

Quantum Properties of Dielectric Losses Spectra in Lamellar Crystals at Extra-low Temperatures

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Quantum mechanism of interlayer polarization in condensed mediums in alternating electric field in the limits of low and extra-low temperatures is studied. Unbalanced density matrix is calculated for the ensemble of noninteracting protons, moving in one-dimension multipit potential image of rectangular shape in variable polarizing field. With the help of unbalanced density matrix, anomalous effects are studied, connected with the move of low-temperature maximum loss tangent of dielectric in lamellar crystals towards the temperatures of liquid helium. Results of quantum-mechanical calculation of spectra of complex dielectric permittivity (SCDP) may be used in the study of tunnel mechanism of spontaneous polarization of ferrielectrics (KDP, DKDP).

Key – words: hydrogen – bonded crystals (HBC); interlayer polarization; proton relaxation; unbalanced proton density matrix; quantum statistic for the ensemble of non - interacting protons; spectra of complex dielectric permittivity (SCDP); anomalous effects during the proton relaxation

Electro-physical properties of lamellar crystals (crystallohydrates, layered silicates) in temperature range $T = 70 - 450$ K, in range of low fields $E \approx 10^5 - 10^6 \frac{V}{\mu m}$, are shown in protonic conductivity, resulted in jump diffusion of protons along the hydrogen links towards the polarizing field¹⁻².

Relaxational protons movement in layered minerals (hydrosulphates of bivalent metals, mica, vermiculites, talcum, pyrophyllite) in marginal electric field (at polarization) and in the field of decomposable electret charge (at depolarization) allows classifying the materials of this class as protonic semiconductors and dielectrics^{1,3-5}.

Polarization of lamellar crystals may be considered as interlayer one⁶⁻⁸.

Kinetics of interlayer polarization of hydrogen-bonded crystals (HBC) is carried due to both thermally activated protons transitions (Maxwell relaxation), and their tunnelling (diffusional relaxation)^{1,3}.

Theoretical researches of dielectric relaxation in HBC, in the range of high temperatures (100 – 450 K), are made by methods of quasiclassical kinetic theory, based upon the combined solving of set of equations of Focker – Planck and Poisson, at defined electrode model¹. To describe the proton relaxation subject to hydrogen bonds at the temperatures higher than critical, linear approximation at small parameter at the solving equations of Focker – Planck is enough, as in high temperature range thermally activated proton transfers, distributed according to Boltzmann statistics according to levels of quasicontinuous

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spectrum energy make the dominant contribution to migration polarization^{3,9}.

At low temperatures (70-100 K), due to significant transparency of potential barrier, distance between neighboring energy levels is increased, energy spectrum of relaxed protons becomes quasisdiscreet, which leads them to quantum distribution^{10,11}.

In the area of low temperatures ($T \leq 100\text{K}$) expansion parameter is increased significantly $\gamma \approx 0,01 \div 0,1$, contribution of non-linear members in field into the situation of proton relaxation is increased, which, in the limits of quasiclassic approach¹⁰, requires more strict consideration of proton tunneling influence on defect migration kinetics of Bierrum.

Calculation of theoretical spectra of the thermostimulated currents of depolarization (TCDP) in quadratic approximation¹⁰, as in works [3, 9], is based upon the solving of equation of Focker – Planck, at blocking electrodes. In¹⁰, exactness of quantum-mechanical approach at tunneling calculation is in the use of density matrix apparatus for the calculation of TCDP density.

Authors of^{12,13} apply the results of non-linear quantum theory of thermostimulated depolarization to the study of dimensional effects in nanometric layers (3 – 30 nm) of crystallohydrates (chalcantite) and layered silicates (phlogopite). Upon the base of quantum-mechanical formula for TCDP density by varying the thickness of crystal layer, it was defined, that low-temperature theoretical maximum of TCDP density is moved from the sphere of low temperatures (94 K – chalcantite 100 K - phlogopite) at 30 mkm to extra-low temperatures (25 K - chalcantite, 29K - phlogopite) at 3 nm, which is conditioned by abnormal structural changes of energy spectra of protons at temperatures of liquid helium (4 – 25K). Solving of transcendent spectral equation for protons shows, that at blocking contacts in the margin of crystal decreasing of layer thickness from 30000 nm to 3 nm conditions the decreasing of maximal number of energy layers of low-temperature relaxation oscillators in chalcantite from 2000 to 3, and from 3500 to 30 in phlogopite. Defined electrophysical features of nanocrystal state of proton semiconductors and dielectrics emphasize the

defining role of proton tunneling in nanoclusters (1-10 nm) at dielectric relaxation in layered crystals in the sphere of helium temperatures¹⁴.

