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ANALYTICAL INVESTIGATION INTO THE MECHANISM OF DIELECTRIC LOSSES DUE TO INTERLAYER POLARIZATION

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The theory of dielectric space-charge polarization losses describes well both the model of an inhomogeneous dielectric [1] and the polarization resulting from mosaic blocks of alkali-halide crystals [2]. The Debye frequency dependences ε(ω) and tan δ(ω) with non-Arrhenius relaxation time are calculated in the first approximation of perturbation theory [3, 4] with the use of a nonlinear system of the Fokker–Planck and Poisson equations for the interlayer polarization with allowance for tunnel transitions of relaxation oscillators. For the Maxwell mechanism of space-charge relaxation, tan δ(ω) also has the Debye form [5]. It should be noted that in studies cited above the electric field was considered uniform, and the nonlinearity of the initial system of equations was not investigated. This paper removes these restrictions and elaborates a theory of relaxation mechanism.*

1. COMPLEX PERMITTIVITY

The general solution of the nonlinear system of the Fokker–Planck and Poisson equations analyzed in [6] demonstrated that the space-charge distribution obtained by expansion in a Fourier series in relaxation modes demonstrates that at times considerably exceeding the relaxation time of the first mode with wavelength $2l$ (l is the thickness of the dielectric), the process of space-charge relaxation is stationary periodic. In this case, the space-charge distribution is expressed as a series

$$\rho(x,t) = \sum_{n=1}^{\infty} \gamma^n \sum_{k,s=1}^{\infty} A_n^{(s\omega)}(k) e^{is\omega t} \cos\left(\frac{\pi k x}{l}\right) \tag{1}$$

with $\gamma << 1$, where $A_n^{(s\omega)}(k)$ is the amplitude of the kth mode in the nth approximation at the frequency $s\omega$ [6].

The energy of the electric field scattered in unit volume over the oscillation period is described by the formula

$$Q = \overline{\mathrm{Re}(E)\,\mathrm{Re}\frac{\partial P}{\partial t}}, \tag{2}$$

where E is the external electric field and P is polarization.

From Eqs. (1) and (2) it follows that multiple frequency harmonics with $s > 1$ do not contribute to dielectric losses. In this connection, the charge distribution was calculated at the fundamental frequency. From [6] it follows that the nonlinear interaction between the relaxation modes of a stationary periodic process generates multiple frequency harmonics; therefore, in the recursion relation we consider only linear terms [6]:

$$A_n(k,\tau) = \int_0^{\tau} \exp\left[\left(\theta + \frac{\pi^2 k^2 a^2}{l^2}\right)(t'-\tau)\right]\left(\frac{8n_0\psi}{\pi^2}\right)\sin^2\left(\frac{\pi k}{2}\right)\sum_{p=1}^{\infty} A_{n-1}(p,t')\frac{\sin^2\left(\frac{\pi p}{2}\right)}{p^2}dt', \tag{3}$$

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where

$$A_1(p,t') = -\left(\frac{4a}{l}\right) n_0 \sin^2\left(\frac{\pi p}{2}\right) \frac{e^{i\omega_1 t'}}{\left(\theta + \frac{\pi^2 p^2 a^2}{l^2} + i\omega_1\right)}. \tag{4}$$

Since in the *n*th approximation of the perturbation theory the amplitudes are expressed through the amplitudes in the $(n-1)$th approximation, from Eq. (3) we obtain

$$A_n(k,\tau) = -\left(\frac{4a}{l}\right)\left(\frac{8\psi}{\pi^2}\right)^{n-1} n_0^n B^{n-1} \sin^2\left(\frac{\pi k}{2}\right) \frac{e^{i\omega_1 \tau}}{\theta + \frac{\pi^2 k^2 a^2}{l^2} + i\omega_1}, \tag{5}$$

where

$$B = \sum_{k=1}^{\infty} \frac{\sin^2\left(\frac{\pi k}{2}\right)}{k^2} \frac{1}{\left(\theta + \frac{\pi^2 k^2 a^2}{l^2} + i\omega_1\right)}. \tag{6}$$

Here ω_1 is the dimensionless electric field frequency equal to $\frac{\omega a^2}{D}$.

