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NON – LINEAR QUANTUM EFFECTS DURING MIGRATORY POLARIZATION IN RANGE OF EXTRA – LOW TEMPERATURES

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The use the limb - difference scheme for calculating of the thermally stimulated current of depolarization allows to identify the characteristic of low temperature relaxators size effects. These effects were caused by anormal displacement of the theoretical maximum termo depolarization current density at lower temperatures of (12 – 14) K with increasing of amplitude maximum on one - two orders of magnitude on a nanometer crystal layers with hydrogen bonds. On the model of a multi pit potential of relief with rectangular shape and ohmic contacts at the boundaries of the crystal it is shown that decreasing of potential pits number energy band width is decreasing. But the minimum distance between adjacent energy bands is increasing, the energy spectrum becomes quasi discrete, potential barrier transparency is increasing, the tunneling causes quantum effects are enhancing. It was established that with locking pins at the boundary of crystal layers in the nanometer layers (3 nm) in comparing with crystals of thickness 30microns the maximum number of associated energy levels of relaxators with low temperature is decreasing by 99% from the current thermo depolarization theoretical maximum displacement toward low temperature of (65 -75) K. Whereas increasing of density amplitude TSDC on (3 – 4) orders of magnitude, while the high-temperature defects of Bjerrum increase only on 1% when and temperature shift is on (0.1 – 1) K at a constant amplitude. Therefore it can be argued that in the nanometer crystals with hydrogen ties of polarization at very low temperatures (4 – 25) K is caused by nanoclusters.

Keywords: Maxwell relaxation; quantum effects; diffusion; depolarization; temperatures; protons electromigration; crystal layers; electrodes.

Introduction

Studies of the last decade in last century have greatly expanded understanding of the effects associated with the size of the crystallites in solids. Particular attention is drawn to nanoclusters, whose properties are intermediate between isolated atoms and polycrystalline solid body [1 - 3]. An important role in studying the properties of nanomaterials can play not only the grain size but also the structure and condition of the grain boundaries [1]. Reducing the size of crystallites below a certain threshold results in a significant change in the properties of the solid. These effects arise when the average crystal grain size is not greater than 100 nm, they are most clearly pronounced when the grain size is less than 10 nm [1].

1. Anomalous effects in crystalline layers of nanometer-size (10 - 100 nm)

The possibility of proton relaxation anomalies in crystalline layers of nanometer size lies in the equation that defines the relaxation time τ_n and the resulting solution of the kinetic equation [1], [4], [5]

$$1/\tau_n = 1/\tau_M + 1/\tau_{nD},$$

where τ_n - relaxation time.

Since diffusion relaxation time corresponding to the n-th space harmonic, in the linear approximation depends on the thickness d of the sample [1]

$$\tau_{nD} = d^2/\pi^2 Dn^2.$$

Maxwell relaxation time does not depend on d - the total length of all the space-charge region in this direction [1].

$$\tau_M = \varepsilon_0 \varepsilon / N_0 q \mu.$$

where d - the total length of all the space-charge region in this direction; D - the diffusion coefficient; N_0 - number of water molecules in ice crystal; q - ion charge; ε - permeability; μ - coefficient of mobility of charge carriers.

Since the diffusion relaxation dominates at low temperatures, when the main contribution to the polarization of migration make tunnel junctions based on the diffusion time relaxation dependence on the thickness of the crystal we can assume that the size effects in hydrogen-bonded crystals are created due to the quantum properties of the proton subsystem, manifested in materials of this class at the temperatures below the critical (near the nitrogen).