Defined interest is attracted by the study of kinetics of low-temperature dielectric relaxation in layered crystals in alternate polarization field¹⁵⁻¹⁷.

Direct quantum-mechanical calculation of theoretical spectra of complex dielectric permittivity allows exact defining of proton tunneling influence on frequency and temperature spectra of tangent of dielectric losses angle in crystallohydrates and layered silicates in the range of low (about nitrogen) and extra-low temperatures. Application of density matrix to calculation of complex dielectric permittivity allows study of dimensional effects in HBC, quantum mechanism of spontaneous polarization in ferroelectric crystals (KDP, DKDP), magnetic quantum phenomena in antiferromagnetic dielectrics.

Statistical operator for ensemble of noninteracting protons

We consider statistic quantum properties of proton subsystem in HBC anionic sublattice, without external disturbance, in the area of low temperatures (70 – 100K), at mathematical description of defect migration of Bierrum, with the help of density matrix^{18,19}, calculated upon the base of Boltzmann statistics²⁰, and of solving of transient equation of Liouville^{18,19}.

$$\frac{\partial \hat{\rho}_s}{\partial t} + \frac{1}{i\hbar} [\hat{\rho}_s, \hat{H}_s] = 0 \quad \dots(1)$$

For non-disturbed system, composed of interacting subsystems (anionic sublattice and protons, migrating between anions), Hamiltonian looks as follows

$$\hat{H}_i = -\frac{\hbar^2}{2m} \sum_i \Delta_i - \frac{\hbar^2}{2M} \sum_j \Delta_j + \sum_q \hat{U}_q + \sum_{jk} \hat{U}_{jk} + \sum_{is} \hat{U}_{is} \dots(2)$$

In (2) proton mass; ion mass of anion sublattice; \hat{U}_{ij} – interaction energy of i-th proton and j-th proton of lattice; \hat{U}_{jk} – interaction energy j-th and k-th ions of lattice; \hat{U}_{is} – Coulomb energy of i-th and s-th protons.

According to results of experimental study of dielectric losses spectra and currents of thermostimulated depolarization in hydrogen-

Table 1. Temperature positions and amplitudes of tangent of losses angle of talc of Onotskoye deposit at polarization field frequency of 7 MHz depending on thickness of crystal layer

Layer thickness, nm	Amplitudes and temperature positions of theoretical maximums $tg\delta(T)$				
30000	$0,5 \cdot 10^{-4}$ (105)	$2,5 \cdot 10^{-3}$ (160)	$3,2 \cdot 10^{-3}$ (220)	$4,25 \cdot 10^{-3}$ (265)	$4,5 \cdot 10^{-3}$ (310)
3000	$1,9 \cdot 10^{-4}$ (96)	$2,8 \cdot 10^{-3}$ (157)	$3,24 \cdot 10^{-3}$ (219)	$4,25 \cdot 10^{-3}$ (265)	$4,5 \cdot 10^{-3}$ (310)
300	$2,3 \cdot 10^{-4}$ (88)	$5,4 \cdot 10^{-3}$ (146)	$4,2 \cdot 10^{-3}$ (215)	$4,25 \cdot 10^{-3}$ (265)	$4,5 \cdot 10^{-3}$ (310)
30	$4,6 \cdot 10^{-2}$ (50)	$6,8 \cdot 10^{-3}$ (127)	$7,2 \cdot 10^{-3}$ (207)	$4,25 \cdot 10^{-3}$ (265)	$4,5 \cdot 10^{-3}$ (310)
3	0,53 (22)	$5,8 \cdot 10^{-2}$ (103)	$5,5 \cdot 10^{-2}$ (190)	$5,3 \cdot 10^{-3}$ (259)	$4,9 \cdot 10^{-3}$ (308)