Using Eqs. (1) and (5), we write down the space charge distribution $\rho(x, \tau)$ as follows:

$$\rho(x,\tau) = \sum_{n=1}^{\infty} \gamma^n \sum_{k=1}^{\infty} A_n(k,\tau) \cos\left(\frac{\pi k x}{l}\right) = \left[-\sum_{n=1}^{\infty}\left(\frac{4a}{l}\right)\gamma^n \left(\frac{8\psi}{\pi^2}\right)^{n-1} n_0^n B^{n-1}\right] \sum_{k=1}^{\infty} \frac{\sin^2\left(\frac{\pi k}{2}\right) e^{i\omega_1 \tau} \cos\left(\frac{\pi k x}{l}\right)}{\left(\theta + \frac{\pi^2 k^2 a^2}{l^2} + i\omega_1\right)}$$

$$= -\left(\frac{4a}{l}\right) \frac{\gamma n_0 e^{i\omega_1 \tau}}{1 - \frac{8\psi\gamma n_0}{\pi^2} B} \sum_{k=1}^{\infty} \frac{\sin^2\left(\frac{\pi k}{2}\right) \cos\left(\frac{\pi k x}{l}\right)}{\left(\theta + \frac{\pi^2 k^2 a^2}{l^2} + i\omega_1\right)}. \tag{7}$$

We now find the electric field strength in the dielectric at the fundamental frequency from the Poisson equation

$$E(x,\tau) = E_0 e^{i\omega_1 \tau} \left\{1 - \left(\frac{4a}{l}\right)\psi \frac{\gamma n_0}{1 - \frac{8\psi\gamma n_0}{\pi^2} B} \sum_{k=1}^{\infty} \frac{\sin^2\left(\frac{\pi k}{2}\right)}{\left(\theta + \frac{\pi^2 k^2 a^2}{l^2} + i\omega_1\right)}\right.$$

$$\left. \times \frac{l}{\pi k a}\left[\sin\left(\frac{\pi k x}{l}\right) - \frac{2\sin^2\left(\frac{\pi k}{2}\right)}{\pi k}\right]\right\}, \tag{8}$$

where

$$B = \frac{l^2}{8a^2}\frac{1}{\alpha_1 + i\alpha_2}\left[1 - \frac{2}{\pi z_1}\frac{1-\cos\pi z_1}{\sin\pi z_1}\right], \tag{9}$$

$$z_1 = \sqrt{\frac{\beta-\alpha_1}{2}} - i\sqrt{\frac{\beta+\alpha_1}{2}}, \tag{10}$$

$$\beta = \sqrt{\alpha_1^2 + \alpha_2^2}\ .$$

In the diffusion-drift approximation, the current density with allowance for the blocking electrodes can be written as

$$j(0,t) = \varepsilon_0\varepsilon_\infty \frac{\partial E(0,t)}{\partial t}. \tag{11}$$

A comparison of Eq. (11) with the drift current density

$$j(0,t) = \varepsilon_0 i\omega E_0 \exp[i\omega t][\varepsilon' - i\varepsilon'']$$

allows us to calculate its real (ε') and imaginary components (ε'') and the loss tangent:

$$\varepsilon'(\omega) = \varepsilon_\infty \left\{(\omega\tau_M)^2\pi^2\left(\frac{\tau_D}{\tau_M}\right)\sqrt{1+\omega^2\tau_M^2}\,(\cos y_1 + \cosh y_2) + 2(y_1\sin y_1 + y_2\sinh y_2)\right.$$

$$\left. + 2\omega\tau_M(y_2\sin y_1 - y_1\sinh y_2)\right\} \times \left\{(\omega\tau_M)^2\pi^2\left(\frac{\tau_D}{\tau_M}\right)\sqrt{1+\omega^2\tau_M^2}\,(\cos y_1 + \cosh y_2) + 4\omega\tau_M\right.$$

