EXCITON-PHONON INTERACTION AND EXCITON ENERGY IN SEMICONDUCTOR NANOFILMS

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The Bethe variational method has been used to estimate the binding energy of the exciton ground state in a flat semiconductor nanofilm. The Green's function method has been applied to study the dependence of the exciton energy on the film thickness taking the exciton-phonon interaction into account at a temperature of 0 K. Calculations were executed in the framework of the rectangular finite-depth quantum well model and making use of $Al_{0.3}Ga_{0.7}As/GaAS/Al_{0.3}Ga_{0.7}As$ and CdS/HgS/CdS nanofilms as examples.

1. Introduction

The prospect of the creation of modern electron-optical devices on the basis of semiconductor nanostructures [1] stimulates theoretical and experimental researches of their electric, magnetic, and optical properties of the latter. The properties of nanosystems are governed to a great extent by a restriction of quasiparticle spatial motion in them [1], the efficiency of interaction between quasiparticles [2], and external conditions.

The energy spectrum of free charge carriers interacting with phonons in flat semiconducting nanofilms (NFs) with quantum wells (QWs) was studied in the framework of the perturbation [2–4] and Lee–Low–Pines [5] theories. Information concerning the electron and hole energies renormalized by the interaction with phonons in NFs with various thicknesses allows analogous energy transformations for exciton states to be established. Since the latter play an important role in the formation of optical spectra [1, 6], the problem of finding the character and the origins of variation of the exciton energy in NFs with different electron-phonon couplings, different thicknesses, and at different temperatures is challenging.

Exciton states and their interaction with optical vibrations in semiconductor heterostructures with QWs were studied in many experimental and theoretical works. In particular, in works [7, 8], the variational method was used to study the dependence of the binding energy (BE) of an exciton in NFs created on the basis of II–VI and III–V compounds on the NF thickness. The calculation of the exciton BE in NFs $Al_xGa_{1-x}As/GaAs/Al_xGa_{1-x}As$ with QWs characterized by a rectangular or a parabolic profile was also carried out in work [9] on the basis of the two-parameter variational method. The results of theoretical calculations by the authors of both groups agree with the data of experimental measurements [10, 11].

However, neither in the works cited above, nor in other theoretical works, were the temperature variations of the quasiparticle energy in semiconductor NFs with QWs studied. Provided a low concentration of quasiparticles, such a problem can be solved in the framework of the Green's function method [12].

In this paper, the possibilities of the Green's function method have been demonstrated for the theoretical study of transformations of the excitonic ground state energy in NFs, which occur when the NF thickness changes,. The specific calculations were executed for $Al_{0.3}Ga_{0.7}As/GaAs/Al_{0.3}Ga_{0.7}As$ and CdS/HgS/CdS NFs with a finite-depth rectangular QW. The temperature was assumed to be 0 K. The former structure has been studied well both theoretically [7,9] and experimentally [10, 11]; it was chosen to compare our results with the data given in the cited works. The latter structure was studied theoretically in the case of nanostructures of the quantum-dot [13] and quantum-wire [14] types. Hence, the reported results comprise an extension of such researches to the case of flat NFs with a rectangular QW in the indicated nanoheterosystem.

The reduction of a NF thickness was shown to give rise to a nonlinear growth of the excitonic transition energy due to the raising of the electron (hole) ground level in the QW, to its shift toward lower energies due to electron-phonon interaction (mainly, with the interface and confined phonons), and to the nonmonotonous dependence of the exciton BE on the NF thickness. The role of exciton-phonon interaction in the formation of a specific BE in the nanoheterostructures under consideration is weak in comparison with the influence of spatial confinement.

The method of theoretical research, which is proposed here, can be easily modified for studying the

temperature-induced variations of the exciton energy as a result of the interaction between excitons and phonons in the NF.

2. Exciton in a Flat Semiconductor Nanofilm

We consider a flat semiconductor NF (medium 0) embedded into another massive semiconductor (medium 1) with a wider energy gap. The Cartesian coordinate system is so chosen that its origin is located in the middle of the film (the film thickness is a), and the plane XOY is parallel to the NF surface.

As usual, theoretical researches of the electron and hole states in semiconductor nanoheterostructures are carried out in the effective mass approximation, whereas the phonon states are considered in the dielectric continuum one [2–5, 7–9]. Our further calculations were carried out in the framework of indicated approximations, by assuming that the energy spectrum of quasiparticles is non-degenerate and isotropic; we also use the model of rectangular QW with a finite depth. Therefore, the effective masses m_j and the confining potentials V_j of an electron ($j = e$) and a hole ($j = h$), as well as the dielectric permittivity ε of the medium, where the electron and the hole are located, are assumed to be known functions of the z-component of the quasiparticle radius-vector $\mathbf{r}_j = (\boldsymbol{\rho}_j, z_j)$:

$$m_j(z) = \begin{cases} m_j^{(0)}, \\ m_j^{(1)}, \end{cases} \varepsilon(z) = \begin{cases} \varepsilon^{(0)}, \\ \varepsilon^{(1)}, \end{cases} V_j(z) = \begin{cases} 0, & |z| \le \frac{a}{2}; \\ V_j, & |z| > \frac{a}{2}. \end{cases}$$

The forces of interaction between charge carriers and their electrostatic images are neglected, because we study the heterostructures with small differences between lattice constants and dielectric permittivities of their components (Table 1).

By separating the free motion of the center of masses of the electron and the hole in directions parallel to the NF plane, we express the Hamiltonian of an exciton in the form

$$\hat{H}_{\rm ex} = \hat{H}_e^{\perp} + \hat{H}_h^{\perp} + \hat{H}_{SS} + \hat{H}_p = \hat{H}_0 + \hat{H}_p. \tag{1}$$

The first two terms

$$\hat{H}_j^{\perp} = -\frac{\hbar^2}{2}\frac{\partial}{\partial z_j}\frac{1}{m_j(z_j)}\frac{\partial}{\partial z_j} + V_j(z_j)\ (j = e, h) \tag{2}$$

describe the confined motion of a free charge carrier along the OZ-axis,

$$\hat{H}_{SS} = -\frac{\hbar^2 \nabla_{\boldsymbol{\rho}}^2}{2\mu} - \frac{\beta e^2}{\varepsilon\rho} \tag{3}$$

is the Shinada–Sugano Hamiltonian [15] modified by introducing the Bethe variational parameter β which describes a two-dimensional (2D) exciton with the reduced mass $\mu = m_e m_h/(m_e + m_h)$;

$$\hat{H}_p = \frac{\beta e^2}{\varepsilon\rho} - \frac{e^2}{\varepsilon|\vec{r}_e - \mathbf{r}_h|} \tag{4}$$

is the perturbation operator which makes allowance for the difference between the motions of 3D and 2D excitons in the NF; and $\boldsymbol{\rho} = \boldsymbol{\rho}_e - \boldsymbol{\rho}_h$.

