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Quantum properties of proton subsystem in proton semiconductors

The quantum mechanism of the relaxation motion of the most mobile charge carriers (protons) in crystals with hydrogen bonds (HBC) in the range of low temperature (70-100 K) is studied. The energy spectrum of the proton in the unperturbed potential field of a crystal lattice modeled as a one-dimensional periodic potential relief of a rectangular shape is investigated in the quasi-classical approximation by the Wentzel – Kramers – Brillouin method (WKB-method) at ohmic contacts at the crystal boundaries (the work function of the proton from the crystal is assumed to be finite). The band structure of the energy spectrum of low-temperature relaxers (protons) in proton materials was discovered, the word parameters of the band structure (width of the forbidden zone, «bottom» and «ceiling» of the energy zone minimum and maximum distances between two fixed energy bands). The populations of quasi-discrete energy levels (within the limits of the corresponding energy bands) by protons are calculated using an balanced (equilibrium) density matrix constructed on the basis of Boltzmann's quantum statistics for protons tunneling through a rectangular potential barrier. With the help of a quasi-stationary equilibrium density matrix, an expression is constructed for the polarization of the proton subsystem perturbed by an external homogeneous harmonic time-varying electric field.

Keywords: crystals with hydrogen bonds, the band structure of the proton energy spectrum in the HBC, quasiclassical approximation in quantum mechanics; the equilibrium density matrix for protons, energy zones of the proton in HBC.

Introduction

Hydrogen bonded crystals (HBC), classified by properties and parameters of crystal lattice as a layered crystals, are characterized, in the limits of low fields in the temperature range T = 70 – 450 K, by proton conductivity includes in diffusion transfer of the protons along the hydrogen links towards the electrical field lines, that allows determine this crystals group as the proton semiconductors and dielectrics [1].

According to kinetic theory of dielectric relaxation [1,2] the mechanism of polarization (and depolarization) in HBC is built just upon based the relaxation movement of the most mobile of the charge carriers (protons) along (parallel) the crystal axis **C** and proton determined as the physical relaxator in HBC [2].

In range of high temperatures (T>100 K) the process of proton relaxation in HBC caused by thermally activated transfer of protons (along the hydrogen links) were studied well experimentally [1]. The solution of linearization kinetic equation type Fokker – Plank built in linear approximation of parameter of perturbation theory $\gamma_{pr,th}$ (for the models of the blocked and ohmic electrodes) [1] and can be used for description of the thermally stimulated currents of depolarization (TCDP) and dielectric losses in the area of T = 100 – 250 K. But the mathematical model of low temperatures proton relaxation in HBC (T=70 – 100 K) [1-3], caused due to quantum tunneling transfer of protons trough the potential barrier (according to the experimental results [1]), remains unsatisfactory [1, 3-5].

1. The calculation of energy spectrum of protons in quasi-classical approximation

Due to the significant transparency of the potential barrier [1,2], quantum effects play the main role in migration processes of the protons in HBC at low (T<100 K) and super – low (T=4-25 K) temperatures [6]. In this case, the theoretical studies of the properties of the proton relaxation movement in the crystal structure of the dielectric must be constructed by methods of quantum theory (based on the wave Schrödinger equation) and statistical properties of the proton subsystem (linked by hydrogen bonds with ionic subsystem) to be described upon based the Gibbs quantum statistics (in the case of a non - degenerated proton gas) with the help of density matrix [1, 2, 6].