2. Investigation of size effects in hydrogen-bonded crystals by numerical solution of the kinetic equation in finite differences

In section 2.5 [1] the mechanism of dielectric relaxation in materials with hydrogen bonds was described by means of the kinetic theory built on the solution of the Fokker-Planck equation (2.13) obtained from the system of kinetic equations of electromigration of protons on hydrogen bonds in the approximation of the collision integral (1.4) [1]. Solution of the nonlinear Fokker-Planck equation (2.21) [1], (2.34) [1] is achieved by expanding the unknown function in powers of the polarizing field (2.15) [1] is superimposed on the crystal in the preparation of thermoelectrets [5], was carried out as a result of linearization, which made it possible to reduce the nonlinear kinetic equation (2.13) [1] to the system of linear kinetic equations. Analysis of the contribution of the quadratic component solution (2.35) [1] in the description of the electrical transport is possible by numerical solution of the kinetic equation and comparison with the results of analytical study, which is valid in weak fields in the temperature range (100 - 290 K), for small values of the expansion parameter [5 - 11]

$$\Gamma = \frac{B_0 q E_0 \delta_0}{A_0} \approx 10^{-3} - 10^{-2}.$$

where q - ion charge; E_0 - the value of a uniform electric field intensity; δ_0 - the low-frequency specific electrical conductivity; A_0 - initial amplituda.

At temperatures of (70 - 100) K, the value of small parameter is markedly being increased [12, 13, 14]. More rigorous investigation of anomalies in the crystalline layers of nanometer size carried out by the shift of the theoretical density maxima of TSDC to low temperatures with thickness decreasing of the layer can be done by expanding the concentration relaxators in powers of the lattice constant ζ in the neighborhood of the i -th potential well [1].

As a result of this procedure, the kinetic equation of protons electromigration in hydrogen bonds (1.4) [1] is reduced to the nonlinear kinetic equation of proton relaxation [15]

$$\frac{\partial N}{\partial t} = \frac{\partial^2}{\partial x^2} \{ \Omega(x, t) N(x, t) \} - \frac{\partial}{\partial x} \{ \mathfrak{R}(x, t) N(x, t) \}, \quad (1)$$

where Ω and \mathfrak{R} are nonlinear functions of the electric field intensity

$$\Omega(x, t) = \frac{v \zeta^2}{2} \left\{ \exp\left(-\frac{U_0}{k_B T}\right) \operatorname{ch}\left(\frac{\Delta U}{k_B T}\right) + \right.$$

$$+ X \left(\frac{\exp(-\Lambda) - \operatorname{ch}\left(\frac{\Delta U}{k_B T}\right) \exp(-X)}{X - \Lambda} \right) + \frac{\Delta U}{k_B T} \left(\frac{\operatorname{sh}\left(\frac{\Delta U}{k_B T}\right) \exp(-X)}{X - \Lambda} \right), \quad (2)$$

$$\mathfrak{R}(x, t) = v\zeta \left\{ \exp\left(-\frac{U_0}{k_B T}\right) \operatorname{sh}\left(\frac{\Delta U}{k_B T}\right) + \right. \\ \left. + X \left(\frac{\operatorname{sh}\left(\frac{\Delta U}{k_B T}\right) \exp(-X)}{X - \Lambda} \right) + \frac{\Delta U}{k_B T} \left(\frac{\operatorname{ch}\left(\frac{\Delta U}{k_B T}\right) \exp(-X) - \exp(-\Lambda)}{X - \Lambda} \right) \right\}. \quad (3)$$

As in paragraph 2.5 [1], the numerical calculation of thermally stimulated depolarization current let's make, determining the number of the initial condition of the kinetic equation solution describing the process of proton relaxation in the crystal is placed in an external uniform electric field of an intensity E_0 at a fixed temperature polarization. The kinetic equation (1) with respect to the excessive concentration of relaxation oscillators in this case has the form [16]

$$\frac{\partial \Delta N}{\partial t} = \omega_1 \frac{\partial^2 \Delta N}{\partial x^2} + \omega_2 E \frac{\partial \Delta N}{\partial x} \Delta N + \omega_3 \Delta N \frac{\partial \Delta N}{\partial x} + \\ + \omega_4 (\Delta N)^3 + \omega_5 E (\Delta N)^3 + \omega_6 \frac{\partial \Delta N}{\partial x} + \omega_7 E \frac{\partial \Delta N}{\partial x} + \\ + \omega_8 (\Delta N)^2 + \omega_9 E (\Delta N)^2 + \omega_{10} E \Delta N + \omega_{11} \Delta N. \quad (4)$$

Describing the thermal depolarization kinetic equation (1) takes the form [16]

$$\frac{\partial \Delta N}{\partial t} = D' \frac{\partial^2 \Delta N}{\partial x^2} + \omega'_1 (\Delta N)^3 + \omega'_2 (\Delta N)^2 + \omega'_3 \Delta N, \quad (5)$$

The coefficients of the equations (4) and (5) are given in [17].