If $\hat{H}_p$ is considered as a small perturbation in the system describing by the Hamiltonian $\hat{H}_0$, the energy of an exciton in the NF can be expressed in the form

$$E_{n_e,n_h,N}(\mathbf{k}_\parallel) = E_{n_e}^{(e)}(\mathbf{k}_\parallel) + E_{n_h}^{(h)}(\mathbf{k}_\parallel) +$$

$$+ E_N + \Delta E_{n_e,n_h,N}(\mathbf{k}_\parallel), \tag{5}$$

where $E_{n_j}^{(j)}(\mathbf{k}_\parallel)$ is the energy of a free charge carrier in the band that is defined by the quantum number n_j and the longitudinal component of the wave vector $\mathbf{k}_\parallel$, $E_N = -\beta^2 R_{\rm ex}/(N + 1/2)^2$ is the energy of a 2D exciton in the state with the principal quantum number N ($N = 0, 1, 2, \ldots$), and $R_{\rm ex}$ is the effective Rydberg constant [15]. The last term in formula (5) is a correction to the eigenvalue of Hamiltonian $\hat{H}_0$, which arises due to the perturbation determined by the operator $\hat{H}_p$.

The normalized wave function of a particle in the ground state of the system with the Hamiltonian $\hat{H}_0$ looks like

$$\Psi(\boldsymbol{\rho}, z_e, z_h) = \sqrt{\frac{8}{\pi a_{\rm ex}^2}} \exp(-\frac{2\rho\beta}{a_{\rm ex}}) \cdot \psi_1(z_e)\psi_1(z_h). \tag{6}$$

Here, $a_{\rm ex}$ is the effective Bohr radius of an exciton,

$$\psi_n(z) = \frac{C_n}{\sqrt{a}} \times$$

$$\times \begin{cases} \mathrm{cs}(k_{0n} z), & |z| \le \frac{a}{2}; \\ \mathrm{cs}[\mathrm{sign}(z) k_{0n} a/2] \exp[k_{1n}(a/2 - |z|)], & |z| > \frac{a}{2} \end{cases} \tag{7}$$

T a b l e 1. Physical parameters of compounds: lattice constant a_0 (Å), dielectric permittivities ε_0 and ε_∞, effective masses of electron and hole $m_{e,h}$ (in terms of free electron mass, m_0, units), optical phonon energies Ω_L and Ω_T (meV), energy gap width E_g (eV), and confining potentials $V_{e,h}$ (eV)

Compound	a_0	ε_0	ε_∞	m_e	m_h	Ω_L	Ω_T	E_g	V_e	V_h
β-HgS	5.851	18.20	11.36	0.036	0.044	27.80	21.96	0.5		
β-CdS	5.818	9.10	5.50	0.20	0.70	57.20	44.47	2.5	1.35	0.8

is the wave function of a free charge carrier in the state with the energy $E_n < V$ $(n = 1, 2, \ldots)$,

$$C_n = \sqrt{2}[1 + (-1)^{n-1}\frac{\sin(k_{0n}a)}{k_{0n}a} + 2\frac{\mathrm{cs}^2(k_{0n}a/2)}{k_{1n}a}]^{-\frac{1}{2}}, \quad (8)$$

$$\mathrm{cs}(x_n) = \begin{cases} \cos(x_n), & \mathrm{n} = 1, 3, 5, \ldots; \\ \sin(x_n), & \mathrm{n} = 2, 4, 6, \ldots, \end{cases}$$

and $k_{0n} = \sqrt{2m_0E_n}/\hbar$ and $k_{1n} = \sqrt{2m_1(V - E_n)}/\hbar$ are the transverse wave vector components of a quasiparticle in the NF and in the barrier medium, respectively. The correction to the eigenvalue of operator $\hat{H}_0$, which is determined with the help of function (6), depends on the NF thickness a and the variational parameter β. Then, the ground state energy $(n_e = n_h = 1, N = 0)$

$$E_{\mathrm{ex}}(a) = E_g^{(0)} + E_1^{(e)}(a) + E_1^{(h)}(a) - E_b(a) \quad (9)$$

and the BE

$$E_b(a) = 4R_{\mathrm{ex}}\beta_0 - \Delta E(a, \beta_0) \quad (10)$$

of an exciton are the functions of the NF thickness a. Here, $E_g^{(0)}$ is the energy gap width in the massive crystal of a substance the NF is made of, $E_1^{(j)}(a) \equiv E_1^{(j)}(\mathbf{k}_\parallel = 0)$ is the quasiparticle ground state energy in the corresponding QW, and β_0 is the value of the variational parameter that minimizes the ground state energy of an exciton.

Hence, to determine the exciton energy for a given a, we need to find the correction $\Delta E(a, \beta)$ and then to minimize $E_{\mathrm{ex}}(a)$ with respect to the parameter β. To calculate $\Delta E(a, \beta)$, we use functions (6) which contain the wave functions of the quantized states of an electron and a hole, $\psi_n(z_j)$.

We found the correction $\Delta E(a, \beta)$ in two models:
(a) Similarly to what was done in works [7,8], we neglect the probability for the electron and the hole to penetrate outside the QW boundaries. In this case, we obtain

$$\Delta E(a, \beta) = 8R_{\mathrm{ex}}^{(0)}\beta^2\Bigg(1 - \frac{2a}{\pi a_{\mathrm{ex}}^{(0)}S_e(a)S_h(a)}\times$$

$$\times\int_0^{\pi/2}\frac{D_e(a,x)D_h(a,x)}{x^2 - (2a\beta/a_{\mathrm{ex}}^{(0)})^2}\ln\frac{1 + (\frac{\pi a_{\mathrm{ex}}^{(0)}}{4a_0\beta})^2}{1 + (\frac{\pi a}{2a_0x})^2}dx\Bigg); \quad (11)$$