$$\left. \times(y_2\sin y_1 - y_1\sinh y_2) + 4(\cosh y_2 - \cos y_1)\right\}^{-1}, \tag{12}$$

$$\varepsilon''(\omega) = \varepsilon_\infty \left\{(\omega\tau_M)\pi^2\left(\frac{\tau_D}{\tau_M}\right)\sqrt{1+\omega^2\tau_M^2}\,(\cos y_1 + \cosh y_2) + 2(y_2\sin y_1 - y_1\sinh y_2)\right.$$

$$\left. - 2\omega\tau_M(y_1\sin y_1 + y_2\sinh y_2)\right\} \times \left\{(\omega\tau_M)^2\pi^2\left(\frac{\tau_D}{\tau_M}\right)\sqrt{1+\omega^2\tau_M^2}\,(\cos y_1 + \cosh y_2) + 4\omega\tau_M\right.$$

$$\left. \times(y_2\sin y_1 - y_1\sinh y_2) + 4(\cosh y_2 - \cos y_1)\right\}^{-1}, \tag{13}$$

$$\tan\delta(\omega) = \left\{(\omega\tau_M)\pi^2\left(\frac{\tau_D}{\tau_M}\right)\sqrt{1+\omega^2\tau_M^2}\,(\cos y_1 + \cosh y_2) + 2(y_2\sin y_1 - y_1\sinh y_2)\right.$$

$$\left. - 2\omega\tau_M(y_1\sin y_1 + y_2\sinh y_2)\right\} \times \left\{(\omega\tau_M)^2\pi^2\left(\frac{\tau_D}{\tau_M}\right)\sqrt{1+\omega^2\tau_M^2}\,(\cos y_1 + \cosh y_2)\right.$$

$$\left. + 2(y_1\sin y_1 + y_2\sinh y_2) + 2\omega\tau_м(y_2\sin y_1 - y_1\sinh y_2)\right\}^{-1}. \tag{14}$$

Here we have used the designation

$$y_{1,2} = \frac{\pi}{\sqrt{2}}\left[\left(\frac{\tau_D}{\tau_M}\right)\left[\left(\sqrt{1+\omega^2\tau_M^2}\right)^{1/2} \mp 1\right]\right]^{1/2}. \quad (15)$$

Proceeding to the limit at $\omega \to 0$, we obtain the static permittivity:

$$\varepsilon_s = \frac{\pi\varepsilon_\infty}{2}\left(\frac{\tau_D}{\tau_M}\right)^{1/2} \coth\left[\frac{\pi}{2}\left(\frac{\tau_D}{\tau_M}\right)^{1/2}\right]. \quad (16)$$

The quantity (τ_D/τ_M) depends on the thickness l of the dielectric, concentration of the mobile charge carriers n_0, and temperature T:

$$\frac{\tau_D}{\tau_M} = \frac{q^2 n_0 l^2}{\pi^2 \varepsilon_0 \varepsilon_\infty kT}; \quad (17)$$

otherwise,

$$\frac{\tau_D}{\tau_M} = \left(\frac{l}{r_D}\right)^2. \quad (18)$$

Here $r_D = \sqrt{\frac{\pi^2\varepsilon_0\varepsilon_\infty kT}{q^2 n_0}}$ is the Debye shielding radius

Formula (18) describes the dimensional effects resulting from the space-charge relaxation.