The initial condition for thermally stimulated depolarization, as in the paragraph 2.5 [1], we present the sum of excess concentrations of hetero- and homocharge (2.33) [1]. The initial distribution of heterocharge we obtain in the result of the numerical solution of equation (4) in blocking electrodes. Finite-difference form of the equations (4), (5), defining for the corresponding model of the electrodes [18] is also given in [17]. Writing current density of thermal depolarization in accordance with the results of the kinetic theory of [4, 19, 20] in the form of a time derivative of polarized crystal [15, 16]

$$J(x, t) = -qx \frac{\partial \Delta N}{\partial t} \quad (6)$$

averaging (6) over the thickness of the crystal with the finite - difference scheme [1], we obtain the equation [16]

$$\langle J_k \rangle = -\frac{q}{L} \sum_{i=0}^L \zeta_i \left\{ (D')_i^k \frac{\Delta N_{i+1}^k + \Delta N_{i-1}^k - 2\Delta N_i^k}{dx^2} + \right. \\ \left. + (\omega'_1)_i^k (\Delta N_i^k)^3 + (\omega'_2)_i^k (\Delta N_i^k)^2 + (\omega'_3)_i^k \Delta N_i^k \right\}, \quad (7)$$

$$\text{where } \zeta_i = \frac{2k-1}{2} dx.$$

Application of finite - difference scheme (7) to the calculation of the theoretical spectra of thermally stimulated depolarization currents at blocking electrodes allowed to establish a non-linear dependence of the density of the TSDC intensity of the polarizing field and at a higher level, in contrast to the results of paragraph 2.5 [1], to identify the size effects in nanometer layers of bluestone (Table 1) and phlogopite mica (Table 2). Comparison of tables 15, 16 [1] and tables 1 and 2 shows that the use of the finite difference method to the solution of the kinetic equation of proton relaxation displaces of the density of the thermally stimulated current low-temperature relaxation oscillators theoretical maximum by 12 - 14 K to lower temperatures in comparison with the measurement results, while as a quadratic approximation of the maximum displacement provided only 8 - 9 K.

Table 1. Amplitude and temperature position of the theoretical maximum density of the thermally stimulated depolarization current bluestone calculated by the method of finite differences for different thicknesses of the crystalline layer [21]

The thickness of the layer, nm	Amplitude and position of the thermally stimulated current theoretical maximum temperature					
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	$8,4 \cdot 10^{-10}$ (90)	$9,6 \cdot 10^{-10}$ (137)	$2,3 \cdot 10^{-9}$ (167)	$2,1 \cdot 10^{-10}$ (206)	$3 \cdot 10^{-10}$ (230)	10^{-9} (246)
300	$8,6 \cdot 10^{-10}$ (89)	10^{-9} (135,5)	$2,5 \cdot 10^{-9}$ (166)	$2,3 \cdot 10^{-10}$ (205)	$3 \cdot 10^{-10}$ (230)	10^{-9} (246)
30	$5,5 \cdot 10^{-9}$ (85)	$1,4 \cdot 10^{-9}$ (130)	$2,9 \cdot 10^{-9}$ (165)	$2,35 \cdot 10^{-10}$ (205)	$3,14 \cdot 10^{-10}$ (229)	10^{-9} (246)
3	10^{-8} (80)	$2,5 \cdot 10^{-9}$ (125)	$3 \cdot 10^{-9}$ (160)	$2,5 \cdot 10^{-10}$ (202)	$3,3 \cdot 10^{-10}$ (228)	$1,3 \cdot 10^{-9}$ (245)

Table 2. Amplitude and temperature position of the theoretical maximum density of the thermally stimulated depolarization current in phlogopite mica calculated by the method of finite differences for different thicknesses of the crystalline layer [21]