(b) In the case where the electron and the hole can penetrate into the barrier medium, we obtain

$$\Delta E(a, \beta) = 8R_{\mathrm{ex}}(a)\beta^2\Bigg(1 - \frac{a}{2\pi a_B W(a)}\times$$

$$\times\int_0^{\pi/2}\Bigg[\frac{\mu_{00}^2}{\tilde{\varepsilon}_{00}^3}P_{00}(a,\beta,x)D_e(a,x)D_h(a,x)+$$

$$+\frac{\mu_{01}^2}{\tilde{\varepsilon}_{01}^3}\cos^2\frac{k_{01}^{(h)}a}{2}P_{01}(a,\beta,x)D_e(a,x)Q_h(a,x)+$$

$$+\frac{\mu_{10}^2}{\tilde{\varepsilon}_{10}^3}\cos^2\frac{k_{01}^{(e)}a}{2}P_{10}(a,\beta,x)D_h(a,x)Q_e(a,x)+$$

$$+\frac{\mu_{11}^2}{\tilde{\varepsilon}_{11}^3}\cos^2\frac{k_{01}^{(e)}a}{2}\cos^2\frac{k_{01}^{(h)}a}{2}P_{11}(a,\beta,x)\times$$

$$\times Q_e(a,x)Q_h(a,x)\Bigg]dx\Bigg). \quad (12)$$

Here,

$$W(a) = \frac{1}{4}[\frac{\mu_{00}}{\tilde{\varepsilon}_{00}^2}S_e(a)S_h(a) + \frac{\mu_{01}}{\tilde{\varepsilon}_{01}^2}\frac{\cos^2\frac{k_{01}^{(h)}a}{2}}{\frac{k_{11}^{(h)}a}{2}}S_e(a) +$$

$$+\frac{\mu_{10}}{\tilde{\varepsilon}_{10}^2}\frac{\cos^2\frac{k_{01}^{(e)}a}{2}}{\frac{k_{11}^{(e)}a}{2}}S_h(a) + \frac{\mu_{11}}{\tilde{\varepsilon}_{11}^2}\frac{\cos^2\frac{k_{01}^{(e)}a}{2}}{\frac{k_{11}^{(e)}a}{2}}\frac{\cos^2\frac{k_{01}^{(h)}a}{2}}{\frac{k_{11}^{(h)}a}{2}}];$$

$$S_j(a) = 1 + \frac{\sin(k_{01}^{(j)}a)}{k_{01}^{(j)}a};$$

$$D_j(a,x) = \frac{\sin x}{x} + \frac{1}{2}[\frac{\sin(k_{01}^{(j)}a + x)}{k_{01}^{(j)}a + x} + \frac{\sin(k_{01}^{(j)}a - x)}{k_{01}^{(j)}a - x}];$$

$$Q_j(a,x) = 2\frac{k_{11}^{(j)}a\cos x - x\sin x}{x^2 + (k_{11}^{(j)}a)^2}(j = e, h);$$

$$P_{ll'}(a,\beta,x) = \frac{1}{x^2 - (\frac{2a\mu_{ll'}\beta}{a_B\tilde{\varepsilon}_{ll'}})^2}\ln\frac{1 + (\frac{\pi a_B\tilde{\varepsilon}_{ll'}}{4a_0\mu_{ll'}\beta})^2}{1 + (\frac{\pi a}{2a_0x})^2};$$

$$\mu_{ll'} = \frac{1}{m_0}\frac{m_e^{(l)}m_h^{(l')}}{m_e^{(l)} + m_h^{(l')}}; \quad \tilde{\varepsilon}_{ll'} = \sqrt{\varepsilon^{(l)}\varepsilon^{(l')}};$$

$$R_{\mathrm{ex}}(a) = R_yW(a)(C_1^eC_1^h)^2; \quad (13)$$

a_B and R_y are the Bohr radius and the Rydberg constant, respectively, for the hydrogen atom; $a_{\rm ex}^{(0)} = a_B\varepsilon^{(0)}/\mu^{(0)}$ and $R_{\rm ex}^{(0)} = R_y\mu^{(0)}/\varepsilon^{(0)2}$ are the same parameters for an exciton in the NF; C_1^e (C_1^h) is the normalizing factor for the wave function of an electron (hole) in the ground state; $\mu^{(l)}$ is the reduced mass of an exciton (in terms of free electron mass, m_0, units) in the medium with the dielectric permittivity $\varepsilon^{(l)}$ ($l = 0, 1$); and a_0 is the crystal lattice constant of medium 0.

3. Exciton-Phonon Interaction in a Flat Semiconductor Nanofilm

The Hamiltonian of the exciton-phonon system in a NF looks as like

$$\hat{H} = \hat{H}_{\rm ex} + \hat{H}_{\rm ph} + \hat{H}_{\rm int}. \tag{14}$$

Here,

$$\hat{H}_{\rm ph} = \hat{H}_{L0} + \hat{H}_{L1} + \hat{H}_I = \sum_{\lambda,\mathbf{q}_\parallel} \Omega_{L0}(\hat{b}^+_{\lambda\mathbf{q}_\parallel}\hat{b}_{\lambda\mathbf{q}_\parallel} + 1/2) +$$

$$+ \sum_{q_\perp,\mathbf{q}_\parallel} \Omega_{L1}(\hat{b}^+_{q_\perp\mathbf{q}_\parallel}\hat{b}_{q_\perp\mathbf{q}_\parallel} + 1/2) +$$

$$+ \sum_{\sigma=S,A}\sum_{p=\pm}\sum_{\mathbf{q}_\parallel} \Omega_{\sigma p}(\mathbf{q}_\parallel)(\hat{b}^+_{\sigma p\mathbf{q}_\parallel}\hat{b}_{\sigma p\mathbf{q}_\parallel} + 1/2) \tag{15}$$

is the Hamiltonian of the system of longitudinal optical polarization phonons: confined in the NF medium ($L0$), semiconfined in barrier medium 1 ($L1$), and interface (I) ones; Ω_{L0}, Ω_{L1}, and $\Omega_{\sigma p}(\mathbf{q}_\parallel)$ are the energies; and $\hat{b}^+_{\Lambda\mathbf{q}_\parallel}$ ($\hat{b}_{\Lambda\mathbf{q}_\parallel}$) is the operator of creation (annihilation) of the corresponding phonon state with a continuous ($q_\perp$) or discrete ($q_\lambda = \lambda\pi/a$ ($\lambda = 1, 2, \ldots, N$) or $q_\perp = \{\sigma p\}$) transverse components of the wave vector $\mathbf{q} = (\mathbf{q}_\parallel, q_\perp)$ [4].