The Schrödinger equation for the particle (proton) with mass m moving in unperturbed one-dimensional periodic potential field of hydrogen links (multi-well potential image in HBC) $\hat{W}_{C,[H^+]}$ [1] can be shown in simple form [1, 7]

$$-\frac{\hbar^2}{2\,m}\frac{d^2\psi}{dx^2}+\hat{W}_{C,[H^+]}(x)\,\psi=E^{(0)}\,\psi\,. \qquad (1)$$

In this model, the direction of the coordinates axes OX is chosen in the direction of the crystal axis **C**. The changing the coordinates of the particle range is $-\infty<x<\infty$. The unperturbed energy levels of the particles varies in the area $0\le E^{(0)}<\infty$, where in the bound states of the particle (proton) correspond to energy values $0\le E^{(0)}\le U_0$, where U_0- respectively the activation energy of the proton localized at the hydrogen bond. The range of energies $U_0\le E^{(0)}\le U_{max}$ respected to the stationary states of the particles moving outside of the local field of the hydrogen bonds but in potential field of a crystal lattice. Here $U_{max}-$ work function of the proton from the modeling crystal.

The method of analytical solving of equation (1) for given model [2] can be simplified, since for the relaxing protons condition of quasi-classical holds [1]

$$m\omega_0\delta_0^2/4\hbar>>1\,. \qquad (2)$$

Here ω_0- cyclic frequency of natural oscillations of the proton in an isolated potential well, δ_0- the potential barrier width [1].

So, the wave function of the proton in the j-th potential well in the range of $a_j\le x\le b_j$, according to method of Wentzel–Kramers–Brillouin (WKB -method), has the form [1, 7]

$$\breve{\psi}_j(x)=\frac{\breve{C}_j}{\sqrt{p(x)}}\exp\left(-\frac{i}{\hbar}\int_{a_j}^{x}p(x)dx\right)+\frac{\breve{D}_j}{\sqrt{p(x)}}\exp\left(\frac{i}{\hbar}\int_{a_j}^{x}p(x)dx\right). \qquad (3.1)$$

Respectively, of the j-th barrier in $b_j\le x\le a_{j+1}$ is

$$\hat{\psi}_j(x)=\frac{\hat{C}_j}{\sqrt{|p(x)|}}\exp\left(-\frac{1}{\hbar}\int_{b_j}^{x}|p(x)|dx\right)+\frac{\hat{D}_j}{\sqrt{|p(x)|}}\exp\left(\frac{1}{\hbar}\int_{b_j}^{x}|p(x)|dx\right). \qquad (3.2)$$

The relation between the coefficients of the exp. (3.2) of j-th and j +1- th barriers [1, 7]

$$\begin{pmatrix}\hat{C}_{j+1}\\ \hat{D}_{j+1}\end{pmatrix}=B\cdot\begin{pmatrix}\hat{C}_j\\ \hat{D}_j\end{pmatrix},\ B=\begin{pmatrix}\beta_{11}&\beta_{12}\\ \beta_{21}&\beta_{22}\end{pmatrix}. \qquad (4)$$

Here $\beta_{11}=\frac{e^{-\eta}\cos\varphi}{2}$, $\beta_{12}=e^{\eta}\sin\varphi$, $\beta_{21}=-e^{-\eta}\sin\varphi$, $\beta_{22}=2e^{\eta}\cos\varphi$; $\varphi=\frac{1}{\hbar}\int_{a_j}^{b_j}p(x)dx$, $\eta=\frac{1}{\hbar}\int_{b_j}^{a_{j+1}}|p(x)|dx$.

On basis of exp. (4), with the help of expression [1,7]

$$B^j=\frac{1}{\lambda_1-\lambda_2}\cdot\begin{pmatrix}(\lambda_1-\beta_{11})\lambda_2^j-(\lambda_2-\beta_{11})\lambda_1^j & -\frac{(\lambda_1-\beta_{11})(\lambda_2-\beta_{11})}{\beta_{21}}\left(\lambda_1^j-\lambda_2^j\right)\\ \beta_{21}\left(\lambda_1^j-\lambda_2^j\right) & (\lambda_1-\beta_{11})\lambda_1-(\lambda_2-\beta_{11})\lambda_2^{N_w}\end{pmatrix}, \qquad (5)$$

