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Spatial confinement, self-polarization and exciton–phohon interaction effect on the location of exciton line in lead iodide nanofilms

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Theoretical investigation of the spatial confinement, self-polarization and exciton–phonon interaction influence on the exciton state in plane double nanoheterostructure (nanofilm)–lead iodide in polymeric matrix is performed within the effective mass approximation for the electron and dielectric continuum for the phonons in the framework of infinitely deep single quantum well. It is shown that spatial confinement is the dominating feature determining the energy of the bottom of exciton ground band and its binding energy. The relationship of two others depends on nanofilm thickness: in ultrathin films the influence of self-polarization effect is essentially bigger than the role of exciton–phonon interaction.

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1. Introduction

The thin films and low-dimensional nanostructures at the base of lead iodide are the perspective materials for the fabrication of temperature sensors, photodetectors, biomedical sensors and detectors of x-ray and γ-radiation operating in the wide range of temperatures (from –200 till +130 °C) [1]. The large values of charge numbers of Pb and I atoms, band gap widths and exciton binding energies in these structures determine the display of exciton effects in the spectra of their optical absorption, transmission and luminescence [2].

It is well known that the spatial confinement (SC) of quasiparticles in low-dimensional structures causes the additional quantization of their states characteristics. The nature, character and magnitude of variation of quasiparticles states are defined by the characteristic sizes of the structure, reflected at the experimentally observed size dependences of its optical properties including the exciton range of the spectrum [3]. The theoretical investigation of exciton states in semiconductor nanoheterostructures with single quantum wells (QWs) was performed by several authors using different methods and approximations (see, for example [4–7]). However, they did not observe QWs fabricated at the base of layered semiconductors.

In this paper we present the results of theoretical study of SC, self-polarization (SP) and exciton–phonon interaction (EPI) effect on the magnitude of the energy of the ground exciton state and on the location of exciton line in the plane nanofilm (NF) of lead iodide embedded into the organic dielectric medium — copolymer of ethylene-methacrylic acid (E-MAA). The low-dimensional ultra thin crystal structures of such type are fabricated and investigated by the authors of the papers [8,9]. In particular, in [8] the location of exciton peaks in low temperature (T = 2 K) absorption spectra of PbI_2 microcrystallites having the shape of hexagonal plates embedded into E-MAA are experimentally defined. It is proven that the locations of exciton peaks depend on the thickness of the plate — when the latter increases, the maximum of exciton line shifts into the long-wave region of the spectrum.

Assuming that the width of the plate is essentially smaller than its cross sizes, it can be considered as a quasi-two-dimensional structure. Using the model of NF as a plane double heterostructure of type I, we obtained the analytical expressions for the calculation of the ground exciton state energy and its binding energy too.

The exciton energy calculated in such model for the nanoheterostructure E-MAA/PbI_2/E-MAA is characterized by the nonlinearly decreasing dependence on NF thickness. The SC performs the main contribution into the exciton energy at any magnitude of the thickness. The influence of SP and EPI effects is sufficiently weaker and depends on NF

thickness — decreases at its increasing. The contribution of SP effect into the exciton energy in ultra-thin NF is essentially bigger than the one of EPI. The SP effect decreases and EPI — increases when the NF thickness increases.

2. The model

We consider the NF with thickness a consisting of the layered semiconductor crystal embedded into the organic dielectric medium. The layered crystals have the atomic-smooth surface and low number of broken bonds [10], that allows us to consider the heterojunction as unstrained one and the QW — rectangular and, inside of the dielectric medium, — infinitely deep.

The Hamiltonian of exciton–phonon system in NF

$$\hat{H} = \hat{H}_{\text{ex}} + \hat{H}_{\text{ph}} + \hat{H}_{\text{int}}$$

had been discussed in [11]. Also, expression to compute the exciton energy

$$E_{\text{ex}} = E_g + E^{(e)} + E^{(h)} - E_b \tag{1}$$

as a function of the NF thickness taking into account the SC and SP effects been obtained there. Here E_g is a gap energy of NF material, E_b — exciton binding energy, and $E^{(e)}$ ($E^{(h)}$) — ground state energy of electron (hole) in QW.