The thickness of the layer, nm	Amplitude and position of the thermally stimulated current theoretical maximum temperature					
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^{-9} (257)
3000	$7,3 \cdot 10^{-9}$ (95)	$8,5 \cdot 10^{-9}$ (125)	$3,3 \cdot 10^{-8}$ (176)	$2,14 \cdot 10^{-8}$ (206)	$8,5 \cdot 10^{-9}$ (235)	10^{-9} (257)
300	$7,4 \cdot 10^{-9}$ (93)	10^{-8} (122)	$3,5 \cdot 10^{-8}$ (174)	$2,3 \cdot 10^{-8}$ (206)	$8,5 \cdot 10^{-9}$ (235)	10^{-9} (257)
30	$9 \cdot 10^{-9}$ (89)	$1,7 \cdot 10^{-8}$ (120)	$3,6 \cdot 10^{-8}$ (170)	$2,4 \cdot 10^{-8}$ (205)	$8,55 \cdot 10^{-9}$ (234)	10^{-9} (257)
3	$6 \cdot 10^{-8}$ (88)	$4 \cdot 10^{-8}$ (118)	$4 \cdot 10^{-8}$ (169)	$2,7 \cdot 10^{-8}$ (203)	$8,7 \cdot 10^{-9}$ (232)	$1,5 \cdot 10^{-9}$ (256)

In the third peak (170 K chalcantite, 178 K in phlogopite) is to be calculated in the quadratic approximation to the external field shift was 4 - 5 K (Tables 15 [1], 16 [1]), and by numerical calculation increases up to 9 - 10 K (Tables 1,2). Even with the high-temperature relaxation due to ionization defects OH^- (230 K for the bluestone, 235 K in phlogopite) equation (7) leads to a shift of the maximum density TSDC on 2 - 3 with a decrease in thickness of the crystal of 3 nm to 30000 nm (Tables 1,2).

From tables 15 in [1], 16 in [1] and 1, 2 there is one important law related to the fact that the displacement of the theoretical maximum thermal depolarization current accompanied by an increase of its amplitude. Finite difference method clearly revealed this anomaly.

For example, in chalcantite, low temperature measured at the maximum temperature of 94 K and equal amplitude $8 \cdot 10^{-10} \text{ A/m}^2$ with decreasing layer thickness of 30000 to 3 nm shifting to 80 K reaches amplitude 10^{-8} A/m^2 (Table 1). In phlogopite respectively maximum measured at 100 K is equal to the amplitude $7 \cdot 10^{-9} \text{ A/m}^2$ shifted to 88 K, and increased to the amplitude $6 \cdot 10^{-8} \text{ A/m}^2$ (Table 2).

Displacement of the thermally stimulated current theoretical maxima in crystalline layers of nanometer size in the region of low temperatures, can be explained by the diffusion relaxation, the role of which increases substantially when the crystal thickness is 3 - 30 nm, and when the diffusion relaxation time is by 5 - 10 orders less than the Maxwell and migration polarization flows in mainly due to the tunneling protons.

3. Investigation of size effects in nanometer crystal layers by the density matrix method

In subparagraphs 3.1.4.3 [1] and 3.1.4.4 [1] numerical calculation quasi-discrete proton spectrum in hydrogen-bonded crystals have a substantial dependence on the energy bands populations at the ohmic electrodes (3.59) [1] (Tables 11 [1], 12 [1]) and the energy levels of quasi-discrete spectrum for blocking electrodes (3.60) [1] (Tables 13 [1], 14 [1]) on the parameters of the potential relief (activation energy, the width of the potential barrier).

Against the background of the identified in 3.1.4.3 [1] and 3.1.4.4 [1] laws (Table 9 – 14 [1]) can be assumed that in the low, especially ultra-low temperatures the quantum nature of the statistical distribution of protons over the energy levels affect the mechanism of size effects [18].

From the classical course in quantum mechanics we know that the change in size of the region of localization of the microparticles significantly affects on the structure of its energy spectrum in a

given force field. For example, particle in potential pit with infinitely high walls has energy spectrum which depends strongly on the width of the pit [18]

$$E_n = \frac{\pi^2 \hbar^2 n^2}{2ma^2}.$$

where m - is the number of potential wells; n - an integer; a - the distance between adjacent positions of equilibrium of defects in the crystal lattice.