where λ_1,λ_2- the roots of the characteristic determinant $\begin{vmatrix}\beta_{11}-\lambda&\beta_{12}\\ \beta_{21}&\beta_{22}-\lambda\end{vmatrix}=0$, writing the amplitudes of the 0-th barrier as $\begin{pmatrix}\hat{C}_0\\ \hat{D}_0\end{pmatrix}\equiv\begin{pmatrix}0\\ Ce^{-\eta}\end{pmatrix}$, we can build the matrix

$$\begin{pmatrix}\hat{C}_j\\ \hat{D}_j\end{pmatrix}=B^j\cdot\begin{pmatrix}0\\ Ce^{-\eta}\end{pmatrix}=\begin{pmatrix}-Ce^{-\eta}\frac{(\lambda_1-\beta_{11})(\lambda_2-\beta_{11})\left(\lambda_1^j-\lambda_2^j\right)}{b_{21}(\lambda_1-\lambda_2)}\\ Ce^{-\eta}\frac{(\lambda_1-\beta_{11})\lambda_1^j-(\lambda_2-\beta_{11})\lambda_2^j}{\lambda_1-\lambda_2}\end{pmatrix}. \qquad (6)$$

So, the characteristic equation $\lambda^2-\left(\frac{e^{-\eta}}{2}+2e^{\eta}\right)\lambda\cos\xi+1=0$, according to quasi-classical condition $\eta\rangle\rangle 1$, when $2\cos u=\left(\frac{1}{2}e^{-\eta}+2e^{\eta}\right)\cos\varphi\approx 2e^{\eta}\cos\varphi$, given the form $\lambda^2-2e^{\eta}\lambda\cos\xi+1=0$, and characteristic roots, respectively $\lambda_{1,2}=\exp(\pm iu)$. Then, the exp. (6), according to the designations $\beta_{11}+\beta_{22}=2\cos u$, $\beta_{11}\beta_{22}-\beta_{12}\beta_{21}=1$, may be shown as

$$\begin{pmatrix}\hat{C}_j\\ \hat{D}_j\end{pmatrix}=Ce^{-\eta}\begin{pmatrix}\dfrac{\beta_{12}\sin(ju)}{\sin u}\\ \dfrac{\sin((j+1)u)-\beta_{11}\sin(ju)}{\sin u}\end{pmatrix}. \quad (7)$$

In (7) $C-$ constant determined with the help of normalization condition $\int_{-\infty}^{\infty}|\psi|^2=1$.

Upon based the exp. (7), taking for N_W-th potential barrier the matrix $\begin{pmatrix}\hat{C}_{N_W}\\ \hat{D}_{N_W}\end{pmatrix}\equiv\begin{pmatrix}\hat{C}_{N_W}\\ 0\end{pmatrix}$, when $\begin{pmatrix}\hat{C}_{N_W}\\ \hat{D}_{N_W}\end{pmatrix}=Ce^{-\eta}\begin{pmatrix}\dfrac{\beta_{12}\sin(N_W u)}{\sin u}\\ \dfrac{\sin((N_W+1)u)-\beta_{11}\sin(N_W u)}{\sin u}\end{pmatrix}$, according to $\beta_{11}=\frac{e^{-\eta}\cos\varphi}{2}\to 0$, at finally, we have equation $\frac{\sin((N_W+1)u)}{\sin u}=0$, where N_W- full quantity of the potential wells in the model. So, the parameter u may be determined with the help of expression $u_s=\pm\frac{\pi s}{N_W+1}$, where $s\neq 0, s\neq N_W+1$.