When the temperature is low (formally, at $T = 0$ K), only the virtual phonons exist in the system. Since, the EPI can be manifested only in the processes of their radiation, causing the long-wave shift of the energy of stationary states. The magnitude of the shift of quasiparticle energy level in crystal systems with arbitrary power of its binding with phonons at $T = 0$ K can be found using the method of Green's functions. In particular, the renormalized due to phonons energy $\hbar\omega$ of electron from nth mini-band in QW is fixed by the location of the pole of Fourier-image of Green's function

$$G_n(\mathbf{k}_\perp, \omega) = [\hbar\omega - E_n(\mathbf{k}_\perp) - M_n(\mathbf{k}_\perp, \omega)]^{-1},$$

where $E_n(\mathbf{k}_\perp)$ — its magnitude without taking into account of interaction with phonons and $M_n(\mathbf{k}_\perp, \omega)$ — mass operator, determining the magnitude of the shift of the bottom of electron (hole) nth mini-band in QW

$$\Delta_n = -M_n(\mathbf{k}_\perp = 0, \hbar\omega = E_n).$$

Then the energy of exciton created by electron and hole, being in the ground state in QW ($n_e = 1$, $n_h = 1$), renormalized due to the interaction with phonons is fixed by the expression

$$E = E_{\text{ex}} - \Delta^{(e)} - \Delta^{(h)}, \tag{2}$$

where $\Delta^{(e)}(\Delta^{(h)})$ is a shift of the bottom of the ground electron's (hole's) energy mini-band in QW caused by this interaction.

2. Discussion of results

2.1. The influence of self-polarization effect

The energy of the ground ($n = 1$) state of the carrier in its QW is

$$E^{(j)} = \frac{h^2}{8m_j^{\parallel} a^2} + \Delta E_s, \tag{3}$$

where

$$\Delta E_s = \frac{e^2}{\varepsilon_{\infty\parallel}^{(0)} a} \sum_{n=0}^{\infty} \left[\xi^{2n+1} \left(\int_0^{\pi/2} \frac{\cos^2 x\, dx}{x + \pi(n+1/2)} - \right.\right.$$

$$\left.\left. - \int_0^{\pi/2} \frac{\cos^2 x\, dx}{x - \pi(n-1/2)} \right) + \frac{\xi^{2n+2}}{2n+2} \right] \tag{4}$$

— correction due to SP, $m_j^{\parallel}(m_j^{\perp})$ — the effective mass of quasiparticle, characterizing its movement along C axis of layered crystal (in the plane of layered packet),

$$\xi = (\varepsilon_\infty^{(0)} - \varepsilon_\infty^{(1)})/(\varepsilon_\infty^{(0)} + \varepsilon_\infty^{(1)}),$$

and 0 (1) — index of well (barrier) material.

Using the wave function of ground state ($n = 0$, $m = 0$) of 2D-exciton [12]

$$\psi(\boldsymbol{\rho}, z_e, z_h) = \frac{4\sqrt{2}}{\sqrt{\pi} a a_{\text{ex}}} \exp\left(-\frac{2\rho\beta}{a_{\text{ex}}}\right) \cos\left(\frac{\pi z_e}{a}\right) \cos\left(\frac{\pi z_h}{a}\right), \tag{5}$$

we obtain the analytical expression for the exciton binding energy

$$E_b = 4R_{\text{ex}}\beta_0^4 \left\{ 1 - \frac{64a}{\pi a_{\text{ex}}} \left[I_0(a, \beta_0) + \frac{\varepsilon_{0\parallel}^{(0)}}{\varepsilon_{0\perp}^{(0)}} \sum_{n=1}^{\infty} \xi^n I_n(a, \beta_0) \right] \right\}. \tag{6}$$

Here a_{ex} and R_{ex} — radius and Rydberg constant, respectively for the exciton in NF with thickness a;

$$I_n(a, \beta) = \int_0^{2\pi} \cos nx \cdot \sin^2 \frac{x}{2} \left[\frac{1}{x} - \frac{x}{x^2 + 4\pi^2} \right]^2 \frac{\ln[(a_{\text{ex}} x)/(4a\beta^2)]}{x^2 - [(4a\beta^2)/a_{\text{ex}}]^2} dx \tag{7}$$

— function, taking into account the correction taking into account the difference between the exciton in NF and 2D-exciton at $n = 0$ and at $n = 1, 2, \ldots$ — influence of the effect of NF surface polarization by exciton; β_0 — variational parameter, minimizing value of E_{ex} [7].

The calculations performed using the parameters of the crystal $2H$-PbI_2 [2] and polymer E-MAA [13], prove that

SP-potential increases the binding energy of ground exciton state in NF (Fig. 1). It is clear that the magnitude of the correction essentially increases when NF thickness decreases. Herein, the energy of exciton transition increases too (Fig. 2). It is explained by the prevail increase of carriers energies in QW both due to the SC and SP effect.