In this case, the distance between the adjacent energy levels increases with decreasing pit's width [18]

$$E_{n,n+1} = \frac{\pi^2 \hbar^2 (2n+1)}{2ma^2}.$$

For the model of the double symmetric potential pit with a rectangular shape and blocking contacts on its borders in accordance with (3.36) [1], assuming $N_{\text{я}} = 2$ we obtain the expression

$$E_{n,n+1} = \frac{\pi^2 \hbar^2}{4ma^2} (n+1),$$

which implies that the decreasing of this pit in two times leads to the decreasing of distance between the first two energy levels in two times [18]

$$\frac{E_{0,1}^{1-\text{яМ}}}{E_{0,1}^{2-\text{яМ}}} = 2,$$

at an elementary example we see that reducing the model size is accompanied by increasing of average distance between adjacent energy levels.

For the model of a multipit potential relief with rectangular shape and ohmic contacts at the boundaries of the crystal size effects can be traced analytically for an arbitrary number of potential pits ($N_{\text{я}} > 1$). Thus, according to the equation (3.15), the distance between the ceiling of k -th and the bottom of n -th energy band, when $n > k$, we find with a help of expression [22]

$$E_{k,n}^{(-)} = \frac{\pi^2 \hbar^2 (n^2 - k^2 + n - k)}{2ma^2} - \frac{\hbar \omega}{\pi} (\exp(-\eta_k) + \exp(-\eta_n)) \cos\left(\frac{\pi}{N_{\text{я}} + 1}\right). \quad (8)$$

where m is the number of potential wells; k -th and the bottom; n -th energy band; a - the distance between adjacent positions of equilibrium of defects in the crystal lattice; ω -the dimensionless frequency of the external electric field. $N_{\text{я}}$ - number of potential pits

Then, from (4.1), for the model of two potential pits ($N_{\text{я}} = 2$)

$$E_{k,n}^{(-)}(2) = \frac{\pi^2 \hbar^2 (n^2 - k^2 + n - k)}{2ma^2} - \frac{\hbar \omega}{2\pi} (\exp(-\eta_k) + \exp(-\eta_n)), \quad (9)$$

and for an infinite number of potential pits ($N_{\text{я}} \gg 1$)

$$E_{k,n}^{(-)}(\infty) = \frac{\pi^2 \hbar^2 (n^2 - k^2 + n - k)}{2ma^2} - \frac{\hbar\omega}{\pi} (\exp(-\eta_k) + \exp(-\eta_n)), \quad (10)$$

According to the formulas (8) - (10) multiple-pits symmetric model ($N_{\text{p}} \rightarrow \infty$) gives the minimum distance between ceiling of k-th and the bottom of n-th energy band, and 2 – pits model corresponds to the maximum of this n distances, which implies that the reduction in the amount of ohmic contacts potential pits leads to a narrowing of the energy bands. The distance between adjacent energy bands increases.

Numerical study of the energy spectrum of the protons in the field of multipits potential relief with rectangular shape with blocking electrodes, according to the transcendental spectral equation (3.61) [1] enables us to establish the dependence of maximum number of energy levels in the potential pit on the theoretical position of the density maximum TSDC for different thicknesses of the crystalline layer bluestone (Table 3) and in phlogopite (Table 4). The range of layer thicknesses chosen in the range of 30 mcm to 3 nm. In tables 3, 4 in the brackets there are the equivalent temperature of the thermal depolarization current density theoretical maximum.

Thus, in blue stone, measured at a temperature of 94 K and a crystal thickness of 30 microns, a theoretical maximum of thermally stimulated current in the direct result of quantum - quantum - mechanical calculation shifted to 50 K at a thickness of 30 nm and 25 K at 3 nm (Table 3). Total displacement of the corresponding maximum in phlogopite (100 K) was 71 K (Table 4). The second maximum in blue stone (138 K) is shifted to 53 K (Table 3), and in 50 phlogopite K (Table 4). In the field of relaxation high temperature Bjerrum defects of noticeable shift of the theoretical density profile TSDC with decreasing thickness of the crystal to the nanometer range have been identified.