Table 2. Temperature positions and amplitudes of tangent of losses angle in gypsum at polarization field frequency of 7 MHz depending on thickness of crystal layer

Layer thickness, nm	Amplitudes and temperature positions of theoretical maximums $tg(T)$				
30000	$0,9 \cdot 10^{-4}$ (97)	$1,8 \cdot 10^{-3}$ (145)	$3,9 \cdot 10^{-3}$ (210)	$3,3 \cdot 10^{-3}$ (270)	$4,1 \cdot 10^{-3}$ (320)
3000	$1,6 \cdot 10^{-4}$ (89)	$2,3 \cdot 10^{-3}$ (142)	$4,3 \cdot 10^{-3}$ (209)	$3,3 \cdot 10^{-3}$ (270)	$4,1 \cdot 10^{-3}$ (320)
300	$4,5 \cdot 10^{-4}$ (80)	$5,4 \cdot 10^{-3}$ (138)	$4,9 \cdot 10^{-3}$ (200)	$3,3 \cdot 10^{-3}$ (270)	$4,1 \cdot 10^{-3}$ (320)
30	$6,6 \cdot 10^{-2}$ (47)	$7,4 \cdot 10^{-3}$ (130)	$9,6 \cdot 10^{-3}$ (190)	$3,5 \cdot 10^{-3}$ (267)	$4,1 \cdot 10^{-3}$ (320)
3	0,76 (15)	$3,4 \cdot 10^{-2}$ (102)	$5,1 \cdot 10^{-2}$ (183)	$4,9 \cdot 10^{-3}$ (264)	$4,5 \cdot 10^{-3}$ (317)

bonded crystals assumptions are obvious [1,3]: 1) equilibrium density of relaxation oscillators is small ($N_0 \approx 10^{16} - 10^{18} \text{ m}^{-3}$), which allows not to consider their Coulomb energy, being limited to model of ideal proton gas; 2) mass of ions of anion sublattice is much bigger than proton mass, which allows ignoring the ion motion and move to adiabatic approximation; 3) as times of ion subsystem relaxation are 2-3 times next larger than times of proton relaxation, let us study proton migration with some ionic background

$$\hat{H}_I = \sum_{jk} \hat{U}_{jk} = \text{Const}$$

Considering the accepted assumptions, Hamiltonian operator (2) of system becomes significantly simpler

$$\hat{H}_S = -\frac{\hbar^2}{2m} \sum_i \hat{\Delta}_i + \sum_{ij} \hat{U}_{ij} + \text{Const} \quad \dots(3)$$

Hamiltonian of undisturbed system may be shown as

$$\hat{H}_S = \hat{H}_{pr}^{(0)} + \hat{H}_{ph} + \hat{H}_{pr,ph} \quad \dots(4)$$

In (4) $\hat{H}_{pr}^{(0)}$ - Hamiltonian of proton subsystem;

\hat{H}_{ph} - Hamiltonian of phonon subsystem;

$\hat{H}_{pr,ph}$ - operator of proton-phonon interaction.

According to assumptions, accepted in HBC for proton relaxation [1,3]: 1) we ignore proton-phonon interaction $\hat{H}_{pr,ph} \rightarrow 0$; 2) Hamiltonian of phonon subsystem shall be considered as numerical operator $\hat{H}_{ph} \rightarrow \text{const}$; 3) we shall be limited to model of ideal proton gas.

So, Liouville equation (1), considering (5), looks as follows

$$\frac{\partial \hat{\rho}_{pr}^{(0)}}{\partial t} + \frac{1}{i\hbar} [\hat{\rho}_{pr}^{(0)}, \hat{H}_{pr}^{(0)}] = 0 \quad \dots(5)$$

Proton mass, significant in comparison with electron mass and small equilibrium defects density of Bierrum allows considering of

degeneration temperature of proton ensemble as close to absolute zero¹⁰⁻¹¹. Fermi energy of proton gas rushes to zero as well.

