - \frac{p_0^4}{45k^3T^3} + \dots .$$

From whence, we have $\alpha_0 = \frac{p_0^2}{3kT}$, $\alpha_1 = 0$, and $\alpha_2 = -\frac{p_0^4}{45k^3T^3}$.

1.2.2. Thermal ionic polarization

The ionic polarization is associated with thermally induced vibrations of the crystal lattice. Its mechanism consists in hoppings of weakly bound (as a rule, impurity) ions in a certain local space of the crystal lattice. Therefore, this polarization is mainly typical of solid insulators with a pronounced defective structure, such as glasses, pyroceramics, and ceramics, which are characterized by a high concentration of structural defects. However, the thermal ionic polarization is also observed in single crystals, in vicinities of structural defects.

Interstitial ions and ion vacancies can change their location under the influence of the fluctuations of thermal vibrations. In the course of those displacements, which are usually confined by structural defects, the ions overcome potential barriers and stay at new positions for some time, which gives rise to the emergence of electric dipoles. If the external electric field is absent, the locally confined displacement of charged particles is disordered and random and does not result in a macroscopic polarization. The external electric field makes changes in the distribution of ions over the defective sites of the crystal lattice, so that a polarization induced by the electric field arises. The establishment time for this kind of the polarization, τ, depends on the temperature, features of the insulator structure relaxation, and type of defects.

To analyze the relaxation mechanisms of polarization and to calculate the thermal ionic polarizability α_{it}, a statistical model has to be used. Let us consider the polarization in an insulator that contains n_0 weakly bound ions in a unit volume. The value of n_0 is much less than the total concentration of ions in the insulator, n, because not all but only some ions take part in this form of polarization.

Thermally activated local hoppings are possible only for weakly bound ions localized in vicinities of structural defects. During the thermal chaotic motion, the weakly bound ions overcome a definite average potential barrier U, which separates two (or more) probable sites for an ion. It is clear that the temporary localization of such ions can survive only in the case of not very high temperatures, for which $U \gg k_\mathrm{B}T$.

On the average, only $n_0/3$ weakly bound ions moves along any selected direction in the insulator. The average distance δ between the probable localization positions for such ions is of the order of the crystal lattice constant ($\delta \approx 10^{-9}$ m). The quantity δ can be called the mean "free" path length. The probability that, in the course of vibrations at the temperature T, the ion, being at the equilibrium position in potential well 1 or 2, can acquire an energy larger or equal to the barrier height U equals $\exp(-U/k_\mathrm{B}T)$. Let ν be the Debye frequency of thermal vibrations of ions [Hz], let subscripts 1 and 2 denote the position in either of the potential wells, and let n be number of ions per second that overcome the barrier and transit from position 1 into position 2 or vice versa:

$$n_{12} = n_{21} = \frac{n}{6}\nu \exp\left(-\frac{U}{kT}\right).$$

If the probabilities of transitions are equal, the polarization does not arise.

If an electric field F is applied to the insulator along a selected axis x, the probability of transitions of weakly bound ions from position 1 into position 2 increases, whereas the probability of inverse transitions should decrease:

$$\Delta U = \frac{qF\delta}{2}. \tag{20}$$

In some time after the electric field has been switched-on, it turns out that $n_2 > n_1$, namely, $n_1 = n_0/6 - \Delta n$, and $n_2 = n/6 + \Delta n$. In the framework of the considered thermal polarization model, only some part of all n_0 weakly bound ions, Δn, participates in jumps over the barrier. Let us calculate the average elementary polarizability α_{it} per one impurity ion. The electric moment induced by the field equals $P = \Delta nq\delta = np = n\alpha_{it}F$. From the expressions given above, it is possible to determine the polarizability,

$$\alpha_{it} = \frac{\Delta nq\delta}{n_0F}. \tag{21}$$

Hence, the further calculations are reduced to the determination of the quantity Δn, which depends on the temperature and the electric field strength. In order to determine the establishment time for the thermal ionic polarization, the temporal dependence of Δn has to be taken into account as well: $d(\Delta n)/dt = dn_1/dt$.

