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Excitons in Nanosystems Consisting of Semiconductor Quantum Dots

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As found, within the band gap of the quantum dot of zinc selenide, a zone of exciton states located at the bottom of the conduction band appears. As shown, a decrease in the band gap width for this nanosystem is conditioned by transition of the electron from quantum-dimensional level within the valence band of the quantum dot to the levels of the zone of exciton states. The dependence of the energy of a ground state of an exciton on the radius of quantum dot is obtained using a modified method of the effective mass.

Було встановлено, що в межах ширини забороненої зони квантової точки з селеніду цинку з'являється зона екситонних станів, розташована в нижній частині зони провідности. Було показано, що зменшення ширини забороненої зони цієї наносистеми зумовлене переходом електрона з квантово-розмірного рівня у валентній зоні квантової точки до рівнів зони екситонних станів. Залежність енергії основного стану екситона від радіюса квантової точки було одержано з використанням модифікованої методи ефективної маси.

Было установлено, что в пределах ширины запрещённой зоны квантовой точки из селенида цинка появляется зона экситонных состояний, расположенная в нижней части зоны проводимости. Было показано, что уменьшение ширины запрещённой зоны этой наносистемы обусловлено переходом электрона из квантово-размерного уровня в валентной зоне квантовой точки к уровням зоны экситонных состояний. Зависимость энергии основного состояния экситона от радиуса квантовой точки была получена с использованием модифицированного метода эффективной массы.

Key words: exciton states, quantum dot, quantum-dimensional level, band gap.

Ключові слова: екситонні стани, квантова точка, квантово-розмірний рівень, ширина забороненої зони.

Ключевые слова: экситонные состояния, квантовая точка, квантово-размерный уровень, ширина запрещённой зоны.

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1. INTRODUCTION

The solid-state technology developments lead to the fabrication of the quasi-zero-dimensional nanostructures, which are a semiconductor quantum dots (QDs) of spherical shape with a radius $a \approx 1–10$ nm grown in the transparent dielectric (or semiconductor) matrix [1–4]. Such linear dimensions of the QD are comparable with the de Broglie wavelength of an electron and a hole, or (and) their Bohr radius.

The mentioned characteristics lead to the fact that the phenomenon of spatial size quantization of charge carriers plays an important role in the optical and electrooptical processes in these nanosystems [5–12].

Optical and electrooptical properties of those quasi-zero-dimensional nanostructures are largely determined by the energy spectrum of a spatially bounded electron-hole pair (exciton) [1–11]. The energy spectrum of charge carriers in the QD, since the size a is of the order of the Bohr radius of the electron a_e or the hole a_h and less, is fully discrete. Therefore, those QDs are called 'superatoms' [1, 3, 4, 11]. In these conditions, the effect of a spherical surface of interface (QD–dielectric matrix) can cause the size quantization of the energy spectrum of electron and hole in the QD, which is associated with a purely spatial limitation of field quantization, and polarization interaction of charge carriers with the surface of the QD [1, 3–11].

A novel modified method of the effective mass approximation was recently suggested [5] to describe the exciton energy spectrum in semiconductor QDs with radii $a \approx a_{ex}^0$ (a_{ex}^0 —the Bohr radius of exciton in the semiconductor material of the bulk of QDs.). As shown, within the framework of the QD model, in which QD was simulated by limitlessly deep potential well, the effective mass approximation is liable in description of exciton with QD with radius a comparable with the Bohr radius of exciton a_{ex}^0, considering an adduced effective mass of exciton $\mu = \mu(a)$ as a function of QD radius a.

The optical properties of the samples containing of QDs of zinc selenide placed in air was reported earlier [12]. The average radii $\bar{a}$

of such QDs were not exceeding 21 nm. At low concentrations of QDs, when the optical properties of samples are mainly determined by the optical properties of the single QD in the air, the decrease of the band gap ($E_g \approx 2.61$–2.68 eV) was detected in comparison with the band gap for bulk single crystal of zinc selenide ($E_g = 2.7$ eV). The mechanism of such a decreasing in the band gap of zinc selenide QDs is not clear yet.