Solving of equation (5) shall be written down according to Boltzmann statistics for noninteracting protons, distributed according to energy levels of quasisdiscreet spectrum in field of crystal electric image

$$\hat{\rho}_{pr}^{(0)} = N_F \left\{ \sum_{n=0}^{\infty} \exp\left(-\frac{E_n}{k_B T}\right) \right\}^{-1} \times \exp\left(-\frac{\hat{H}_{pr}^{(0)}}{k_B T}\right) \dots(50)$$

where N_F - full quantity of the protons moving with the defined activation energy. Statistic operator of proton subsystem in presence of polarization field is calculated upon the base of transient equation of Liouville

$$\frac{\partial \hat{\rho}_{pr}}{\partial t} + \frac{1}{i\hbar} [\hat{\rho}_{pr}; \hat{H}_{pr}] = 0 \quad \dots(6)$$

where $\hat{H}_{pr} = \hat{H}_{pr}^{(0)} + \hat{W}_{el}$ - proton Hamiltonian,

disturbed by external field; $\hat{H}_{pr}^{(0)}$ - non-disturbed proton Hamiltonian; \hat{W}_{el} - disturbed allowance;

$\hat{\rho}_{pr} = \hat{\rho}_{pr}^{(0)} + \delta\hat{\rho}_{pr}$ - unbalanced proton statistic operator; $\delta\hat{\rho}_{pr}$ - unbalanced allowance for non-disturbed statistic operator (50).

Let operators $\frac{\partial \hat{\rho}_{pr}}{\partial t}$ and $\frac{1}{i\hbar} [\hat{\rho}_{pr}; \hat{H}_{pr}]$

influence the wave function of proton in n stationary state, excluding the second-order terms in field $\delta\hat{\rho}_{pr}(\hat{W}_{el}, \Psi_n)$, $\hat{W}_{el}(\delta\hat{\rho}_{pr}, \Psi_n)$. Than, basing upon (6) we see

$$\frac{\partial \delta\hat{\rho}_{pr}}{\partial t} + \frac{1}{i\hbar} [\delta\hat{\rho}_{pr}, (\hat{H}_{pr}^{(0)} + \hat{W}_{el})] - \hat{H}_{pr}^{(0)}(\delta\hat{\rho}_{pr}, \Psi_n) + \delta\hat{\rho}_{pr}(\hat{W}_{el}, \Psi_n) - \hat{W}_{el}(\delta\hat{\rho}_{pr}, \Psi_n) = 0 \dots(7)$$

Inserting the scalar operator into (7), we get the equation

$$\frac{\partial \hat{u}_n}{\partial t} + \frac{E_n}{i\hbar} \hat{u}_n - \frac{1}{i\hbar} \hat{H}_{pr}^{(0)} \hat{u}_n + \frac{1}{i\hbar} [\hat{\rho}_{pr}^{(0)}; \hat{W}_{el}] \Psi_n = 0 \quad \dots(8)$$

For model of rectangular image in the area of s - th potential pit

$$\frac{\partial \hat{u}_{ns}}{\partial t} + \frac{E_n}{i\hbar} \hat{u}_{ns} + \frac{\hbar}{2mi} \frac{\partial^2 (\hat{u}_{ns})}{\partial x^2} + \frac{1}{i\hbar} [\hat{\rho}_{pr}^{(0)}; \hat{W}_{el}] \Psi_{ns} = 0 \quad (8.0)$$

Table 3. Thermo stimulated currents of depolarization in chalcantite calculated by a method density matrixes at various of crystal layers' thickness