Table 3. Maximum number of calculated energy levels of Bjerrum defects in the bluestone crystals potential pits in the at temperatures of experimental peaks of thermally stimulated depolarization current for different thicknesses of the crystalline layers [22, 23]

The thickness of the layer, nm	The maximum number of energy levels in the potential pits N_{max}					
30000	$2 \cdot 10^3$ (94)	$3,5 \cdot 10^4$ (138)	$2,5 \cdot 10^5$ (170)	$5 \cdot 10^5$ (206)	$7,5 \cdot 10^5$ (230)	$0,9 \cdot 10^6$ (246)
3000	10^3 (90)	$5 \cdot 10^3$ (130)	10^5 (167)	$4,9 \cdot 10^5$ (205)	$7,5 \cdot 10^5$ (230)	$0,9 \cdot 10^6$ (246)
300	$3 \cdot 10^2$ (60)	10^3 (115)	$0,5 \cdot 10^5$ (165)	$4,5 \cdot 10^5$ (204,5)	$7,5 \cdot 10^5$ (230)	$0,9 \cdot 10^6$ (246)
30	100 (50)	900 (95)	10^4 (165)	$4,4 \cdot 10^5$ (202)	$7,49 \cdot 10^5$ (229)	$0,9 \cdot 10^6$ (246)
3	30 (25)	700 (85)	$0,9 \cdot 10^4$ (159)	$4,3 \cdot 10^5$ (200)	$7,48 \cdot 10^5$ (228)	$0,89 \cdot 10^6$ (245)

On the example of how the bluestone (Table 3), and phlogopite (Table 4) we can see that as the thermally stimulated current experimental maximum temperature increasing (the thickness is 30 microns) the maximum number of energy levels in the potential pits increases. For example, in blue stone this number increases from 2,000 at 94 K to 900 000 at 246 K, in phlogopite from 3500 at 100

K to 1.3 million at 257 K. This pattern can be explained by the influence of the parameters of the potential barrier (activation energy, the width of the potential barrier, the lattice constant) on the structure of the energy spectrum of relaxation oscillators with blocking electrodes. At low temperatures (70 - 100 K), when the migration mechanism of polarization is realized due to the tunneling of protons in the protonated anions, the parameters of the potential barrier such that the probability of large sub-barrier transition and the proton moves the tunnel, and the relaxation is diffusive. According to the tables 3, 4 the reduction of crystal layer thickness to the nanometer size (3 - 30 nm) is accompanied by a significant decrease of the maximum number of energy levels in the potential pits of low-temperature relaxation oscillators that successfully consistent with regularity established by the formulas (9) - (10) for ohmic electrodes.

Table 4. Maximum number of calculated energy levels of Bjerrum defects in the potential pits in the phlogopite crystals at temperatures of thermally stimulated depolarization current experimental peaks for different thicknesses of the crystalline layers [22, 23]

The thickness of the layer, nm	The maximum number of energy levels in the potential pits N_{\max}					
30000	$3,5 \cdot 10^3$ (100)	$5,3 \cdot 10^4$ (130)	$1,5 \cdot 10^5$ (178)	$4,3 \cdot 10^5$ (206)	$5,5 \cdot 10^5$ (235)	$1,3 \cdot 10^6$ (257)
3000	$1,7 \cdot 10^3$ (88)	$7,3 \cdot 10^3$ (122)	$0,5 \cdot 10^5$ (174)	$4,2 \cdot 10^5$ (206)	$5,5 \cdot 10^5$ (235)	$1,3 \cdot 10^6$ (257)
300	$0,55 \cdot 10^3$ (57)	$2,45 \cdot 10^3$ (108)	$1,5 \cdot 10^4$ (172)	$4,25 \cdot 10^5$ (206)	$5,5 \cdot 10^5$ (235)	$1,3 \cdot 10^6$ (257)
30	185 (48)	1990 (89)	10^4 (169)	$4 \cdot 10^5$ (204)	$5,5 \cdot 10^5$ (233)	$1,3 \cdot 10^6$ (257)
3	63 (29)	1500 (80)	$0,9 \cdot 10^3$ (168)	$3,8 \cdot 10^5$ (200)	$5,4 \cdot 10^5$ (232)	$1,29 \cdot 10^6$ (256,9)