2. MAXWELL AND DIFFUSION RELAXATION OF THE SPACE CHARGE

If the thickness of a dielectric sample is much greater than the Debye shielding radius $\tau_D \gg \tau_M$ (which is the case for high concentration of structural defects and large sample thicknesses at low temperatures), the space-charge relaxation is determined by the Maxwell mechanism. The $\tan\delta(\omega)$ maximum is in the region $\omega\tau_M < 0.1$, and we can assume that $\omega^2\tau_M^2 \ll 1$. In this case, formulas (12), (13), and (14) assume the form

$$\varepsilon'(\omega) = \varepsilon_\infty \frac{2 + \pi\omega^2\tau_M^2\sqrt{\frac{\tau_D}{\tau_M}}}{\frac{4}{\pi}\sqrt{\frac{\tau_M}{\tau_D}} + \pi\omega^2\tau_M^2\sqrt{\frac{\tau_D}{\tau_M}}}, \quad (19)$$

$$\varepsilon''(\omega) = \varepsilon_\infty \frac{\pi\omega\tau_M\sqrt{\frac{\tau_D}{\tau_M}}}{\frac{4}{\pi}\sqrt{\frac{\tau_M}{\tau_D}} + \pi\omega^2\tau_M^2\sqrt{\frac{\tau_D}{\tau_M}}}, \quad (20)$$

$$\tan\delta(\omega) = \frac{\omega\tau_M}{\frac{2}{\pi}\sqrt{\frac{\tau_M}{\tau_D}} + \omega^2\tau_M^2}. \quad (21)$$

In the above approximation, $\coth \pi(\tau_D/\tau_M)^{1/2} \approx 1$; therefore, according to Eq. (16), ε' is equal to

$$\varepsilon_s = \frac{\pi\varepsilon_\infty}{2}\sqrt{\frac{\tau_D}{\tau_M}}. \tag{22}$$

It can be seen that Eq. (22) is transformed into Eq. (19) at $\omega = 0$, and $\varepsilon''(\omega)$ has a maximum at

$$\left(\omega\tau_M\right)_{max} \approx \frac{2}{\pi}\sqrt{\frac{\tau_M}{\tau_D}}. \tag{23}$$

The maximum of the loss tangent is then determined by the expression

$$\tan\delta_{max} \approx \sqrt{\frac{\pi}{8}\sqrt{\frac{\tau_D}{\tau_M}}}, \tag{24}$$

and

$$\left(\omega\tau_M\right)_{max} \approx \sqrt{\frac{2}{\pi}\sqrt{\frac{\tau_M}{\tau_D}}}. \tag{25}$$

From Eq. (24) it follows that

$$\omega_{max} = \sqrt{2}\left(\frac{\sigma}{\varepsilon_0\varepsilon_\infty}\right)^{3/4}\frac{D^{1/4}}{l^{1/2}}. \tag{26}$$

With increase in l, the maximum of $\tan\delta(\omega)$ is shifted toward lower frequencies for constant σ, T, and D values:

$$\frac{\omega_{max\,2}}{\omega_{max\,1}} = \sqrt{\frac{l_1}{l_2}}, \tag{27}$$

and with increase in the conductivity σ for constant T, D, and l values it is shifted toward higher frequencies:

$$\frac{\omega_{max\,2}}{\omega_{max\,1}} = \left(\frac{\sigma_2}{\sigma_1}\right)^{3/4}. \tag{28}$$

The above dependences allow us to explain quantitatively the experimentally observed effects of shift of the $\tan\delta(\omega)$ maximum when the conductivity of the dielectric cahnges.

In [7] it was experimentally established that $\frac{\omega_{max\,2}}{\omega_{max\,1}} = 1.48$ as the thickness of the dielectric is halved; theoretical formula (27) gives $\frac{\omega_{max\,2}}{\omega_{max\,1}} = 1.41$. Formulas (19)–(21) are similar to the Debye formulas with the effective relaxation time $\tau = \left(\frac{\varepsilon_s}{\varepsilon_\infty}\right)\tau_M$.