Thickness of a layer, nanometer	Amplitudes and temperature provisions of theoretical maxima of thermo stimulated current					
30000	$8 \cdot 10^{-10}$ (94)	$9 \cdot 10^{-10}$ (138)	$2 \cdot 10^{-9}$ (170)	$2 \cdot 10^{-10}$ (206)	$3 \cdot 10^{-10}$ (230)	10^{-9} (246)
3000	$9 \cdot 10^{-9}$ (90)	$9 \cdot 10^{-9}$ (130)	$2,5 \cdot 10^{-9}$ (167)	$2 \cdot 10^{-10}$ (205)	$3 \cdot 10^{-10}$ (230)	10^{-9} (246)
300	$5 \cdot 10^{-8}$ (60)	$8,5 \cdot 10^{-8}$ (115)	$7,5 \cdot 10^{-8}$ (165)	$3 \cdot 10^{-10}$ (204,5)	$3 \cdot 10^{-10}$ (230)	10^{-9} (246)
30	$9 \cdot 10^{-7}$ (50)	10^{-6} (95)	10^{-7} (165)	$3,5 \cdot 10^{-10}$ (202)	$4,5 \cdot 10^{-10}$ (229)	10^{-9} (246)
3	10^{-5} (25)	$3 \cdot 10^{-6}$ (85)	$9 \cdot 10^{-5}$ (159)	$5,2 \cdot 10^{-10}$ (200)	$5 \cdot 10^{-10}$ (228)	$1,35 \cdot 10^{-7}$ (245)

Table 4. Thermo stimulated currents of depolarization in phlogopite calculated by a method density matrixes at various of crystal layers' thickness

Thickness of a layer, nanometer	Amplitudes and temperature provisions of theoretical maxima of thermo stimulated current					
30000	$7 \cdot 10^{-9}$ (100)	$8 \cdot 10^{-9}$ (130)	$3 \cdot 10^{-8}$ (178)	$2 \cdot 10^{-8}$ (206)	$8,5 \cdot 10^{-9}$ (235)	10^{-8} (257)
3000	$8 \cdot 10^{-8}$ (88)	$9 \cdot 10^{-8}$ (122)	$3,8 \cdot 10^{-8}$ (174)	$2 \cdot 10^{-8}$ (206)	$8,5 \cdot 10^{-9}$ (235)	10^{-8} (257)
300	$3 \cdot 10^{-7}$ (57)	$3,5 \cdot 10^{-7}$ (108)	$8,5 \cdot 10^{-7}$ (172)	$2 \cdot 10^{-8}$ (206)	$9 \cdot 10^{-9}$ (235)	10^{-8} (257)
30	$5 \cdot 10^{-8}$ (48)	$8,3 \cdot 10^{-8}$ (89)	10^{-8} (169)	$7 \cdot 10^{-8}$ (204)	$9,5 \cdot 10^{-9}$ (233)	10^{-8} (257)
3	$3,5 \cdot 10^{-5}$ (29)	$7,5 \cdot 10^{-5}$ (80)	$9,4 \cdot 10^{-5}$ (168)	$9,2 \cdot 10^{-8}$ (200)	$1,2 \cdot 10^{-8}$ (232)	$1,3 \cdot 10^{-8}$ (256, 9)

and s -th potential barrier

$$\frac{\partial \hat{u}_{ms}}{\partial t} + \frac{E_s - U_s}{i\hbar} \hat{u}_{ms} + \frac{\hbar}{2mi} \frac{\partial^2 (\hat{u}_{ms})}{\partial x^2} + \frac{1}{i\hbar} \left[\hat{D}_{s,r}^{(0)}; \hat{W}_{s,r} \right] \hat{u}_{ms} = 0 \dots (8.b)$$

Upon the base of (6), we obtain the one-dimensional continuity equation

$$q \frac{\partial (\delta \hat{N}_{s,r})}{\partial t} + \frac{\partial \hat{j}_{s,r}}{\partial x} = 0 \dots (9)$$

and there we find the operator of proton flow density

$$\hat{j}_{s,r}(\mathbf{x}; t) = -q \frac{\partial}{\partial t} \int \delta \hat{N}_{s,r}(\mathbf{x}; t) d\mathbf{x} + \hat{j}_{s,r}(t) \dots (10)$$

For model of blocking electrodes

$$\hat{j}_{s,r}(\mathbf{d}; t) = \hat{j}_{s,r}(0; t) = 0 \dots (11)$$

In zero time polarization is absent

$$\hat{u}_{ms}(\mathbf{x}; 0) = 0, \hat{u}_{ms}(\mathbf{x}; 0) = 0 \dots (12)$$

Solving of equations (8.0, 8.b) shall be made together with Poisson equation [10,11]

$$\frac{\partial \hat{E}}{\partial x} = \frac{q}{\epsilon_0 \epsilon} \delta \hat{N}_{s,r}(\mathbf{x}; t) \dots (13)$$

considering the boundary condition [1]

$$\int_0^d \hat{E}(\mathbf{x}; t) d\mathbf{x} = V_0 \exp(i\omega t) \dots (14)$$

where V_0 , ω - amplitude and frequency of external field respectively.