3.2. Influence of interaction with phonons

In order to evaluate the magnitude of the shift of the electron (hole) ground state due to EPI, we use the one-phonon approximation and electron-phonon binding functions obtained in [7] and transformed for the case of infinitely deep QW. Herein, the mass operator of electron–phonon system in NF takes the form

$$M_1(\omega) = \sum_n [M_{1n}^{(LO)}(\omega) + M_{1n}^{(\sigma)}(\omega)], \tag{8}$$

where the terms

$$M_{1n}^{(LO)}(\omega) = \frac{4e^2}{\pi^2 \varepsilon^{(0)} a} \sum_{\lambda} \frac{\lambda^2}{\dfrac{\hbar\omega - E_n}{\Omega_{LO}} + \dfrac{\pi^2\hbar^2\lambda^2}{2m_\perp a^2 \Omega_{LO}} - 1} \ln \frac{1 + [a/(\lambda a_0)]^2}{1 - \dfrac{\pi^2\hbar^2}{2m_\perp a_0^2 \Omega_{LO}\left(\dfrac{\hbar\omega - E_n}{\Omega_{LO}} - 1\right)}} \times$$

$$\times \begin{cases} \left(\dfrac{\cos\dfrac{1-n}{2}\pi}{\lambda^2 - (1-n)^2} + \dfrac{\cos\dfrac{1+n}{2}\pi}{\lambda^2 - (1+n)^2} \right)^2 & (\lambda = 1, 3, \ldots;\ \text{odd } n); \\ \left(\dfrac{\sin\dfrac{1-n}{2}\pi}{\lambda^2 - (1-n)^2} - \dfrac{\sin\dfrac{1+n}{2}\pi}{\lambda^2 - (1+n)^2} \right)^2 & (\lambda = 2, 4, \ldots;\ \text{even } n); \end{cases} \tag{9}$$

$$M_{1n}^{(\sigma)}(\omega) = \frac{2e^2}{a^3} \int_0^{\pi a/a_0} \frac{\Omega_\sigma(y) \,|\, f^\sigma(y) \,|^2}{\in^{(0)}(y) \varsigma_\sigma(y) \left[\hbar\omega - E_n - \dfrac{\hbar^2}{2m_\perp a^2} y^2 - \Omega_\sigma(y) \right]} dy \tag{10}$$

take into account the change of the carrier ground state energy due to the radiation of virtual confined (LO) or interface (I_σ) phonon from the state E_n. Here

$$f_{nn'}^{\sigma}(\mathbf{q}_\perp) = a^2 \sqrt{1 + \exp(-q_\perp a)} \cdot \delta_{\sigma S} \cdot q_\perp \cdot \tanh \frac{q_\perp a}{2} \left\{ \frac{\cos\dfrac{(n-n')\pi}{2}}{[(n-n')\pi]^2 + [q_\perp a]^2} \pm \frac{\cos\dfrac{(n+n')\pi}{2}}{[(n+n')\pi]^2 [q_\perp a]^2} \right\} \tag{11}$$

if the parity of n and n' is the same or

$$f_{nn'}^{\sigma}(\mathbf{q}_\perp) = -a^2 \sqrt{1 - \exp(-q_\perp a)}\, \delta_{\sigma A}\, q_\perp \operatorname{cotanh} \frac{q_\perp a}{2} \left\{ \frac{\sin\dfrac{(n-n')\pi}{2}}{[(n-n')\pi]^2 + [q_\perp a]^2} + (-1)^{n+1} \frac{\sin\dfrac{(n+n')\pi}{2}}{[(n+n')\pi]^2 + [q_\perp a]^2} \right\}, \tag{12}$$

$$\frac{1}{\varepsilon^{(0)}} = \frac{1}{\varepsilon_0^{(0)}} - \frac{1}{\varepsilon_\infty^{(0)}}, \quad \in^{(0)}(q_\perp) = \varepsilon_\infty^{(0)} [1 - \exp(-q_\perp a)],$$

$$\varsigma_\sigma(q_\perp) = \frac{\varepsilon^{(0)} \Omega_\sigma^2(q_\perp)}{\varepsilon_0^{(0)} \Omega_{\mathrm{TO}}^2} \left(\frac{\Omega_{\mathrm{LO}}^2 - \Omega_{\mathrm{TO}}^2}{\Omega_{\mathrm{TO}}^2 - \Omega_\sigma^2(q_\perp)} \right)^2;$$

$\delta_{\sigma\sigma'}$ — Kronecker symbol; $y = aq_\perp$.