Under such conditions, as noted in paragraph 3.1.4.3 [1] on the model of ohmic electrodes transmittance of 10 - 12 orders of magnitude higher than that at high temperatures, which provides a large energy band width low-temperature relaxation oscillators (tables 9, 10 [1]). During the blocking of contacts, as can be seen from Tables 13, 14 [1] and 3,4, due to the tunneling effect of the broadening of spectral lines of quasi-discrete spectrum of the protons is manifested in a greater degree, which leads to a marked reduction in the number of associated stationary states at temperatures near the nitrogen (70 - 100 K).

Size effects associated with a significant reduction in the number of levels in the potential pits of low-temperature relaxation oscillators with nanometer-thick layers, ohmic electrodes are explained, according to (9) - (10), the influence of the crystal size and the distance between adjacent zones of energy. When electrodes are blocked numerical investigation of spectral transcendental equation (3.60) [1] reduces the amount of bound levels at bluestone from 2000 at 94 K to 30 K at 25 (Table 3) and in phlogopite from 3500 at 100 K to 63 K at 29 (Table 4). During the relaxation of ionization Bjerrum defects as can be seen from Tables 3 and 4 also appear dimensional effects, which indicates a significant role of tunneling and at temperatures above nitrogen. In bluestone for L - defects at the maximum measured thermally stimulated current (246 K, 30 mcm) is localized in the potential pit of 900,000 and a crystal thickness of 3 nm, when the theoretical position of the maximum temperature shifted to the left by 1 K, in the pit is 890000 energy levels (table 3). A

similar situation is shown in phlogopite, in which the thickness of the crystal measured at 30,000 nm maximum density with temperature TSDC 257 K at a number of energy levels associated with a decrease of 130,000 crystal thickness to 3 nm is shifted to lower temperatures by 3.1 K, and the maximum number of energy levels in potential is reduced to 1290000 (Table 4). It turns out that the low-temperature relaxation oscillators reducing chip size from 30,000 to 3 nm leads to a decrease in the number by about 99%, and for L - defects only 1%, that is, the high-temperature relaxation, flowing mainly due to thermally activated transitions of protons to the value of the thickness of the crystal substantially not sensitive.

The numerical processing of equation (3.114) [1] in conjunction with the non-equilibrium density matrix (3.111) [1] allows to calculate the theoretical peak values of and temperature position of the current density maxima of thy thermally stimulated depolarization for each type of Bjerrum defects in Chalcantite (Table 5) and in the phlogopite (Table 6). Theoretical values of relaxators parameters were taken according to the results of quantum - mechanical calculation of the termodepolarization current density (Tables 15, 16 [1]).

Table 5. The amplitudes and temperature positions of theoretical maximum density of bluestone depolarization thermally stimulated current calculated by the density matrix for different thicknesses of the crystalline layer [22, 23]

Layer thickness, nm	Amplitudes and thermal positions of the theoretical thermally stimulated current maximum					
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)	$1,35 \cdot 10^{-9}$ (245)

As noted above in L – defects in phlogopite with the crystal thickness 30 microns when the peak temperature is 257 K in the pit 1300000, and at 3 nm 1290000 levels remained. Against the background of such a huge number of possible energy states of the proton the change of this number at 10,000 - 20,000 levels practically don't effect on the picture of the relaxation oscillators energy spectrum, the populations of the energy levels do not change, and the maximum density deviates from the TSDC measured only 0.5 - 1 K, and its amplitude increases by $(0,3 \div 0,35) \cdot 10^{-9}$ K (Table 6) . With crystal temperature decreasing to very low in L - defects although growing population of the levels near the bottom of the potential well, but because of the low transparency of the potential barrier the proton transfer can be occurred only due to the thermal motion that is impossible near absolute zero of temperature.

Comparing the tables 3, 4 and 5, 6 shows that for low temperature relaxators size effects caused displacement of the termodepolyarization current theoretical maximum to the field of

ultralow temperatures is accompanied by increasing of the TSDC density amplitude in four orders in comparison with those calculated at the experimental maximum [24].