Solving of operational differential equations (8.0, 8.b) was built in finite differences.

2. Theoretical spectra of complex dielectric permittivity

Upon the base of quantum-mechanical expression for excess concentration of relaxation oscillators (protons) [10], let us write down the polarization operator of proton subsystem

$$\hat{P} = q \sum_{n=0}^{\infty} (\Psi_n^* \hat{x}) \hat{u}_n \dots (15)$$

Averaging (15) subject to coordinate and energy shall be executed with the help of unbalanced polarization density matrix

$$\langle \hat{P} \rangle = \int_0^d \Psi^* \hat{P}(\mathbf{x}, t) \Psi d\mathbf{x} \dots (16)$$

Crystal polarization in alternating field [3]

$$\langle \hat{P} \rangle = \epsilon_0 (\epsilon^* - \epsilon_\infty) E_0 \exp(i\omega t) \dots (17)$$

Upon the base of (16), (17), let us write down theoretical spectrum of complex dielectric permittivity

$$\epsilon^*(\omega, T) = \epsilon_\infty + \frac{1}{\epsilon_0 E_0} \exp(-i\omega t) \int_0^d \Psi^* \hat{P}(\mathbf{x}, t) \Psi d\mathbf{x} \dots (18)$$

Quantum-mechanical calculation of relaxation oscillator parameters in proton semiconductors and dielectrics

First experimental studies of dielectric losses in complex hydrogen-bonded crystals (layered silicates, crystalhydrates, hydrous micas, layered nonstoichiometric minerals) were started by Vodopianov K.A., who measured frequency and temperature spectra of tangent of dielectric losses angle $\text{tg} \delta$ and dielectric permittivity of ϵ' row of crystals at temperatures higher than 190 K and frequencies of 50 - 10⁷ Hz [3].

In works of Tonkonogov M.P., Blistanov ..., Poplavko Yu. "., V. "., Timokhin, V., Mironov spectra precised measurements of frequency and temperature spectra $\text{tg} \delta$ were executed at crystals of muscovite $\text{KAl}_2(\text{AlSi}_2\text{O}_{10})(\text{OH})_2$, talc of Onotskoye deposit $\text{Mg}_3(\text{Si}_4\text{O}_{10})(\text{OH})_2$, phlogopite $\text{KMg}_3(\text{Si}_3\text{O}_{10})(\text{OH})_2$, chalcantite $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and gypsum CaSO_4 ¹⁻³.

In frequency spectra of tangent of losses angle of talc and gypsum in wide temperature range (80 – 400 K) 1 - 3 monorelaxation maximums were found, conditioned by Bierrum defects relaxation and refocusing of water molecules in electric field. In crystals $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in temperature range of 100 – 130 , proton conductivity was found experimentally, which is overlaid by high ion conductivity in the area of high temperatures (130 – 450 K)³.

In frequency spectra $\text{tg} \delta$ of talc of Onotskoye deposit, measured at temperature $T = 80$ K (low temperature spectrum), three maximums are found, at Hz, Hz and Hz, whose positions are almost unchangeable subject to frequency at higher temperatures ($T = 98$ K, 112 K, 125 K), and amplitudes of maximums increase 1,5-fold and 2-fold. In gypsum maximums Hz, Hz 8 Hz correspond to low-temperature branch (86 K) of frequency spectra $\text{tg} \delta$ [1]. At transfer to frequency spectra at

higher temperatures (112 K, 124 K, 150 K) of measurement, in gypsum, as well as in talc, maximums of $\text{tg}\delta$ are almost immovable along the frequency axis, and increase 1,3-fold (112 K), 1,45-fold (124 K) in amplitude. In high temperature branches ($T = 150 - 270$ K), in both talc and gypsum, all the three maximums are moved with the temperature increasing towards higher frequencies and increase in amplitude on 50 – 100 %.