The results of numeric calculations performed for E-MAA/2*H*-PbI_2/E-MAA NF prove that the magnitude of the shift of electron (hole) ground level caused by the interaction with LO-phonons nonlinearly increases when NF becomes thicker (curves *1* in Fig. 3) from $N = 1$ till $N = 10$. Herein, the contribution of higher phonon states ($\lambda \geq 2$) is smaller comparing to the main one ($\lambda \geq 1$). The

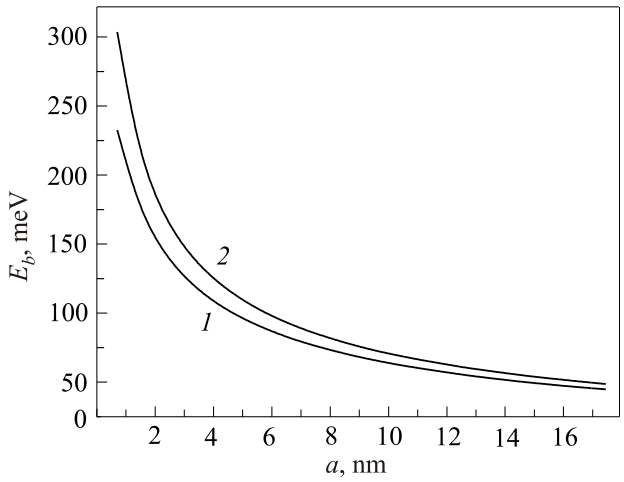

Fig. 1. Exciton binding energy as function of NF thickness without (curve *1*) and taking into account SP effect (curve *2*).

contribution of higher electron states ($n \geq 2$) into the magnitude of the ground level shift increases for the thicker NF. It is explained by smaller distance between the levels for the thicker NF and, thus, bigger mutual influence of the levels in the process of interaction with phonons.

The character of the I-phonons influence at the location of carrier ground level in QW is the other — the magnitude of long-wave shift decreases when HF thickness increases (curves *2* in Fig. 3). The role of higher ($n \geq 2$) levels also increases when NF becomes thicker and due to the same reason as for the case of interaction with LO-phonons.

The dependences of the total shift caused by the interaction with phonons of both types on NF thickness (N) are shown by curves *3* in Fig. 3. It is clear that at increasing NF thickness, the total shift increases, staying essentially smaller comparing to the shifts of opposite direction

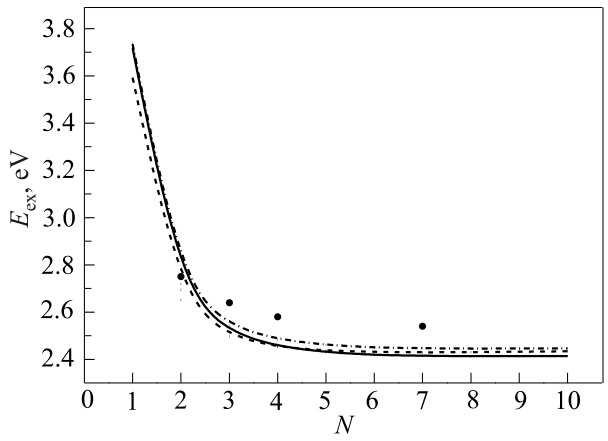

Fig. 2. Energy of the ground exciton state in NF consisting of N layers of 2*H*-PbI_2, calculated without SP effect and EPI (dotted curve), considering SP (dash-dotted curve), and taking into account SP and EPI (solid curve). Dots designate the location of exciton's peaks obtained from experimental data [8].