Let us consider the rate of variation of the redundant ion concentration in position 1, when the electric field is switched-on. Changing their positions, the particles overcome the potential barrier of the height $U - \Delta U$ in one direction and $U + \Delta U$ in the opposite one. Substituting the values of n_1 and n_2, we obtain

$$\frac{dn_1}{dt} = \nu e^{(-U/kT)} \times \left(\frac{n_0}{6}\left(e^{(-\Delta U/kT)} - e^{(\Delta U/kT)}\right) + \right.$$
$$\left. + \Delta n\left(e^{(-\Delta U/kT)} + e^{(\Delta U/kT)}\right)\right). \tag{22}$$

For weak fields ($\Delta U \ll kT$),

$$\exp\left(\frac{\pm\Delta U}{kT}\right) = 1 \pm \frac{\Delta U}{kT} = 1 \pm \frac{q\delta F}{2kT}. \tag{23}$$

Substituting Eq. (23) into Eq. (22), we obtain

$$\frac{dn_1}{dt} = -2\left(\frac{n_0 qF\delta}{12kT}\right)\nu e^{\frac{-U}{kT}} + 2 \times \Delta n \nu e^{\frac{-U}{kT}}. \tag{24}$$

To simplify the expression, we make the following substitutions and introduce the following notation: $dn_1/dt = d(\Delta n)/dt$, $\tau = \frac{1}{2\nu}\exp\left(\frac{U}{kT}\right)$, and $A = \frac{nq\delta F}{12kT}$. As a result, we obtain the differential equation

$$\frac{d\,(\Delta n)}{dt} = \frac{\Delta n - A}{\tau},$$

which has the solution $\Delta n = Ce^{-t/\tau} + A$. From the conditions that $\Delta n = 0$ at $t = 0$, it follows that $C = -A$. Hence, we have

$$\Delta n = \frac{n_0 q\delta F}{12kT}\left(1 - e^{-t/\tau}\right). \tag{25}$$

Substituting expression 25) into Eq. (21), we obtain

$$\alpha_{im} = \frac{q\delta}{12kT}\left(1 - e^{-t/\tau}\right).$$

If the field acts for a long enough time ($t \to \infty$),

$$\alpha_{it} = \frac{q^2\delta^2}{12kT}. \tag{26}$$

1.2.3. Determination of nonlinearity

If the electric field is strong enough, the nonlinear properties of any polarization mechanism have to reveal themselves. The ionic polarization is not an exception in this sense. The nonlinearity should arise when a strong electric field stimulates ions to overcome the potential barrier. Consider once more Eq. (23), by keeping its additional terms at the simplification:

$$\frac{dn_1}{dt} = \nu e^{\left(\frac{-U}{kT}\right)} 2\left[\frac{-n_0}{6}\sinh\left(\frac{\Delta U}{kT}\right) + \Delta n \cosh\left(\frac{\Delta U}{kT}\right)\right]. \tag{27}$$

Introducing the notation $2\nu\exp(-U/kT) = 1/\tau$ and substituting it into the expression

$$\frac{d\,(\Delta n)}{dt} = \frac{1}{\tau_0}\cosh\left(\frac{\Delta U}{kT}\right)\left(-\Delta n + \frac{n_0}{6}\tanh\left(\frac{\Delta U}{kT}\right)\right),$$

we obtain the formula

$$\Delta n = \left[1 - \exp\left(\frac{-t}{\tau_0}\cosh\left(\frac{\Delta U}{kT}\right)\right)\right]\left(\frac{n_0}{6}\tanh\left(\frac{\Delta U}{kT}\right)\right). \tag{28}$$

Substituting it into the formula for the polarizability, we have

$$\alpha_{im} = \left[1 - \exp\left(\frac{-t}{\tau_0}\cosh\left(\frac{\Delta U}{kT}\right)\right)\right]\left(\frac{q\delta}{6F}\tanh\left(\frac{\Delta U}{kT}\right)\right).$$

If the field acts for a long-term period ($t \to \infty$),

$$\alpha_{it} = \frac{q\delta}{6F}\tanh\left(\frac{\Delta U}{kT}\right).$$

Expanding the hyperbolic tangent in a series, $\tanh(x) = x - x^3/3 + 2x^5/15 + ...$, we obtain a formula for the polarizability in the form of a series

$$\alpha_{it} = \frac{(q\delta)^2}{12kTF} + \frac{(q\delta)^4}{144k^2T^2F^2} + \dots\,.$$

The expansion coefficients are $\alpha_0 = \frac{(q\delta)^2}{12kT}$, $\alpha_1 = 0$, $\alpha_2 = -\frac{(q\delta)^4}{144(kT)^2}$, and $\alpha_3 = 0$.