Regularities of temperature behavior of spectra defined experimentally, allow confirming that low-temperature branches (80 – 112 K) of spectra of losses angle tangent are mainly defined by tunnel relaxation of Bierrum defect and are slightly sensitive to temperature subject to frequency parameter, and increasing of maximums amplitude No. 1-3 with temperature measuring increase in the range 80 – 125 K is conditioned by insignificant increase of structure defects concentration. Thickness of experimental samples was 30 μm [1,3].

In measuring of temperature spectra $\text{tg}\delta$ of talc of Onotskoye deposit at polarization frequency 4 Hz 4 maximums were found at temperatures 160 K, 220 K, 265 K, 310 K, and in gypsum – at temperature 145 K, 210 K, 270 K, 320 K. At frequency decreasing from 4 Hz to 1 Hz first maximum in talc (160 K) moved to 75 K, and in gypsum – from 145 K to 79 K. Experimental activation energy of first maximum $\text{tg}\delta(T)$ in talc amounted 0,53 eV, and in gypsum - 0,25 eV.

Comparison of activation energies, calculated subject to temperature and frequency spectra allows confirming, that the first maximum $\text{tg}\delta(T)$ of talc crystals and in gypsum is connected with relaxation of Bierrum ionization defects, the second maximum is conditioned by refocusing of crystallization water molecules, the third peak is connected with relaxation of Bierrum defects, and the fourth maximum was connected with Bierrum orientation defects VL, VD.

Due to weak resolving power of resonant device, method of losses angle tangent does not allow finding low-temperature maximums in spectra $\text{tg}\delta(T)$, connected with proton tunneling inside and between ions of anion sublattice.

Upon the base of (18) we have carried the analytical study of spectra and $\text{tg}\delta(T)$ by method of comparison function minimization and parameters of relaxation oscillators in talc of

Onotskoye deposit and gypsum in temperature range 70 – 350 K were calculated. In calculation of theoretical spectra experimental temperatures were accepted: for talc $T = 80, 98, 112, 125, 150, 218, 250, 298$ K; for gypsum $T = 86, 112, 124, 150, 200, 273, 293$ K. In calculation of theoretical dependences $\text{tg}\delta(T)$ frequency of alternating field varied from 4 Hz till 1 Hz. Crystal thickness was accepted as 30 μm .

Expression (18) allowed, by density matrix method, calculate the activation energy, temperature position and amplitude of low-temperature maximum $\text{tg}\delta(T)$ at 4 Hz. Subject to results of numerical calculation, for talc of Onotskoye deposit: $E_a = 0,53$ eV, and for gypsum: $E_a = 0,25$ eV.

Upon the base of (19), by variation of crystal layer thickness from 30 μm to 3 nm moves of theoretical temperature maximums $\text{tg}\delta(T)$ were defined at 4 Hz for talc of Onotskoye deposit and gypsum (tables 1,2).

According to tables 1,2, low-temperature maximum is the most sensitive to change of thickness of crystal layer, and in the result of this: low-temperature theoretical maximum in talc with decreasing of layer thickness from 30 μm to 3 nm is moved from low (105 K) towards extra-low temperatures (22 K), and amplitude of maximum is increased from 0,53 to 0,75; in gypsum maximum is moved from 97 K to 15 K with increasing of amplitude from 0,25 at 30 μm to 0,45 at 3 nm.

Increasing of experimental temperature of monorelaxational peak, according to tables 1,2, leads to attenuation of dependence of maximum parameters on layer thickness. Parameters of high-temperature maximums (310 K – in talc of Onotskoye deposit, 320 K – in gypsum) at varying of crystal layer thickness are almost unchangeable.

Regularities, found in quantum-mechanical calculation of $\text{tg}\delta(\omega, T)$ spectra, confirm, that abnormally high dielectric losses in layered crystals (crystallohydrates, layered silicates) at extra-low (helium) temperatures are conditioned by proton tunneling in nano-clusters (1- 10 nm), which play the intermediate role between isolated atoms and flakes of polycrystalline structures. Apparatus of density matrix (expression 18) allows studying non-linear kinetic phenomena in proton semiconductors at extra-low temperatures, considering the quantum distribution of protons according to energy levels of quasisdiscreet

spectrum considering the alternating polarization field.