If the thickness of the dielectric is much less than the Debye shielding radius (this is the case for small concentration of relaxation oscillators, small thicknesses of the dielectric, and high temperatures), $\tau_D \ll \tau_M$, and the space-charge relaxation is governed by the diffusion mechanism. In this case, the $\tan\delta(\omega)$ maximum is in the region $\omega\tau_M \gg 1$, and $\tan\delta(\omega)_{max} \ll 1$. From Eq. (15) it follows that $y_{1,2} \approx \pi\sqrt{\frac{\omega\tau_D}{2}}$; then from Eqs. (12)–(14) we have

$$\varepsilon'(\omega) \approx \varepsilon_\infty, \tag{29}$$

$$\varepsilon''(\omega) = \varepsilon_\infty \left(\frac{\tau_D}{\tau_M}\right) \frac{(\omega\tau_D)^{1/2} - \frac{\sqrt{2}}{\pi}}{(\omega\tau_D)^{3/2}}, \tag{30}$$

$$\tan\delta(\omega) = \left(\frac{\tau_D}{\tau_M}\right) \frac{(\omega\tau_D)^{1/2} - \frac{\sqrt{2}}{\pi}}{(\omega\tau_D)^{3/2}}. \tag{31}$$

Formulas (30) and (31) hold true in the region of the $\tan\delta(\omega)$ maximum whose position is determined by the relation $\omega\tau_D \approx 0.5$ and whose magnitude is $\tan\delta(\omega)_{max} \approx 0.74\left(\frac{\tau_D}{\tau_M}\right)$.

3. CALCULATION OF THE PARAMETERS OF DIELECTRIC SPACE-CHARGE RELAXATION IN IH ICE CRYSTALS

The dielectric relaxation of the space charge in the Ih ice crystals was experimentally established in [8]. The space-charge relaxation time $\tau_{sp.ch}$, low-frequency (LF) conductivity $\sigma_{sp.ch}$, and Debye relaxation conductivity σ_{0D} derived from the temperature dependences of these quantities in the Ih ice crystals with the high-frequency (HF) impurity concentration $n \approx 6\cdot10^{20}$ m^{-3} are given in Table 1. The parameters of defects were calculated from the formulas for the Maxwell relaxation mechanism:

$$\varepsilon_s = \frac{\sigma_{0D}\cdot\tau_{sp.ch}}{\varepsilon_0}, \quad \varepsilon_\infty = \frac{\sigma_{sp.ch}\cdot\tau_{sp.ch}}{\varepsilon_0}, \tag{32}$$

$$\left(\frac{\tau_D}{\tau_M}\right) = \frac{4}{\pi^2}\left(\frac{\varepsilon_s}{\varepsilon_\infty}\right)^2, \tag{33}$$

$$n_0 = \frac{4\varepsilon_0\varepsilon_s^2 kT}{q^2 l^2 \varepsilon_\infty}, \tag{34}$$

$$D = \frac{l^2}{\pi^2\tau_D}, \tag{35}$$

$$\mu = \frac{\varepsilon_0\varepsilon_\infty}{n_0 q\tau_M}. \tag{36}$$

We took $q = 1.6\cdot10^{-19}$ C and $l = 2\cdot10^{-3}$ m.

TABLE 1. Experimental Parameters of Space-Charge Relaxation in Ice Crystals with HF Impurity

Parameter	Designation	Parameter values				
Temperature	T, K	234	238	245	255	264
Relaxation time	$\tau_{sp.ch}$, s	$2.64\cdot10^{-3}$	$2.34\cdot10^{-3}$	$2\cdot10^{-3}$	$1.72\cdot10^{-3}$	$1.69\cdot10^{-3}$
LF Debye conductivity	σ_{0D}	$2\cdot10^{-6}$	$2.43\cdot10^{-6}$	$2.86\cdot10^{-6}$	$2.97\cdot10^{-6}$	$3.23\cdot10^{-6}$
LF space-charge conductivity	$\sigma_{sp.ch}$	$5\cdot10^{-7}$	$5.35\cdot10^{-7}$	$6.95\cdot10^{-7}$	$1\cdot10^{-6}$	$1.44\cdot10^{-6}$

TABLE 2. Calculated Temperature Dependences of the Relaxation Oscillator Parameters