The model of thermal electronic polarization is similar to the ionic one. The corresponding calculations bring about the same results [2].

2. Nonlinearity in Paraelectrics

Film-like ferroelectrics were earlier studied from the viewpoint of their application as nonlinear capacitors, controllable filters, microwave phase inverters, and so on. Thin layers of ferroelectric materials can also be used in controllable transistors as gate insulators in ferroelectric memory units. In recent years, the interest in thin ferroelectric films has been renewed, because there emerged a possibility to control the temperature of phase transitions, as well as other parameters, in them [1]. For example, the temperature of a phase transition in a strontium titanate film can be raised from 4 to 400 K.

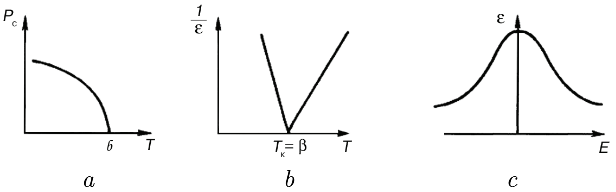
As a rule, the electric fields, at which a considerable dielectric nonlinearity is observed, are higher than the dielectric breakdown strength, which makes their application complicated. The revival of the interest in this phenomenon is connected with the appearance of new technologies allowing nano-sized dielectric layers to be created. In such layers, the dielectric nonlinearity is by an order of magnitude larger, and the layers become more controllable. For instance, 100-nm layers with a high dielectric permittivity and very low losses of the control can be used.

Since such materials as $SrTiO_3$, $BaTiO_3$, BST, and $EuTiO_3$ [4, 8] became promising for applications, it is necessary to reconsider the theory of dielectric nonlinearity and to verify theoretical calculations made earlier for some mechanisms that take place in ferroelectrics in order to determine the operational conditions of units and devices based on thin ferroelectric films more exactly.

The paraelectric is the phase of a ferroelectric above the phase transition point, which is characterized by high values of dielectric permittivity, whose temperature dependence obeys the Curie–Weiss law.

2.1. Phase transition in a ferroelectric

Ferroelectrics anomalously change their dielectric properties at the phase change. Phase transitions in the ferroelectric have specific features in every crystal and can be similar to a phase transition of the first or second kind. Their main classification is based on the displacement type and whether the ferroelectric structure is ordered or disordered.



a *b* *c*

Fig. 6. Temperature dependences of the spontaneous polarizability (a) and the inverse dielectric permittivity (b), and dielectric nonlinearity in the nonpolar phase (c) [2]

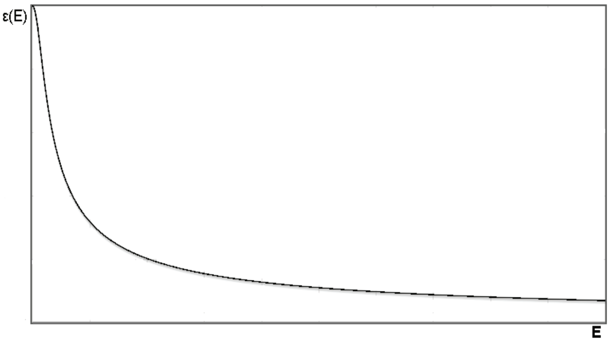


Fig. 7. Dependence of the dielectric permittivity on the electric field strength. Obtained for formula (29) using characteristics [4] of Barium Titanate

At the phase transition of the displacement type, if the temperature is above the Curie point, the crystal becomes unstable with respect to one type of vibrations called a soft mode. As the temperature decreases and approaches the phase transition point, the frequency of those vibrations also decreases and can reach the zero value. This circumstance is responsible for the emergence of a spontaneous relative displacement of the crystal sublattices and the appearance of a spontaneous polarization.