Dimensional effects at the thermo stimulated depolarization in nanometer layers of proton semiconductors and dielectrics

The abnormal regularities of temperature behavior of low-temperature ranges $\text{tg}\delta(T)$ above in nanometer layers of proton semiconductors (onotsky talc, 105 K; plaster, 97 K) investigated earlier found dimensional effects confirm at thermo stimulated depolarization in layers chalcantite (94 K) and phlogopite (100 K) at a variation of thickness of a layer from 30 microns to 3 nanometers.

On the basis of full averaging of the density's operator of TSTD on the coordinate and energies by means of a matrix density's device received quantum – mechanical expression for the measured of density's quantity of thermostimulated currents of depolarization (TCDP) [12]

$$\langle \bar{J} \rangle = \sum_{n=0}^{\infty} \rho_{nn} \langle E_n, t \rangle \times \int_0^d \Psi_n^* \hat{J}(x, t) \Psi_n dx \dots (19)$$

in square approach on a polarizing field [12]

$$\langle \bar{J} \rangle = \langle \bar{J}_0(t) \rangle + E_0 \langle \bar{J}_1(t) \rangle + E_0^2 \langle \bar{J}_2(t) \rangle \dots (20)$$

At calculation of relaxation oscillator's parameters in phlogopite's crystal depolarization's experimental range of thermo stimulated current of phlogopite's model is used. Its thickness is $d=30$ of the micron. It previously calcinated at a temperature of 873 K and polarized in electric field by intensity $E=10^6$ V/m at a polarization's temperature of $T=373$ [12]. Speed of linear heating in experiment made with $\dot{T}=0,1$ K/mines, the lattice constant in mathematical model was accepted by $a=0,85$ ú.

For calculation of relaxation oscillators' parameters in a chalcantite crystal results of precision measurements of polarized models in electric field by intensity $E=2.10^5$ V/m at a polarization's temperature of $T=300$ were used [1,2]. Speed of linear heating in experiment made $\dot{T}=5,5$ K/mines [12].

Results of density's theoretical ranges' numerical calculation of TSTD in chemically pure chalcantite $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and natural phlogopite $\text{KMg}_3(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$ at a variation of a crystal layer's thickness from 3 nanometers to 30000

nanometers are given in tables 3,4.

According to results of numerical calculation in chalcantite of a crystal layer's thickness's reduction from 30 microns to 3 nanometers provides to shift of a low-temperature maximum from 94 to 25 K, and amplitude of density

of TCDP thus increases from $8.10^{-10} \frac{\text{A}}{\text{m}^2}$ to $10^{-5} \frac{\text{A}}{\text{m}^2}$

(table 3), and amplitude of a theoretical maximum in phlogopite grows from 7.10^{-9} at a thickness of crystal of 30 microns to at 3 nanometers (table 4), that points to of a power range's structure essential influence of protons on kinetics of low-temperature proton conductivity in nanometer layers of HBC (proton superconductivity)

CONCLUSIONS

1. At low temperatures (70 – 100 K), mechanism of dielectric losses in layered crystals is defined by proton tunneling in anion sublattice.
2. Quantum-mechanical formulae for numerical calculation of theoretical spectra $\text{tg}\delta(\omega, t)$ in layered crystals at low temperatures (70 – 100 K) were composed.
3. With the help of apparatus of density matrix parameters of low-temperature maximum of tangent of dielectric losses angle $\text{tg}\delta(T)$ at frequency of polarization field of 7 MHz in talc of Onotskoye deposit and gypsum were studied.
4. Effects of nano-crystal state of talc of Onotskoye deposit and gypsum were studied. Extremely high theoretical amplitudes of losses angle tangent with move of low-temperature (80 – 100 K) maximum $\text{tg}\delta(T)$ towards the extra-low (10 – 25 K) temperatures at nanometric thicknesses of crystal layers were found.

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