Supposing that exciton-phonon coupling is realized through the interaction between phonons, on the one hand, and the electron and the hole, on the other hand, the interaction Hamiltonian can be expressed in the form

$$\hat{H}_{\rm int} = \hat{H}_{{\rm ex}-L0} + \hat{H}_{{\rm ex}-L1} + \hat{H}_{{\rm ex}-I} =$$

$$= \sum_{j=e,h}\eta_j[\sum_{n_j,n'_j,\mathbf{k}_\parallel}\sum_{\lambda,\mathbf{q}_\parallel} F^\lambda_{n_jn'_j}(\mathbf{q}_\parallel)\hat{a}^+_{n'_j\mathbf{k}_\parallel+\mathbf{q}_\parallel}\hat{a}_{n_j\mathbf{k}_\parallel}\hat{B}_{\lambda q_\parallel} +$$

$$+ \sum_{q_\perp,\mathbf{q}_\parallel} F^{q_\perp}_{n_jn'_j}(\mathbf{q}_\parallel)\hat{a}^+_{n'_j\mathbf{k}_\parallel+\mathbf{q}_\parallel}\hat{a}_{n_j\mathbf{k}_\parallel}\hat{B}_{q_\perp q_\parallel} +$$

$$+ \sum_{\sigma,p,\mathbf{q}_\parallel} F^{\sigma p}_{n_jn'_j}(\mathbf{q}_\parallel)\hat{a}^+_{n'_j\mathbf{k}_\parallel+\mathbf{q}_\parallel}\hat{a}_{n_j\mathbf{k}_\parallel}\hat{B}_{\sigma pq_\parallel}], \tag{16}$$

where $\eta_e = 1$; $\eta_h = -1$; $\hat{a}^+_{n_j\mathbf{k}}$ and $\hat{a}_{n_j\mathbf{k}}$ are the operators of creation and annihilation, respectively, of an electron ($j = e$) or hole ($j = h$) state with the wave vector $\mathbf{k}$ in the n_j-th band; $\hat{B}_{\Lambda\mathbf{q}_\parallel} = \hat{b}_{\Lambda,\mathbf{q}_\parallel} + \hat{b}^+_{\Lambda,-\mathbf{q}_\parallel}$ ($\Lambda = q_\lambda, q_\perp$, or $\{\sigma p\}$ is the subscript that distinguishes the phonon type and, simultaneously, determines the transverse component $q_\perp$ of its wave vector $\mathbf{q}$); and $F^\Lambda_{n_jn'_j}(\mathbf{q}_\parallel)$ are the functions, which describe the coupling with the corresponding phonon state. The explicit forms for the dependences of coupling functions on the NF thickness a and the longitudinal component $\mathbf{q}_\parallel$ of the wave vectors are given in work [16] for $L0$- and $L1$-phonons, as well as for I-phonons belonging to the symmetric ($\sigma = S$) and antisymmetric ($\sigma = A$) branches.

The interaction with phonons shifts the bottom of the ground band of the j-th carrier in the QW by Δ_j and, by varying the transverse components of its wave vector $k^{(j)}_{\rm ln}$ (here, n indicates the band, and l the medium), changes the exciton BE. Then, the transition energy into the ground state of an exciton in the NF with thickness a renormalized by the interaction with phonons is expressed as

$$E_{\rm ex}(a) = E_g^{(0)} + E_1^{(e)}(a) + \Delta_e(a) +$$

$$+ E_1^{(h)}(a) + \Delta_h(a) - E_b(a). \tag{17}$$

In the case of weak electron-phonon coupling, the shift of the bottom, E_1, of the electron ground band can be written down in the form

$$\Delta \equiv M(\mathbf{k}_\parallel = 0, E = E_1) = \Delta_{L0} + \Delta_{L1} + \Delta_I, \tag{18}$$

where $M(\mathbf{k}_\parallel, E)$ is the one-phonon mass operator of Green's function; and Δ_{L0}, Δ_{L1}, and Δ_I are partial shifts due to the interaction with corresponding phonons [16]. Their explicit forms at $T = 0$ K, owing to their cumbersome length, are not given here, but they can be found in work [16].

4. Analysis of the Results Obtained

The plots of the dependence of the exciton BE, E_b, on the NF thickness (the film $Al_{0.3}Ga_{0.7}As$/GaAS/$Al_{0.3}Ga_{0.7}As$) are shown in Fig. 1,*a*. The calculations carried out in the framework of model A give rise to a monotonously decreasing

BE dependence on the NF thickness a (curve *1*), which is similar to the results of work [7]. The values of E_b obtained for films with the thickness of more than 10 nm agree with the results of works [7, 9] and approach the value characteristic of a massive GaAs crystal, $R_{\rm ex}^{(0)} \approx 4.7$ meV, if $a \geq 40$ nm. At smaller film thicknesses, the results obtained in the framework of this model considerably exceed the data of the indicated works.

The calculations executed in the framework of model B brought about a nonmonotonous dependence of the BE on the NF thickness (curve *2*). At thicknesses of more than 20 nm, the results of both models practically do not differ. At $a \geq 10$ nm, the behavior of curve *2* qualitatively agrees with the data of theoretical [7,9] and experimental [10, 11] works. In the range of narrower thicknesses, the dependence $E_b(a)$ also turns out non-monotonous; namely, if a diminishes, the BE drastically grows to reach the maximum in an NF with a thickness of about 2 GaAs monolayers. Then it falls down quickly and attains, at $a \to 0$, the value $R_{\rm ex}^{(1)} \approx 7.3$ meV which is characteristic of a massive $\rm Al_{0.3}Ga_{0.7}As$ crystal.

From the physical reason, the behavior of curve *2* testifies that model B takes the influence of the nanosystem structure into consideration more completely than model A does. The results obtained in the framework of this model are in qualitative agreement with the calculation results [9] and the experimental data [10, 11]. However, in the region of curve *2* maximum, the BE values turn out overestimated. It is quite clear, because the model of dielectric continuum, the effective mass approximation, our assumption on the effective mass isotropy, and our neglect of the interaction between electrons (holes) and their electrostatic images appear rather crude in the case of very narrow films. Nevertheless, this model gives the qualitatively valid result which agrees with the results of calculations in work [9] even at $a \to 0$.