At the phase transition of the order-disorder type, the structural elements of a crystal are characterized by the dipole-dipole interactions, which are described by dipole moments. In the high-temperature phase, the structural elements are disordered, and the energy of such disordered thermal motion is higher than the energy of interaction between the dipoles. Therefore, the dipoles are orientated chaotically, and the total polarization equals zero. In the low-temperature phase, the structural elements are ordered, and a spontaneous polarization emerges.

The Landau theory helps us to describe the phase transitions in ferroelectrics. For this purpose, let us use the series expansion of thermodynamic potential, taking the polarization as the order parameter,

$$\Phi(T,P)=\Phi_0(T)+\frac{1}{2}\alpha P^2+\frac{1}{4}\beta P^4+\frac{1}{6}\gamma P^6+\dots . \quad (29)$$

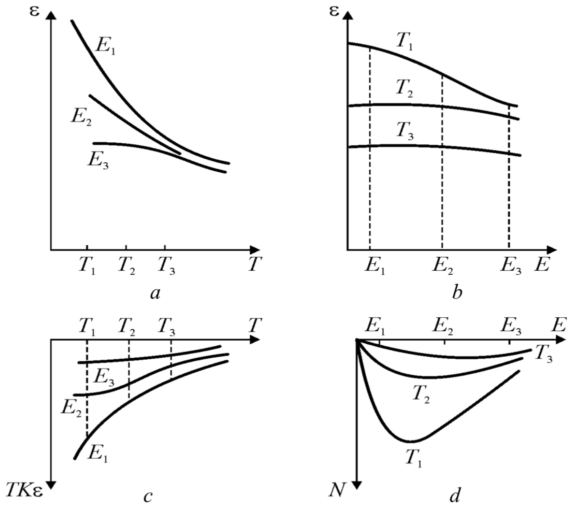


Fig. 8. Main properties of paraelectrics: dependences of the dielectric permittivity on the temperature (a) and the field strength (b), dependence of the quantity $TK\varepsilon$ on the temperature (c), and dependence of the nonlinearity N on the field strength (d) [2]

The choice of polarization as the order parameter is quite natural, because the spontaneous polarization ($P > 0$) appears in the ordered low-temperature phase, whereas the energy of disordered thermal motion in the high-temperature phase exceeds the energy of interaction between the dipoles, so that dipole orientations become chaotic, and their total polarization $P = 0$. In the framework of the Landau theory, the Curie–Weiss law can be obtained, which describes the temperature dependence of the dielectric permittivity $\varepsilon(T)$, as well as the spontaneous polarization $P_s(T)$ and other nonlinear dependences for insulators.

For the phase transition of the second kind, the expression for the electric field strength can be derived by differentiating the thermodynamic potential with respect to the order parameter: $E = \partial\Phi/\partial P = \alpha P + \beta P^3$. Taking the second derivative, we can determine the inverse dielectric susceptibility: $1/\chi = r\partial E/\partial P = \partial^2\Phi/\partial P^2 = \alpha + 3\beta P^2$. The dielectric susceptibility is related to the dielectric permittivity by the expression $\chi = 1+\varepsilon$. However, since the values of dielectric permittivity are very high in a vicinity of the phase transition point, namely, $\varepsilon \gg 1$, we may consider that $\varepsilon \sim \chi$.

Let us consider a nonpolar phase, in which the Curie–Weiss law is satisfied. It exists within a temperature interval above the critical temperature ($T > T_c$), in which the coefficient α in the Landau expansion is positive ($\alpha > 0$). The phase stability is provided by the conditions $\partial\Phi/\partial P = 0$ and $\partial^2\Phi/\partial P^2 = 0$. The former condition is reduced to the equation $\alpha P + \beta P^3 = 0$. Its solutions are $P = 0$ and $P = \pm(-\alpha\beta)^{1/2}$. Taking into account that $\alpha > 0$ and $\beta > 0$ for the phase transitions of the second kind, those solutions are imaginary. Hence, there is no spontaneous polarization above the Curie point.