Using the exp. $\cos(\varphi_{(n;s)})\approx e^{-\eta_n}\cos(u_s)$, according to $\varphi_{(n;s)}=\arccos(\chi_{(n;s)})\approx\arccos(0)\mp\chi_{(n;s)}$, where $\chi_{(n;s)}=e^{-\eta_n}\cos(u_s)<<1$, we can write $\varphi_{(n;s)}=\arccos(\chi_{(n;s)})\approx\arccos(0)\mp\chi_{(n;s)}$ and

$$\varphi_{(n;s)}\approx\mp\pi\left(n+\frac{1}{2}\right)\mp e^{-\eta_n}\cos\left(\frac{\pi s}{N_W+1}\right). \quad (8)$$

Here $\varphi_{(n,s)}=\frac{\sqrt{2m}}{\hbar}\int_{a_{j,(n,s)}}^{b_{j,(n,s)}}\sqrt{E_{n,s}^{(0)}-\breve{W}_{C,[H^+]}(x)}\,dx$, $\eta_n=\frac{\sqrt{2m}}{\hbar}\int_{b_{j,n}}^{a_{j+1,n}}\sqrt{\hat{W}_{C,[H^+]}(x)-E_n^{(0)}}\,dx$; $\breve{W}_{C,[H^+]}(x)$, $\hat{W}_{C,[H^+]}(x)-$ respectively potential energy of the proton calculated in range of the potential well, or barrier.

In exp. (8) the unperturbed energy levels of the proton in the isolated potential well $E_n^{(0)}$ may be calculated by eq. $\varphi_n=\frac{1}{\hbar}\int_{a_{j,n}}^{b_{j,n}}p_n(x)\,dx=\pm\pi\hbar\left(n+\frac{1}{2}\right)$, where accepted $p_n(x)=\sqrt{2m\left(E_n^{(0)}-\breve{W}_{C,[H^+]}(x)\right)}$.

For the model of potential image with rectangular shape write $\hat{W}_{C,[H^+]}(x)=\begin{cases}0, a_j\le x\le b_j\\ U_0, b_j\le x\le a_{j+1}\end{cases}$ [1], where $\hat{W}_{C,[H^+]}(x)=U_{max}>U_0$, when $x<0$, $x>d$; $a_j=(j-1)(a+\delta_0)$, $b_j=a_j+a$. The crystal thickness is $d=(N_W-1)(a+\delta_0)+a$. Here: $a-$ width of the well, δ_0- barrier width; U_0- barrier height (activation energy) [1]. It is obvious that $a+\delta_0=a$.

For the isolated square well in WKB-approximation [1]:

$$\varphi_n \approx \mp\pi\left(n+\frac{1}{2}\right),\ \ \varphi_n = \frac{\sqrt{2m}}{\hbar}\int\limits_{a_{j,n}}^{b_{j,n}} \sqrt{E_n^{(0)} - \breve{W}_{C,[H^+]}(x)}\,dx = \frac{\sqrt{2mE_n^{(0)}}}{\hbar}a\ ;\ E_n^{(0)} \approx \frac{\hbar^2\pi^2}{2ma^2}\left(n+\frac{1}{2}\right)^2.$$

Splitting energy levels $E_n^{(0)}$ parameter η_n for the rectangular relief has the form

$$\eta_n = \frac{\sqrt{2m}}{\hbar}\int\limits_{b_{j,n}}^{a_{j+1,n}} \sqrt{U_0 - E_n^{(0)}}\,dx = \frac{\sqrt{2m\left(U_0 - E_n^{(0)}\right)}}{\hbar}\delta_0\,.$$

The unperturbed energy levels $E_n^{(0)}$ for the proton in potential image of hydrogen links are calculated on basis of (8), with respecting of exp. $\varphi_{(n,s)} = \frac{\sqrt{2mE_{(n,s)}^{(0)}}}{\hbar}a$ and may be shown as

$$E_{(n,s)}^{(0)} = \frac{\hbar^2\pi^2}{2ma^2}\left(\upsilon_{(n,s)} + \frac{1}{2}\right)^2. \tag{9}$$