Similar dependences of the exciton BE on the thickness of CdS/HgS/CdS NF are shown in Fig. 1,*b*. For films, the thickness of which exceeds the polaron radius $R_p \approx 6.2$ nm, the results of both models practically coincide and approach, at $a > 100$ nm, the BE value for a 3D exciton in β-HgS, $R_{\rm ex}^{(0)} \approx 0.8$ meV. At narrower thicknesses, the dependence shown by curve *2* is more abrupt and nonmonotonous: the reduction of a gives rise to the BE growth, which achieves its maximum in films, the thickness of which is one monolayer of β-HgS, and is followed by a decreasing, so that the value of E_b tends to the BE of a 3D exciton in β-CdS, $R_{\rm ex}^{(1)} \approx 25.6$ meV, at $a \to 0$.

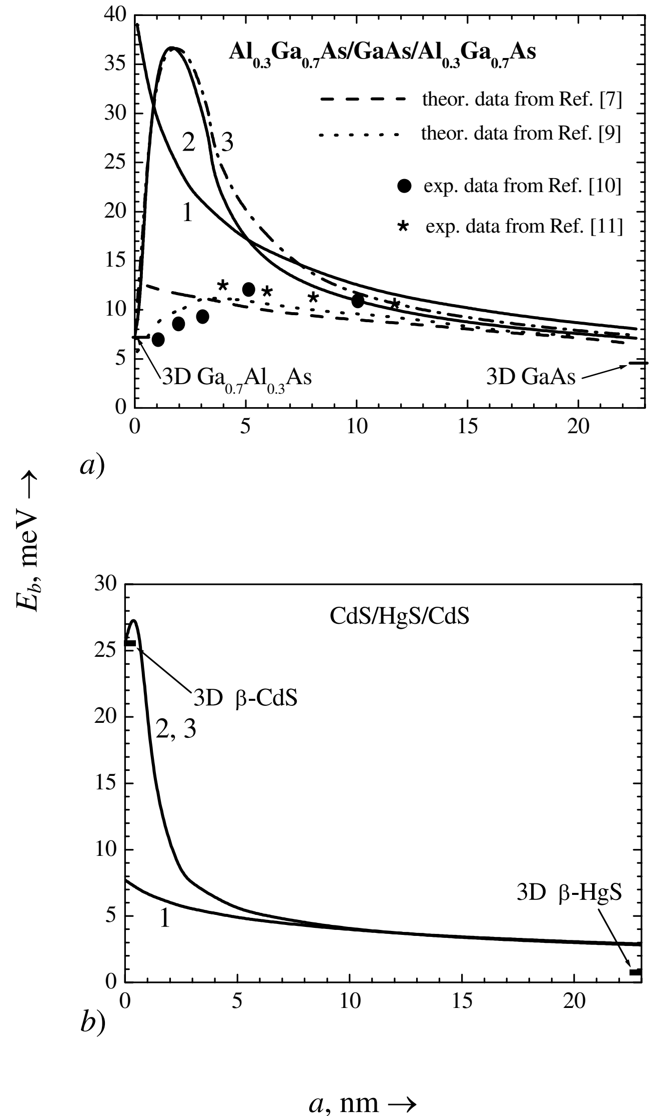

Fig. 1. Dependences of the exciton binding energy E_b on the nanofilm thickness a, calculated in the framework of models A (*1*) and B (*2*), and taking the interaction with phonons into account (*3*)

An essential difference between the results for both nanostructures consists in that both models give practically identical results for the NF CdS/HgS/CdS (except for very small thicknesses, where the application of model A is invalid). It is related to the fact that the height of the potential barrier for an electron and a hole at the heterojunction β-HgS/β-CdS is considerably higher than that at the $\rm GaAs/Al_{0.3}Ga_{0.7}As$ one (Table 1). Hence, at $a > R_p$, we can consider an exciton to be really closed within the NF CdS/HgS/CdS [7]. At