Let us consider the temperature dependence of the dielectric permittivity above the Curie point. Here, $1/\varepsilon \approx 1/\chi = \alpha + 3\beta P^2$. As was said above, the critical dependence on the temperature is inherent only to the coefficient α. Then the coefficient β can be neglected, and α can be written as follows: $1/\varepsilon = \alpha_0(T - \theta)$. Identifying $1/\alpha_0$ as the Curie–Weiss constant, we obtain $\varepsilon = C/(T-\theta)$. From whence, we can see that the phase transition takes place at the Curie–Weiss temperature θ, when the parameter α changes its sign.

In the nonpolar phase, the dielectric permittivity depends not only on the temperature but also on the electric field strength. The expressions for $E(P)$ and $\chi^{-1}(P)$ testify that the nonpolar phase of ferroelectrics has a very considerable and appreciable dielectric nonlinearity, which can be described as $\varepsilon\, \partial P/\partial E$. The general formula for the nonlinearity involves both the temperature and electric-field dependences:

$$\varepsilon\,(T, E) = \frac{\varepsilon\,(T)}{\sqrt[3]{1 + 3\beta\varepsilon_0^3\varepsilon^3\,(T)\,E^2}}, \tag{30}$$

where $\varepsilon(T) = C/(T - \theta)$. Let us analyze this expression. First, let us plot the dielectric permittivity as a function of the electric field strength. The specific parameters at that are the Curie–Weiss constant $C = 1.2 \times 10^5$ K, the critical temperature $T = 400$ K, the Curie–Weiss temperature $\theta = 388$ K, and the coefficient $K \approx 3 \times 10^{-15}$; i.e. close to the parameters of barium titanate [2, 4]. Now, let us determine the coefficient of nonlinearity and the temperature coefficient of the permittivity. For this purpose, we make the substitution $3\beta\varepsilon_0^3 = K$ and expand the function $\varepsilon\,(T, E)$ in a series

$$\varepsilon\,(T, E) = \frac{C}{T - \theta} - \frac{K}{3}\frac{C^4E^2}{(T - \theta)^4} + \frac{2K^2}{9}\frac{C^7E^4}{(T - \theta)^7} - \dots . \tag{31}$$

From whence, we can determine the nonlinearity and the temperature coefficient of the dielectric permit-

Polarizability components obtained in 1.1 and 1.2

Polarization type	α	α_1	α_2	α_3
Elastic				
Electronic	r^3	0	$\frac{3}{2}\frac{r^7}{q^2}$	0
Ionic	$\frac{a^3}{(n-1)}$	$\frac{a^5(n+4)}{q(n-1)^2}$	$\sim\frac{a^7n^2}{q^2(n-1)^3}$	$\sim\frac{a^9n^3}{q^3(n-1)^4}$
Dipole	$\frac{p_0^2\sin^2\theta}{U_0}$	$-\frac{3}{2}\frac{p_0^3\sin^2\theta\cos\theta}{U_0^2}$	$\sim\frac{p_0^4\sin^2\theta}{U_0^3}$	$\sim-\frac{p_0^5\sin^2\theta}{U_0^4}$
Relaxation				
Electronic	$\frac{(e\delta)^2}{12kT}$	0	$-\frac{(e\delta)^4}{144(kT)^2}$	0
Ionic	$\frac{(q\delta)^2}{12kT}$	0	$-\frac{(q\delta)^4}{144(kT)^2}$	0
Dipole	$\frac{p_0^2}{3kT}$	0	$-\frac{p_0^4}{45(kT)^3}$	0

tivity:

$$\frac{\partial\varepsilon}{\partial E} = 0 - \frac{2}{3}\frac{KC^4E}{(T-\theta)^4} + \frac{2}{3}\frac{K^2C^7E^3}{(T-\theta)^7}, \tag{32a}$$

$$N = \frac{1}{\varepsilon}\frac{\partial\varepsilon}{\partial E} \approx \frac{-2}{3}\frac{KC^3E}{(T-\theta)^3} + \frac{2}{3}\frac{K^2C^6E^3}{(T-\theta)^6}, \tag{32b}$$

$$\frac{\partial\varepsilon}{\partial T} = \frac{-C}{(T-\theta)^2} + \frac{4}{3}\frac{KC^4E^2}{(T-\theta)^5} - \frac{14}{3}\frac{K^2C^7E^4}{(T-\theta)^8}, \tag{33a}$$

$$TK\varepsilon = \frac{1}{\varepsilon}\frac{\partial\varepsilon}{\partial T} \approx \frac{-1}{(T-\theta)} + \frac{4}{3}\frac{KC^3E^2}{(T-\theta)^4} - \frac{14}{3}\frac{K^2C^6E^4}{(T-\theta)^7}. \tag{33b}$$