Therefore, in this paper, we show that a decrease in the band gap within such nanosystem detected under the experimental conditions [12] was stipulated by transition of an electron from the quantum-level located in the valence band of the QD on the level of the exciton state zone. The energy of the base state of the exciton, which are moving in volume of QDs of zinc selenide, as a function of radius a of the QD is obtained utilizing the variational method in a context of the modified effective mass approximation [5]. As found, in the band gap of QDs of zinc selenide, a zone of exciton states, which is located at the bottom of the conduction band, appears.

2. VARIATIONAL CALCULATION OF THE EXCITON GROUND-STATE ENERGY IN THE NANOSYSTEM

A model of a quasi-zero-dimensional system as a neutral spherical semiconductor QD of radius a, which contains a semiconductor material in the bulk with a dielectric constant ε_2, surrounded by a media with dielectric permittivity ε_1, is considered. Within the volume of the described QD, electron (e) and hole (h) with the effective masses m_e and m_h, respectively (r_e and r_h—distance of electron and hole from the centre of the QD), are moving. Assuming the electron and hole bands as parabolic, the characteristic quantities for a problem,

$$a_e = \frac{\varepsilon_2 \hbar^2}{m_e e^2}, \; a_h = \frac{\varepsilon_2 \hbar^2}{m_h e^2}, \; a_{ex}^0 = \frac{\varepsilon_2 \hbar^2}{\mu_0 e^2}, \tag{1}$$

are the Bohr radii of the electron, hole, and exciton, respectively, in a semiconductor with the permittivity ε_2 (e is the electron charge, and $\mu_0 = m_e m_h/(m_e + m_h)$ is the reduced exciton mass).

The energy of the polarization interaction $U(r_e,r_h,a)$ with a relative permittivity $\varepsilon = \varepsilon_2/\varepsilon_1 > 1$ can be represented as the algebraic sum of energies of the interactions of an electron and a hole with 'themselves', $V_{hh'}(r_h,a)$, $V_{ee'}(r_e,a)$, and with 'strangers', $V_{eh'}(r_e,r_h,a) = V_{he'}(r_e,r_h,a)$, respectively [5–7]:

$$U(r_e,r_h,a) = V_{hh'}(r_h,a) + V_{ee'}(r_e,a) + V_{eh'}(r_e,r_h,a) + V_{he'}(r_e,r_h,a), \tag{2}$$

$$V_{hh'}\left(r_h, a\right) = \frac{e^2}{2\varepsilon_2 a}\left(\frac{a^2}{a^2 - r_h^2} + \frac{\varepsilon_2}{\varepsilon_1}\right), \tag{3}$$

$$V_{ee'}\left(r_e, a\right) = \frac{e^2}{2\varepsilon_2 a}\left(\frac{a^2}{a^2 - r_e^2} + \frac{\varepsilon_2}{\varepsilon_1}\right), \tag{4}$$

$$V_{eh'}\left(r_e, r_h, a\right) = V_{he'}\left(r_e, r_h, a\right) = -\frac{e^2\beta}{2\varepsilon_2 a}\frac{a}{\left[\left(r_e r_h / a\right)^2 - 2r_e r_h \cos\Theta + a^2\right]^{1/2}}, \tag{5}$$

where $\beta = \left(\varepsilon_2 - \varepsilon_1\right)/\left(\varepsilon_2 + \varepsilon_1\right)$—parameter, $\Theta = r_e, r_h$—angle.