In (9) $\upsilon_{(n,s)} = n + \frac{1}{\pi}e^{-\eta_n}\cos\left(\frac{\pi s}{N_W+1}\right)$. At finally, the energy spectrum of proton in crystalline potential relief with rectangular shape given the form

$$E_{(n,s)}^{(0)} = E_n^{(0)} + \frac{\hbar^2\pi}{ma^2}\left(n+\frac{1}{2}\right)e^{-\eta_n}\cos\left(\frac{\pi s}{N_W+1}\right) + \frac{\hbar^2}{2ma^2}e^{-2\eta_n}\cos^2\left(\frac{\pi s}{N_W+1}\right). \tag{10}$$

Upon based the (10) determine the energy band (zone) number n (respectively to energy level $E_n^{(0)}$) includes the energy levels, beginning the numbers from $s = N_W$:

$$E_{n,min} = E_n^{(0)} - \frac{\hbar^2\pi}{ma^2}\left(n+\frac{1}{2}\right)e^{-\eta_n}\cos\left(\frac{\pi}{N_W+1}\right) + \frac{\hbar^2}{2ma^2}e^{-2\eta_n}\cos^2\left(\frac{\pi s}{N_W+1}\right), \tag{11}$$

to $s = 1$:

$$E_{n,max} = E_n^{(0)} + \frac{\hbar^2\pi}{ma^2}\left(n+\frac{1}{2}\right)e^{-\eta_n}\cos\left(\frac{\pi}{N_W+1}\right) + \frac{\hbar^2}{2ma^2}e^{-2\eta_n}\cos^2\left(\frac{\pi s}{N_W+1}\right). \tag{12}$$

The n- th energy band (zone) width is

$$\Delta E_n = E_{n,max} - E_{n,min} = \frac{2\hbar^2\pi}{ma^2}\left(n+\frac{1}{2}\right)e^{-\eta_n}\cos\left(\frac{\pi}{N_W+1}\right). \tag{13}$$

When $N_W \to \infty$ it gives the form

$$\Delta E_n \to \left(\Delta E_n\right)_{max} = \frac{2\hbar^2\pi}{ma^2}\left(n+\frac{1}{2}\right)\exp\left(-\eta_n\right). \tag{14}$$

The minimum $\Delta E_{n,m}^{(min)} = \Delta E_{n,m}^{(-)} = E_{n,min} - E_{m,max}$ and maximum $\Delta E_{n,m}^{(max)} = \Delta E_{n,m}^{(+)} = E_{n,max} - E_{m,min}$ distances between energy levels of m-th and n-th energy bands, when $n > m$, respectively

$$\Delta E_{n,m}^{(\pm)} = E_{n,m}^{(0)} \pm \frac{\hbar^2\pi}{ma^2}\left[\left(n+\frac{1}{2}\right)e^{-\eta_n} + \left(m+\frac{1}{2}\right)e^{-\eta_m}\right]\cos\left(\frac{\pi}{N_W+1}\right) +$$

$$+ \frac{\hbar^2}{2ma^2}\left[e^{-2\eta_n} - e^{-2\eta_m}\right]\times\cos^2\left(\frac{\pi}{N_W+1}\right). \tag{15}$$

When $N_W \to \infty$, exp. (15) give the form

$$\Delta E_{n,m}^{(\pm)} \to \left(\Delta E_{n,m}^{(\pm)}\right)_{max} = E_{n,m}^{(0)} \pm \frac{\hbar^2\pi}{ma^2}\left[\left(n+\frac{1}{2}\right)e^{-\eta_n} + \left(m+\frac{1}{2}\right)e^{-\eta_m}\right] + \frac{\hbar^2}{2ma^2}\left[e^{-2\eta_n} - e^{-2\eta_m}\right]. \tag{16}$$

Upon based the exp. (15) we can see

$$\Delta E_{n,m}^{(max)} = \Delta E_{n,m}^{(min)} + \Delta E_n + \Delta E_m . \quad (17)$$

The n-th energy band width (13), (14) may be determined in complex with the transparency of potential barrier

$$\Delta E_n = \frac{2\hbar^2 \pi}{ma^2}\left(n+\frac{1}{2}\right)\sqrt{D\left(U_0, E_n^{(0)}\right)}\cos\left(\frac{\pi}{N_W+1}\right),\ \left(\Delta E_n\right)_{max} = \frac{2\hbar^2 \pi}{ma^2}\left(n+\frac{1}{2}\right)\sqrt{D\left(U_0, E_n^{(0)}\right)}. \quad (18)$$

The solutions of quantum wave eq.