In Chalcanthite the reduction of crystalline layer thickness from 30 microns to 3 nm leads to a shift of the maximum low temperature from 94 to 25 K, and thus increases the amplitude of theoretical maximum rises from $8 \cdot 10^{-10} \text{ A/m}^2$ to 10^{-5} A/m^2 (Table 5). At phlogopite the amplitude of theoretical maximum temperature grows from $7 \cdot 10^{-9} \text{ A/m}^2$ with crystal thickness of 30 microns up to $3,5 \cdot 10^{-5} \text{ A/m}^2$ at 3 nm.

Table 6. The amplitudes and temperature position of the thermally stimulated depolarization current theoretical maximum density in phlogopite calculated by the density matrix for different thicknesses of the crystalline layer [22, 23]

Layer thickness, nm	Amplitudes and thermal positions of the theoretical thermally stimulated current maximum					
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^{-9} (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^{-9} (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^{-9} (257)
30	$5 \cdot 10^{-6}$ (48)	$8,3 \cdot 10^{-6}$ (89)	10^{-6} (169)	$7 \cdot 10^{-8}$ (204)	$9,5 \cdot 10^{-9}$ (233)	10^{-9} (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)	$1,3 \cdot 10^{-9}$ (256,9)

Displacement of thermally stimulated current theoretical maximum to ultralow temperatures (in Chalcanthite from 94 K at 30 microns to 25 K at 3 nm (Table 5)? in phlogopite from 100 K at 30 microns to 29 K at 3 nm (table 6)) due to a significant underestimation of the energy levels associated number (from 2000 to 30 in the bluestone (Table 3) and from 3500 to 63 from phlogopite (Table 4)). Because of a small number of stationary energy states the average distance between adjacent levels within the potential well increases, the transparency of the potential barrier is also increasing, in consequence of which significantly the speed of the probability of protons tunneling in hydrogen bonds is increasing and a maximum current of termodepolarization is realized at a lower temperature. At the same time, for low temperature relaxators of population, with are located near the bottom of the potential pit of associated energy levels in the layers of nanometer size are increased, providing background on the high probability of sub-barrier transitions significant concentration of relaxing protons. Under these conditions, migration polarization is being occurred due to the huge number of protons and density of thermally stimulated current is increased by 3 - 4 orders of magnitude.

Conclusions

1. Use the limb - difference scheme for calculating of the thermally stimulated current of depolarization (7) it is possible to identify the characteristic of low temperature relaxators size effects caused by abnormal displacement of the theoretical maximum termodepolarization current density at lower temperatures of 12 - 14 K with increasing of amplitude maximum on one - two orders of magnitude on a nanometer crystal layers with hydrogen bonds (table 1, 2).

2. On the model of a multipit potential of relief with rectangular shape and ohmic contacts at the boundaries of the crystal it is shown that decreasing of potential pits number energy band width is decreasing, and the minimum distance between adjacent energy bands is increasing ((8) - (10)), the energy spectrum becomes quasidiscrete, potential barrier transparency is increasing and tunneling caused quantum effects are enhancing.

3. From the numerical solution of the transcendental spectral equation (3.37) there was defined the dependence of energy levels maximum number in the potential pits (bounded states) on thermally stimulated depolarization current theoretical maximum temperature and amplitude by varying the thickness of the crystal layer in Chalcantite (Table 3.,5) and in the phlogopite (table 4.,6) in the thickness range from 3 nm to 30 mcm.

4. It was established that with locking pins at the boundary of crystal layers in the nanometer layers (3 nm) in comparing with crystals of thickness 30 mcm, the maximum number of associated energy levels of relaxators with low temperature is decreasing by 99% from the current thermo depolarization theoretical maximum displacement toward low temperature of 65 - 75 K with increasing of density amplitude TSDC on 3 - 4 orders of magnitude, while the high-temperature defects of Bjerrum only with 1% when and temperature shift is on 0.1 - 1 K at a constant amplitude, therefore it can be argued that in the nanometer crystals with hydrogen ties of polarization at very low temperatures (4 - 25 K) is caused by nanoclusters.

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