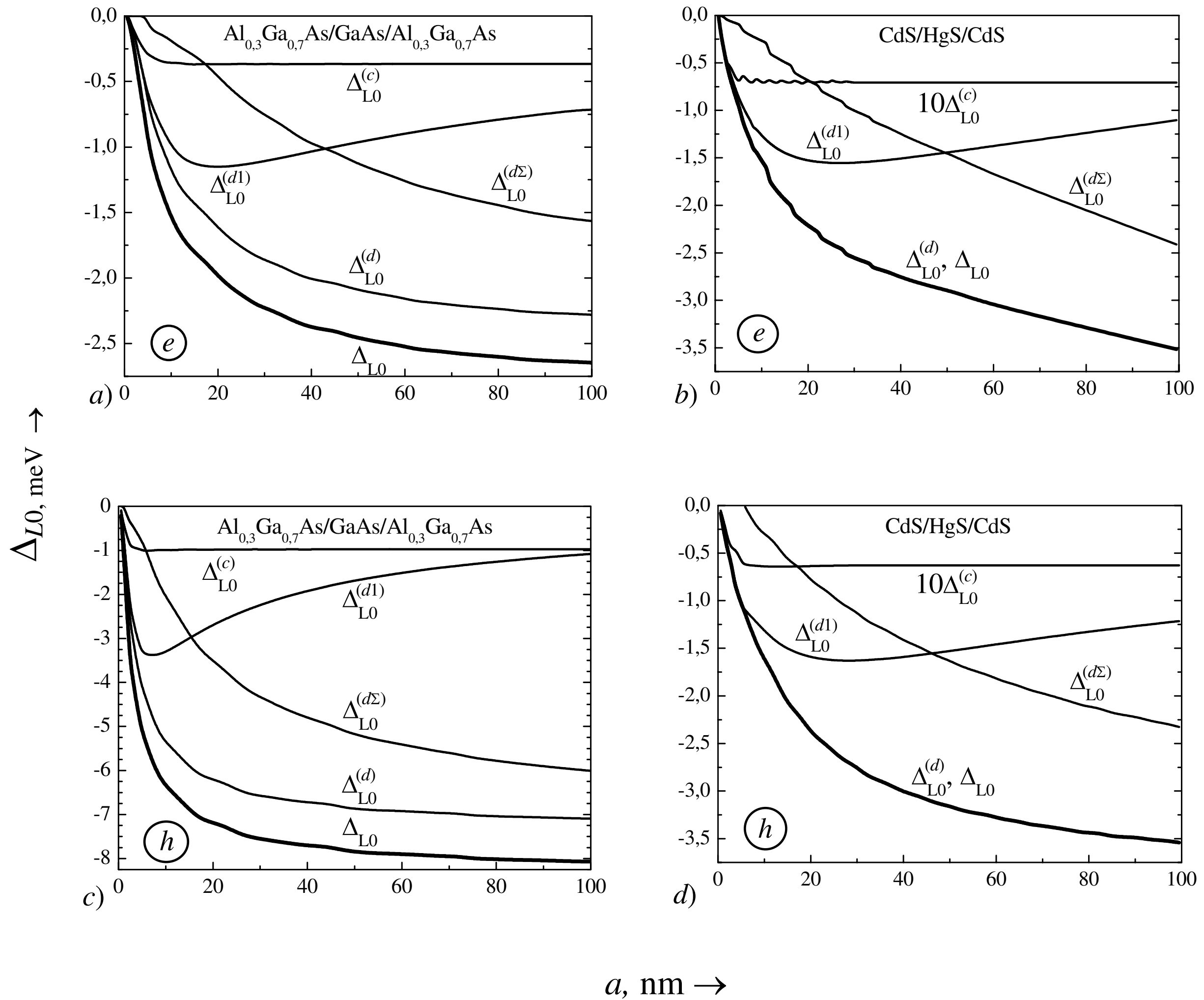

Fig. 2. Dependences of the electron (a, b) and hole (c, d) ground band bottom shift Δ_{L0} due to the interaction with confined phonons and its components associated with the engaging of main ($d1$), other ($d\Sigma$) and all (d) discrete states, as well as continual (c) states, of the electron spectrum, on the nanofilm thickness a

smaller thicknesses, the spatial confinement and barrier medium effects grow, which induces a nonmonotonous behavior of the BE variation. From the physical reason, the behavior of curve *2* looks quite justified, and the quantitative results of model B seem satisfactory in order to analyze the character of exciton energy transformations in the NF, when the NF thickness and the temperature vary.

The renormalization of the ground state energies of an electron and a hole–and, respectively, an exciton–in the QW occurs due to their interaction with optical vibrations of all types, which give different contributions to shift (18). Let us suppose that every partial shift is generated by the interaction between the electron (hole) and phonons through the states in the ground and all higher bands of the discrete and continual parts of the spectrum, and write down them in the form

$$\Delta_{Ll} = \Delta_{Ll}^{(d1)} + \Delta_{Ll}^{(d\Sigma)} + \Delta_{Ll}^{(c)} (l = 0, 1),$$

$$\Delta_I = \Delta_I^{(d1)} + \Delta_I^{(d\Sigma)} + \Delta_I^{(c)}, \qquad (19)$$

where the symbols $d1$, $d\Sigma$, and c denote the contributions of each mentioned mechanisms, in that order. The role of each mechanism in the formation of the total shift of the electron and hole ground state energies depends on the NF thickness.

In Fig. 2, the dependences of the partial shift Δ_{L0} of the bottom of the electron and hole ground bands in

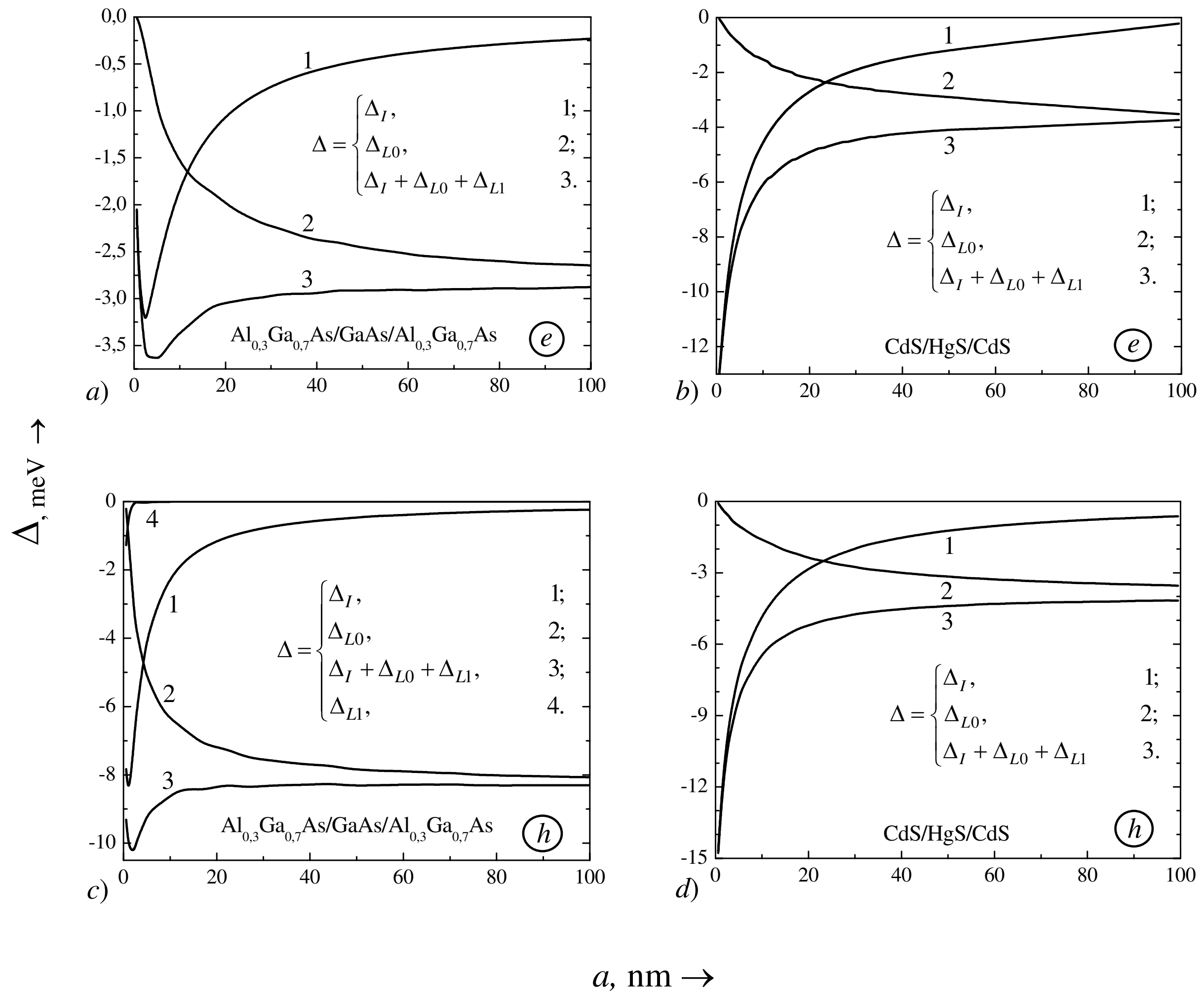

Fig. 3. Dependences of the electron (a, b) and hole (c, d) ground band bottom shift Δ and its partial components associated with the interaction with the interface (Δ_I), confined (Δ_{L0}), and semiconfined (Δ_{L1}) phonons