The most interesting is the temperature, at which the nonlinearity has a maximum. The corresponding electric field strength can be determined from the nonlinearity formula

$$\frac{2}{3}\frac{K^2C^6E^3}{(T-\theta)^6} = \frac{2}{3}\frac{KC^3E}{(T-\theta)^3}.$$

As a result, we obtain

$$E^2_{\max} = (T-\theta)^3/(3KC^3).$$

This parameter is used to select the working electric voltage. It has to be as low as possible to prevent the electric breakdown in the material and reduce the material heating by consumed capacities. For the application of paraelectrics at ultrahigh frequencies, we need a low dielectric permittivity, a high nonlinearity, and a small temperature coefficient.

2.2. Nonlinear paraelectric films

The prospectivity of paraelectrics consists in their application in the UHF technology. Ferroelectric materials in the paraelectric phase with a transition of the displacement type can be used in the form of thin films deposited on a dielectric substrate with a high thermal conductivity. Since the film dielectric permittivity is often required to be made lower, films and substrates with the different coefficients of thermal expansion are selected to produce mechanical stresses.

For a quick inertialess control, the films have to possess the following parameters: a thickness of 0.1÷1 μm (which enables both ε and $\tan\delta$ to be reduced), the film permittivity $\varepsilon = 300\div1000$, and the substrate permittivity $\varepsilon_{sub} = 10$. The ability to control the film by an external electric field, $\Delta\varepsilon/\varepsilon_m$, grows together with the parameter ε. The film thickness is also of importance: the thicker the film, the higher is the control degree [2, 5, 6, 9].

3. Results and Conclusions

Thin films of controllable ferroelectric materials have found more and more applications in the recent time. The analysis of the literature testifies that they can be used as insulators in capacitors and delay lines, and as gate insulators in transistors. Those elements can be used while fabricating UHF phase invertors and filters driven by the electric field, and in a new promising type of non-volatile random-access memory (FRAM).

The executed calculations for relevant mechanisms show that even the simplest model can describe the processes taking place when the electric field penetrates into the insulator. The calculations demonstrate the mechanism of how the polarization grows with the field penetration depth.

Bearing in mind its applications, the expression obtained for the dielectric nonlinearity is analyzed to confirm and to specify the information obtained in earlier calculations. With the help of the Landau theory, the Curie–Weiss for ferroelectric materials in the paraelectric phase is derived. It shows the appreciable dependence of the dielectric permittivity of paraelectrics on the ambient temperature. The approximation of this law is used to derive the law of nonlinearity in the form of the dependence of the ferroelectric dielectric permittivity on the electric field strength. It is this dependence that mainly characterizes the controllability of thin ferroelectric films.

In view of a permanently growing interest in thin ferroelectric films and an increasing demand for devices and units on their basis, we may claim that the technologies based on the application of controllable insulators have to justify the hopes put on them concerning a reduction of the sizes of active elements and the enhancement of their controllability.

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ОСОБЛИВОСТІ ДІЕЛЕКТРИЧНОЇ НЕЛІНІЙНОСТІ У ПАРАЕЛЕКТРИКАХ

Резюме

Виконано розрахунки та аналіз формул поляризовності для основних механізмів поляризації діелектриків. Отримані вирази можуть відобразити ефекти, що виникають при проникненні в кристал електричного поля. Проаналізовано діелектричну нелінійність сегнетоелектрика при переході у параелектричну фазу. Аналітично отримано підтвердження результатів попередніх досліджень параелектриків, які допускають можливість застосування тонких параелектричних плівок у НВЧ техніці та в ролі підзатворних діелектриків.