Parameter	Designation	Parameter values				
Temperature	T	234	238	245	255	264
Static permittivity	ε_s	597	643	646	577	617
HF permittivity	ε_∞	149	141	157	194	275
Absolute deviation	$\Delta\varepsilon$	448	502	489	383	342
Relative permittivity	$\varepsilon_s / \varepsilon_\infty$	4	4.56	4.11	2.97	2.24
Maxwell relaxation time	τ_M	$6.6\cdot10^{-4}$	$5.13\cdot10^{-4}$	$4.87\cdot10^{-4}$	$5.79\cdot10^{-4}$	$7.5\cdot10^{-4}$
Relative relaxation time	τ_D/τ_M	6.56	8.53	6.93	3.62	2.06
Diffusion relaxation time	τ_D	$4.33\cdot10^{-3}$	$4.38\cdot10^{-3}$	$3.37\cdot10^{-3}$	$2.1\cdot10^{-3}$	$1.55\cdot10^{-3}$
Concentration of charge carriers	n_0, m^{-3}	$2.69\cdot10^{15}$	$3.37\cdot10^{15}$	$3.13\cdot10^{15}$	$2.11\cdot10^{15}$	$1.76\cdot10^{15}$
Diffusion coefficient	D	$9.5\cdot10^{-5}$	$9.4\cdot10^{-5}$	$1.2\cdot10^{-4}$	$1.95\cdot10^{-4}$	$2.65\cdot10^{-4}$
Mobility	μ	$4.64\cdot10^{-3}$	$4.5\cdot10^{-3}$	$5.7\cdot10^{-3}$	$8.78\cdot10^{-3}$	$11.5\cdot10^{-3}$

The theoretical temperature dependences of the parameters of relaxation oscillators are tabulated in Table 2. A comparison of the formulas with the experiment was carried out invoking our measurements for the Ih ice polycrystal samples grown from chemically pure twice distilled degassed water [9]. Conditions of our experiment excluded completely the influence of the surface electrical conductivity and electrodes on the measurement accuracy.

The static permittivity ε_s depends weakly on the temperature and coincides by the order of magnitude with the data presented in [10]. The HF permittivity of the space-charge polarization is characterized by a weakly pronounced minimum in the region of crossover ($T_c \approx 238$ K). It is somewhat larger than the value calculated from the Debye variance [8]. The values obtained testify to the dominant role of the $(H_3O)^+$ ions. The calculated results demonstrate a significant role of tunneling.

The diffusion relaxation time τ_D at $T > T_c$ is characterized by an activation energy of ~0.23 eV, which coincides with the activation energy of moving L- and D-defects [11]. Thus, in accordance with theory [12], the diffusion of $(H_3O)^+$ defects at high temperatures is determined by motion of the D-defects. The mobility and diffusion coefficients calculated in this paper noticeably exceed their experimental values. This is most likely due to the influence of the space charge on the saturation current used to calculate these coefficients [13].

CONCLUSIONS

1. The system of the Fokker–Planck and Poisson equations can be linearized for times considerably exceeding the maximum relaxation time of the mode with the longest wavelength equal to the doubled thickness of the dielectric. Only in this case the relaxation process can be considered stationary periodic.

2. The multiple frequency harmonics 2ω, 3ω, etc. (the distribution of space charge on which does not influence the dielectric losses at the fundamental frequency ω) are generated only when the process is stationary periodic.

3. The formulas for calculation of ε', ε'', and $\tan\delta$ for the diffusion and Maxwell relaxation mechanisms are given for the stationary periodic process of space-charge relaxation.

4. Analytical investigations of the dimensional effects accompanying the Maxwell relaxation in dielectrics having high conductivity have allowed us to explain the anomalous shift of the loss tangent maximum toward lower frequencies with increase in the thickness of the dielectric and its shift toward higher frequencies with increase in the conductivity.

5. Theoretically calculated values of the static permittivity and charge-carrier concentration in the Ih ice crystals agree with the measured values, whereas the diffusion coefficient and the mobility considerably exceed their experimental values. This can be explained by incomplete consideration of the influence of the space charge on the saturation current used to estimate these parameters.

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