the QW owing to their interaction with $L0$-phonons on the NF thickness are shown together with the contributions connected with the states in the ground band only ($\Delta_{L0}^{(d1)}$) and with all other states in the discrete ($\Delta_{L0}^{(d\Sigma)}$) and continual ($\Delta_{L0}^{(c)}$) spectral ranges. One can see that, if the film is thin ($a < 20$ nm), the main contribution to Δ_{L0}, irrespective of the specific nanostructure, is given by the electron-phonon interaction through the states in the ground band, and the absolute value of this contribution grows drastically, if the NF thickness increases. The total contribution of all higher states in the discrete part of the spectrum is small, if the film is narrow; however, its magnitude also grows quickly with the thickness a. At the same time, the growth of the film thickness above 20 nm is accompanied by a smooth reduction of the quantity $\Delta_{L0}^{(d1)}$, whereas the total contribution of the higher states increases, and, at $a > 45$ nm, it exceeds $\Delta_{L0}^{(d1)}$.

The contribution of continual states grows firstly drastically as the thickness a increases up to 5 nm; then, weakly oscillating, it saturates, not exceeding 2% of $\Delta_{L0}^{(d)}$ in $Al_{0.3}Ga_{0.7}As/GaAS/Al_{0.3}Ga_{0.7}As$ and 4–5% in CdS/HgS/CdS. The total partial shift Δ_{L0} increases with the film thickness and saturates at $a > 100$ nm, achieving the values characteristic of massive medium 0.

The analysis of partial shifts Δ_I and Δ_{L1} caused by the interaction with interface and semiconfined phonons (Fig. 3) showed the following.

1. Since the wave function of an electron in the ground state is symmetric, the electron interacts only with the

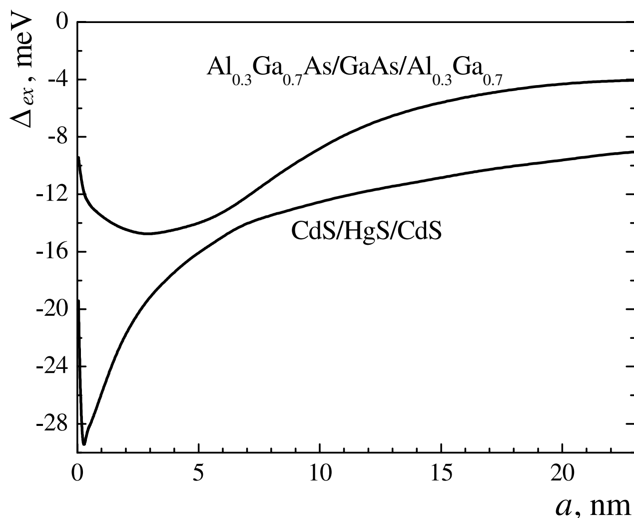

Fig. 4. Exciton level shifts due to the exciton-phonon interaction in nanofilms with various thicknesses

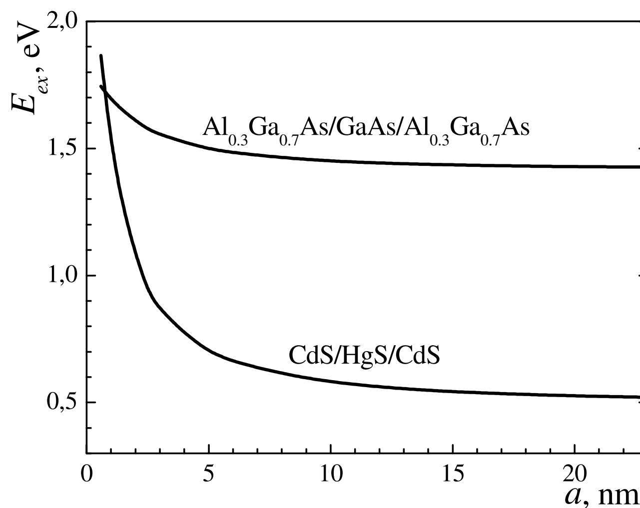

Fig. 5. Exciton energy $E_{\rm ex}$ as a function of the nanofilm thickness a

symmetric branch of I-phonons, whereas the interaction through states in the higher bands of the discrete spectral range gives a contribution that does not exceed $0.05\Delta_I^{(d1)}$. The contribution of states in the continual spectral range is negligibly small. Therefore, the dominant contribution to the Δ_I-magnitude is given by the intraband interaction with symmetric I-phonons.

2. The magnitude of Δ_{L1} is mainly governed by the intraband interaction too; the total contribution of interband interactions through the states in the discrete spectral range is small in comparison with $\Delta_{L1}^{(d1)}$, whereas that through the continual states does not exceed 1% of $\Delta_{L1}^{(d1)}$.

3. The shifts Δ_I and Δ_{L1} (curves *1* and *4* in Fig. 3) quickly decrease as the NF thickness grows over the size of one monolayer of medium 0. In so doing, the dependence of Δ_{L1} on a monotonously falls down for both nanoheterosystems, and the initial values (the interaction between a hole and $L1$-phonons in $Al_{0.3}Ga_{0.7}As/GaAS/Al_{0.3}Ga_{0.7}As$ is an exception) are much less than that of Δ_I. For this reason, the plot of the dependence $\Delta_{L1}(a)$ is shown only for holes in the NF $Al_{0.3}Ga_{0.7}As/GaAS/Al_{0.3}Ga_{0.7}As$ (Fig. 3,*c*).

As is seen from Fig. 3, the long-wave shift of the ground level of an electron and a hole in thin films ($a < 10$ nm for $Al_{0.3}Ga_{0.7}As/GaAS/Al_{0.3}Ga_{0.7}As$ and $a < 25$ nm for CdS/HgS/CdS) is mainly caused by the interaction with I-phonons and, in thicker films, with $L0$-ones. If the film thickness increases substantially, the influence of I-phonons vanishes, and the magnitude of Δ_{L0} approaches the value characteristic of massive medium 0 (2.90 and 8.81 meV for electrons and holes, respectively, in GaAs, and 3.85 and 4.26 meV, respectively, in β-HgS). Such a behavior is completely clear, because the probability to find an electron (hole) at the heterojunction interface decreases with increase of the NF thickness and grows in the region of a quantum well.