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_{(n,s)}}{dx^2} + \hat{W}_{C,[H^+]}(x)\psi_{(n,s)} = E_{(n,s)}^{(0)}\psi_{(n,s)}$$

may be constructed in the form of wave functions $\breve{\psi}_{(n,s)}, \bar{\psi}_{(n,s)}$ earlier calculated by authors of [7]. Here we must with respect the parameters

$$\varphi_{(n,s)} = \frac{\sqrt{2mE_{(n,s)}^{(0)}}}{\hbar}a,\ \eta_n = \frac{\sqrt{2m\left(U_0 - E_n^{(0)}\right)}}{\hbar}\delta_0 .$$

2. The populations of unperturbed energy spectrum levels. Statistically averaging operator of polarization

Balanced proton density matrix $\rho_{pr,n}^{(0)}$ [2] allows us to calculate the populations of unperturbed energy levels $E_{(n,s)}^{(0)}$ helps to construct the occupation numbers in the area of n- th energy band

$$a_{(n,s)}^{(0)+}a_{(n,s)}^{(0)} = \rho_{pr;(n,s)}^{(0)} = N_{pr,F}\left[Z_{pr}^{(0)}\right]^{-1}\exp\left(-\frac{E_{(n,s)}^{(0)}}{k_B T}\right). \quad (19)$$

Here $Z_{pr}^{(0)} = \sum_{n=0}^{\infty}\sum_{s=1}^{N_W}\exp\left(-\frac{E_{(n,s)}^{(0)}}{k_B T}\right)$ – statistical sum of the protons subsystem [2]; $N_{pr,F} = \sum_{n=0}^{\infty}\sum_{s=1}^{N_W}a_{(n,s)}^{(0)+}a_{(n,s)}^{(0)}$ – full quantity of the protons relaxing with predetermined activation energy U_0 in range of given experimental monorelaxation maximum (in HBC) is determined by summing the occupation numbers of the levels $E_{(n,s)}^{(0)}$ [2].

The equilibrium (balanced) density matrix of the proton subsystem perturbed by external (polarizing) field, built in the form [2]

$$a_{(n,s)}^{+}a_{(n,s)} = \rho_{pr;(n,s)} = N_{pr,F}\left[Z_{pr}\right]^{-1}\exp\left(-\frac{E_{(n,s)}}{k_B T}\right). \quad (20)$$

In (20) $Z_{pr} = \sum_{n=0}^{\infty}\sum_{s=1}^{N_W}\exp\left(-\frac{E_{(n,s)}}{k_B T}\right)$ – statistical sum for the protons distributed by perturbed energy levels (disturbed states) $E_{(n,s)} = E_{(n,s)}^{(0)} + \Delta E_{(n,s)}$, where indignant component of energy $\Delta E_{(n,s)}$ is calculated for invent of large periods of oscillation of the external (polarizing) field, in predetermined approximation of indignation theory [2]. In the linear approximation of indignation theory used the expression $\Delta E_{(n,s)}(t) = \int_0^d \psi_{(n,s)}^{+}\hat{W}(x;t)\psi_{(n,s)}\,dx$ [2]. In this formula d – is crystal thickness. For the model of homogeneous harmonic time-varying electrical field we have $\hat{W}(x;t) = -qE_0\hat{x}\cdot e^{i\omega t}$, where E_0, ω– amplitude and frequency of alternating field; q – the proton charge [2]. Here respected the condition of low indignations to $\frac{\Delta E_{(n,s)}(t)}{k_B T} << 1$. So transform (20) into the type

$$\rho^{(\omega)}_{\mathrm{pr};(\mathrm{n,s})}(\mathrm{t}) = \rho^{(0)}_{\mathrm{pr};(\mathrm{n,s})} \times \left[\left\langle \exp\left(-\frac{\Delta E_{(\mathrm{n,s})}(\mathrm{t})}{\mathrm{k_B T}} \right) \right\rangle_0 \right]^{-1} \times \exp\left(-\frac{\Delta E_{(\mathrm{n,s})}(\mathrm{t})}{\mathrm{k_B T}} \right). \quad (21)$$