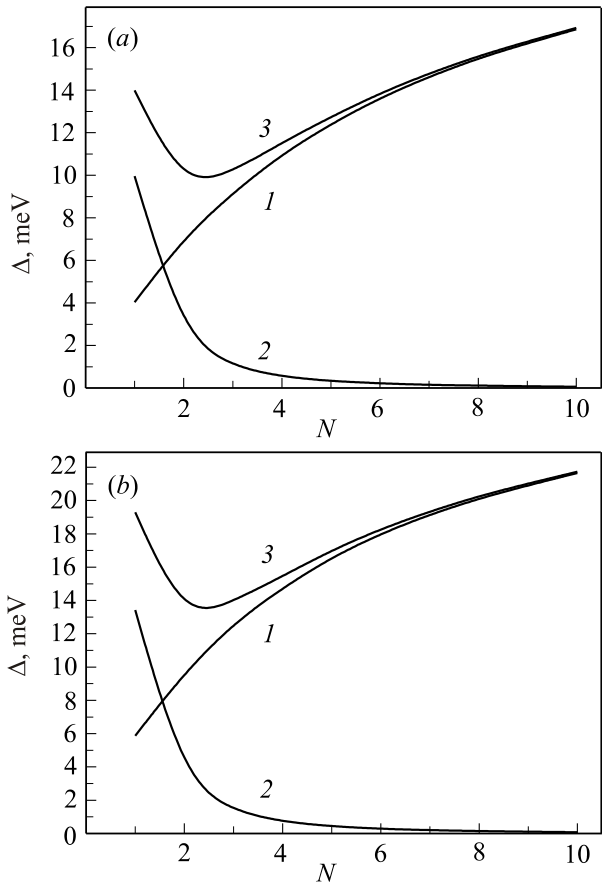

Fig. 3. Magnitude of the shift of the bottom of ground mini-band of electron (a) and hole (b) in NF with thickness N of layers 2*H*-PbI_2 caused by the interaction with LO- (curve *1*) and I-phonons (curve *2*); curve *3* — the total shift.

caused by SC and SP effect. Consequently, the contribution of the latter into the energy of exciton in NF at $N < 10$ is substantially bigger than the same of EPI (Fig. 4).

Finally, the converting of the shape function of the exciton absorption band [2] with NFs thickness changing had been computed (Fig. 5). It can be seen, that the location

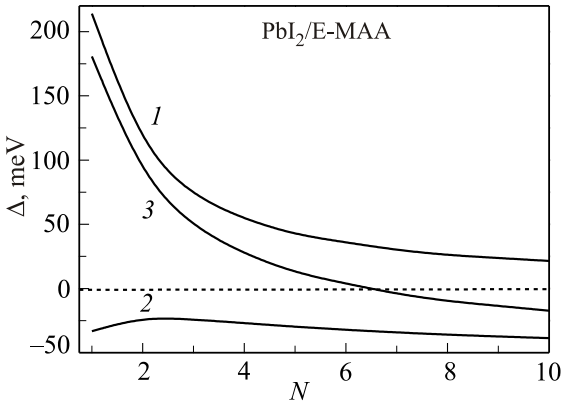

Fig. 4. Shift of the bottom of ground exciton band caused by SP effect (curve *1*) and exciton–phonon interaction (curve *2*); curve *3* — the total shift.

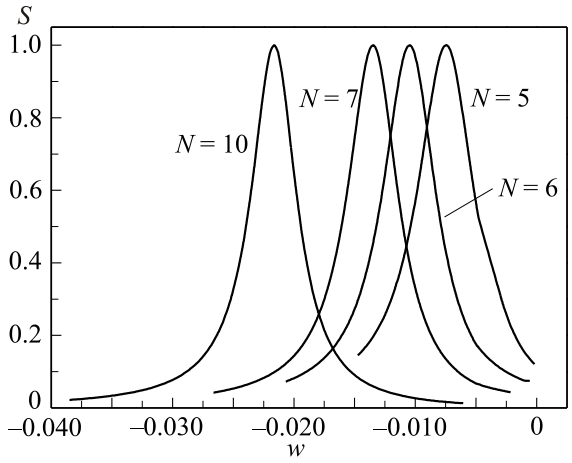

Fig. 5. Spectral dependence of the shape function S of the exciton absorption band in NFs of varying thickness (N — number of layers in the NF; $w = (\hbar\omega - E)/L_{ex}$; $L_{ex} = \pi^2\hbar^2/(2m_{ex}a_0)$ — width of the exciton band).

of the exciton line depends on the NF thickness as well as the bottom of the ground exciton energy band — they are shifting in long-wave range with the thickness growth.

4. Conclusion

Comparing the results of calculations with the experimental data [8] we make the conclusion that the observed differences in the location of exciton peaks are really caused by the differences of the thicknesses of lead iodide plates.

Taking into account the SP effect and EPI bring the magnitudes of the exciton energy, calculated within the model of infinitely deep potential QW, nearer to the experimentally measured ones. The quantitative mismatches of our calculated and measured by the authors of paper [8] energies of exciton transition in nanoheterostructures of different thicknesses can be caused by the fact that for the calculations we used the parameters, typical for the modification 2*H*-PbI_2, while in the cited paper the polytype of lead iodide was not stated. It is also evident that the plane NF rightfully models the micro-crystallites studied in [8] not at any ratio between their thicknesses and transversal sizes.

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