The influence of the phonon system on the exciton BE in the studied nanosystems at $T = 0$ K turned out insignificant (curves *3* in Fig. 1): the BE change does not exceed 2.5 meV in the case of thin $Al_{0.3}Ga_{0.7}As/GaAS/Al_{0.3}Ga_{0.7}As$ NFs and 0.5 meV in the case of CdS/HgS/CdS NFs.

The analytical expressions, which were obtained by us for the exciton BE and the shifts of electron and hole levels in the QW, make it possible to study the dependence of the excitonic ground state energy on the NF thickness. The dependences of the shift $\Delta_{\rm ex}$ of the ground excitonic level, caused by interaction with phonons, and its energy $E_{\rm ex}$ on the NF thickness are plotted in Figs. 4 and 5, respectively. Three factors are responsible for the nonlinear—weak at large and drastic at small a's—growth of $E_{\rm ex}$ with a reduction of the NF thickness. These are 1) the elevation of the electron (hole) level in a QW, when the width of the latter decreases [2–4]; 2) its shift toward lower energies as a result of the electron-phonon interaction, mainly with I- and $L0$-phonons (Fig. 3); and 3) the nonlinear dependence $E_b(a)$ (Fig. 1).

The results of our calculations reported in this paper testify to the presence of a nonlinear nonmonotonous

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dependence of the BE and the ground state energy of exciton on the thickness of NFs under investigation. Its amplitude grows at a reduction of the NF thickness and, in the films thin enough, exceeds the values characteristic of both media: the film itself and the barrier substance. At $T = 0$ K, the dependence $E_b(a)$ is mainly governed by peculiarities in spatially confined motions of the electron and the hole, whereas the values of $E_{\rm ex}$ are driven by both the spatial confinement conditions and the electron-phonon interaction. In particular, in thin CdS/HgS/CdS and $Al_{0.3}Ga_{0.7}As/GaAS/Al_{0.3}Ga_{0.7}As$ NFs, the contribution of the electron-phonon interaction to the exciton energy change achieves 14 and 29 meV, respectively. Certainly, the quantitative coincidence with experimental data should not be expected in the range of ultrathin nanofilms. However, this model gives an idea about the tendencies in the dependence of the excitonic transition energy on the film thickness.

5. Conclusions

1. The theory of the exciton-phonon interaction in flat semiconductor NFs with a weak electron-phonon coupling has been developed. For the first time, the analytical expression for the exciton BE in the ground state in a NF has been obtained, and the dependence of the excitonic transition energy on the NF thickness has been calculated.

2. The BE depends nonlinearly and nonmonotonously on the thickness a of studied NFs: as the thickness diminishes, the BE grows from the value characteristic of a massive substance the QW is made of to a finite value which exceeds the BEs of a 3D exciton in the materials on either side of a heterojunction. This can be explained by both an enhancement of spatial confinement effects and a possibility for an electron or a hole to partially tunnel into the barrier medium in very thin (less than 10 nm) NFs. As $a \to 0$, the BE approaches the value characteristic of a massive barrier substance.

3. The dependence of the excitonic transition energy on the NF thickness is also nonlinear. Its value grows with a reduction of the NF thickness and reaches the maximum in the range of very thin (less than 5 nm) NFs. Such a behavior mainly originates from the change of the influence degree of I- and $L0$-phonons in NFs with different thicknesses.

1. *Confined Electrons and Photons: New Physics and Applications,* edited by E. Burstein and C. Weisbuch (Plenum Press, New York, 1995).
2. L. Wendler and R. Pechstedt, Phys. Status Solidi B **141**, 129 (1987).
3. N. Mori and T. Ando, Phys. Rev. B **40**, 6175 (1989).
4. G.Q. Hai, F.M. Peeters and J.T. Devreese, Phys. Rev. B **48**, 4666 (1993).
5. R. Zheng, S. Ban, and X.X. Liang, Phys. Rev. B **49**, 1796 (1994).
6. D.D. Nolte, J. Appl. Phys. **85**, 6259 (1999).
7. R. Zheng and M. Matsuura, Phys. Rev. B **58**, 10769 (1998).
8. R. Zheng, M. Matsuura, and T. Taguchi, Phys. Rev. B **61**, 9960 (2000).
9. B. Gerlach and M.A. Smondyrev, cond-mat/0002156 v2.
10. M. Gurioli, J. Martinez-Pastor, M. Colocci *et al.*, Phys. Rev. B **47**, 15755 (1993).
11. V. Voliotis, R. Grousson, P. Lavallard *et al.*, Phys. Rev. B **52**, 10725 (1995).
12. M.V. Tkach, *Quasiparticles in Nanoheterosystems. Quantum Dots and Wires* (Chernivtsi Univ. Publ. House, Chernivtsi, 2003) (in Ukrainian).
13. N.V. Tkach and V.P. Zharkoi, Fiz. Tekh. Poluprovodn. **33**, 598 (1999).
14. N.V. Tkach, V.A. Golovatskii, O.N. Voitsekhivskaya *et al.*, Fiz. Tverd. Tela **42**, 1315 (2001).
15. M. Shinada and S. Sugano, J. Phys. Soc. Jpn., **21**, 1936 (1966).
16. M.V. Tkach and V.M. Kramar, Ukr. Fiz. Zh. **53**, 812 (2008).

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ЕКСИТОН-ФОНОННА ВЗАЄМОДІЯ І ЕНЕРГІЯ ЕКСИТОНУ У НАПІВПРОВІДНИКОВИХ НАНОПЛІВКАХ

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Р е з ю м е

Варіаційним методом Бете оцінено енергію зв'язку основного екситонного стану у плоскій напівпровідниковій наноплівці. Методом функцій Гріна досліджено залежність енергії екситону від товщини плівки з урахуванням екситон-фононної взаємодії при 0 К. Розрахунки виконано на прикладі наноплівок $Al_{0,3}Ga_{0,7}As/GaAs/Al_{0,3}Ga_{0,7}As$ та CdS/HgS/CdS у моделі прямокутної квантової ями скінченої глибини.