Here accepted the designation

$$\left\langle \exp\left(-\frac{\Delta E_{(\mathrm{n,s})}(\mathrm{t})}{\mathrm{k_B T}} \right) \right\rangle_0 = \left[Z^{(0)}_{\mathrm{pr}} \right]^{-1} \times \sum_{\mathrm{n}=0}^{\infty} \sum_{\mathrm{s}=1}^{\mathrm{N_W}} \exp\left(-\frac{\Delta E_{(\mathrm{n,s})}(\mathrm{t})}{\mathrm{k_B T}} \right) \times \exp\left(-\frac{E^{(0)}_{(\mathrm{n,s})}}{\mathrm{k_B T}} \right). \quad (22)$$

At finally, the result of full quantum – mechanical averaging of polarization operator (formula (16) in [2]) for the developed in this work statistical model (21) may be shown in the form

$$P^{(\omega)}_{\mathrm{pr,pol}}(t) \approx \mathrm{q} \sum_{\mathrm{k}=0}^{\infty} \sum_{\mathrm{n}=0}^{\infty} \sum_{l=1}^{\mathrm{N_W}} \sum_{\mathrm{s}=1}^{\mathrm{N_W}} \left\{ \rho^{(0)}_{\mathrm{pr};(\mathrm{k},l)}(E^{(0)}_{(\mathrm{k},l)}) \times \rho^{(0)}_{\mathrm{pr};(\mathrm{n,s})}\left(E^{(0)}_{(\mathrm{n,s})}\right) \times \right.$$

$$\left. \times \left\{ \left[\left\langle \exp\left(-\frac{\Delta E_{(\mathrm{k},l)}(t)}{\mathrm{k_B T}} \right) \right\rangle_0 \right]^{-1} \times \exp\left(-\frac{\Delta E_{(\mathrm{k},l)}(t)}{\mathrm{k_B T}} \right) - 1 \right\} \times \int_0^{\mathrm{d}} \left| \psi_{(\mathrm{n,s})} \right|^2 \left| \psi_{(\mathrm{k},l)} \right|^2 \hat{x}\, \mathrm{d}x \right\}. \quad (23)$$

In (23) δ_0 – is potential barrier width.

The more detailed investigating of the quantum mechanism of migratory motions of the protons during tunneling polarization in HBC must be constructed upon based the numerical calculating by the function (23) in complex with the stationary wave functions $\psi_{(\mathrm{n,s})}$, $\psi_{(\mathrm{k},l)}$ [7] and energy spectrum expression (16) and will be made later.

Conclusion

1. In quasi-classical approximation, by the WKB –method, constructed the expression for quasi-discrete energy spectrum (10) of the protons moving in unperturbed one-dimensional periodic multi - well potential field (potential image of hydrogen links in HBC) with rectangular for the model of ohmic contacts at the boundaries of crystal. Detected the zone structure of proton quasi-discrete energy spectra in HBC and built the formulas for numerical calculating of the parameters of band structure (the «bottom» and «ceiling» of energy band (11), (12); energy band width (13), (14); the minimum and maximum distances between predetermined energy bands (15), (16)) of the proton subsystem relaxing in rectangular potential image.

2. The calculating of the populations of the unperturbed energy levels (10) in limits of respectively energy band built with the help of occupation numbers (balanced density matrix) for the protons moving with predetermined activation energy (19). The quasi-equilibrium proton density matrix constructed upon based Boltzmann's quantum statistics (by analogy with the balanced density matrix) for the proton subsystem perturbed by alternating external indignation (21).

3. By method of full quantum – mechanical averaging with the help of quasi-equilibrium proton density matrix constructed the formula (23) for numerical calculating of polarization of the proton subsystem relaxing in homogeneous harmonic time-varying electrical field.

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Протонды жартылай өткізгіштердің протонды қосалқы жүйесінің кванттық қасиеттері

Төменгі температуралар диапазонында (70–100 К) сутекті байланысы бар кристалда (СБК) өте қозғалмалы заряд тасушылардың (протондардың) реакциялық қозғалысының кванттық механизмі зерттелді. Тікбұрыш пішіндес периодты әлеуетті (потенциалды) бедерде үлгіленетін, кристалды тордың ұйытқымаған (тыныш) әлеуетті өрісінде протонның энергетикалық спектрі кристалдың шекарасында омдық қарым-қатынас торы кезінде Вентцел-Крамерс-Бриллюен әдісімен, квазиклассикалық жуықталумен қарастырылды (протон кристалдан шығу жұмысы шеткі шама болып қабыладанды). Протонды жартылай өткізгіштерде төменгі температуралық релаксаторлардың (протондардың) энергетикалық спектрінің аймақтық құрылымдары табылды. Аймақтық құрылымның параметрлері анықталды (жабық аймақ ені, энергетикалық аймақтың «түбі» және «төбесі», энергияның екі бекітілген аймақтарының минималды және максималды арақашықтығы). Квазидискретті энергия деңгейлерінің протондармен толымдылығы тікбұрышты әлеуетті потенциалды кедергі арқылы жүретін протондарға арналған Больцман квант статистика негізінде құрылған, бірөлшемді тығыздық матрицасының көмегімен есептелінді. Бірөлшемді квазистационарлы тепе-теңдік тығыздық матрицасының көмегімен протонды қосалқы жүйесін поляризациялау өрнегі құрылған.

Кілт сөздер: сутекті байланысы бар кристалдар, СБК-дағы протонның энергетикалық спектрінің аймақтық құрылымы, кванттық механикадағы квазиклассикалық жуықтау, протондарға арналған тығыздық тепе-теңдік матрицасы, СБК-дағы протондардың энергетикалық аймақтары.

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Квантовые свойства протонной подсистемы в протонных полупроводниках

Исследуется квантовый механизм релаксационного движения наиболее подвижных носителей заряда (протонов) в кристаллах с водородными связями (КВС) в диапазоне низких температур (70–100 К). Энергетический спектр протона в невозмущенном потенциальном поле кристаллической решетки, моделируемой в виде одномерного периодического потенциального рельефа прямоугольной формы, исследуется в квазиклассическом приближении методом Вентцеля–Крамерса–Бриллюэна (ВКБ - методом) при омических контактах на границах кристалла (работа выхода протона из кристалла принимается конечной величиной). Обнаружена зонная структура энергетического спектра низкотемпературных релаксаторов (протонов) в протонных полупроводниках, определены параметры зонной структуры (ширина запретной зоны, «дно» и «потолок» энергетической зоны, минимальное и аксимальное расстояния между двумя фиксированными зонами энергий). Заселенности квазидискретных уровней энергии (в пределах соответствующих энергетических зон) протонами рассчитываются с помощью равновесной матрицы плотности, построенной на основании квантовой статистики Больцмана для протонов, туннелирующих сквозь прямоугольный потенциальный барьер. С помощью квазистационарной равновесной матрицы плотности построено выражение для поляризации протонной подсистемы, возмущенной внешним однородным, гармонически изменяющимся во времени электрическим полем

Ключевые слова: кристаллы с водородными связями (КВС), зонная структура энергетического спектра протона в КВС, квазиклассическое приближение в квантовой механике, равновесная матрица плотности для протонов, энергетические зоны протона в КВС.

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