Within the studied simple model of quasi-zero-structures within the framework of the above-mentioned approximations as well as the effective mass approximation, using a triangular coordinate system $r_e = |r_e|$, $r_h = |r_h|$, $r = |r_e - r_h|$ with initial point in the centre of the QD, the Hamiltonian of the exciton moving in the QD volume, transforms into [5, 6]:

$$\begin{aligned} H\left(r_e, r_h, a\right) = &-\frac{\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial r_e^2} + \frac{2}{r_e}\frac{\partial}{\partial r_e} + \frac{r_e^2 - r_h^2 + r^2}{r_e r}\frac{\partial^2}{\partial r_e \partial r}\right) - \\ &-\frac{\hbar^2}{2m_h}\left(\frac{\partial^2}{\partial r_h^2} + \frac{2}{r_h}\frac{\partial}{\partial r_h} + \frac{r_h^2 - r_e^2 + r^2}{r_h r}\frac{\partial^2}{\partial r_h \partial r}\right) - \\ &-\frac{\hbar^2}{2\mu_0}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + V_{eh}(r) + U\left(r_e, r_h, a\right) + V\left(r_e, r_h\right) + E_g^0, \end{aligned} \tag{6}$$

where the first three terms are the operators of the kinetic energy of electron, hole and excitons; E_g^0—band gap in the unlimited semiconductor with dielectric permittivity ε_2. In Hamiltonian $H(r_e, r_h, a)$ (6), the energy of polarization interaction $U(r_e, r_h, a)$ is determined by formulas (2)–(5), and the energy of the Coulomb interaction between the electron and the hole $V_{eh}(r)$ is described by the formula:

$$V_{eh}(r) = -\frac{e^2}{\varepsilon_2 r}. \tag{7}$$

In Hamiltonian, the exciton potential (6),

$$V\left(r_e, r_h\right) = 0 \text{ at } r_e, r_h \le a \text{ and } V\left(r_e, r_h\right) = \infty \text{ at } r_e, r_h > a, \tag{8}$$

describes a motion of quasi-particles in the QD volume *via* model of the infinitely deep potential well.

The variation of radial wave function of the base state of an exciton (1*s*-electron state and 1*s*-hole state) in the QD with radius a can

be written as follows [5, 6]:

$$\Psi_0\left(r_e, r_h, r\right) = A \exp\left(-\frac{\mu(a)}{\mu_0}\right) \frac{\sin\left(\pi r_e / a\right)}{r_e} \frac{\sin\left(\pi r_h / a\right)}{r_h} \times \\ \times \frac{\left(a^2 - r_e^2\right)}{a^2} \frac{\left(a^2 - r_h^2\right)}{a^2} \frac{r}{a} \frac{\left|r_e - \left(a / r_h\right)^2 r_h\right|}{a}. \tag{9}$$

To determine the energy of the base state of the exciton $E_{1,0,0;1,0,0}(a)$ within the variational method for the QD radius a, the average value of Hamiltonian of an exciton (6) with wave functions (9) can be written as follows:

$$E_{1,0,0;1,0,0}(a, \mu(a)) = \left\langle \Psi_0\left(r_e, r_h, r\right) \middle| H\left(r_e, r_h, a\right) \middle| \Psi\left(r_e, r_h, r\right) \right\rangle = \\ = \int_0^a dr_e \int_0^a dr_h \int_r^{r_e + r_h} dr\, r_e r_h r\, \Psi_0\left(r_e, r_h, r\right) H\left(r_e, r_h, a\right) \Psi\left(r_e, r_h, r\right). \tag{10}$$

The calculation of the energy–radius dependence, $E_{1,0,0;1,0,0}(a)$, for the QD with radius a in the base state of the exciton ($n_e = 1$, $l_e = m_e = 0$; $n_h = 1$, $l_h \quad m_h = 0$ where n_e, l_e, m_e and n_h, l_h, m_h are principal, orbital and magnetic quantum numbers of the electron and a hole, respectively) was performed via minimization of function $E_{1,0,0;1,0,0}(a, \mu(a))$ (10).

The results of the variational calculation of the base state of the exciton energy $E_{1,0,0;1,0,0}(a)$ (10) of the QD with radius a are shown in Fig. 1. The obtained values of the energy of the base state of the

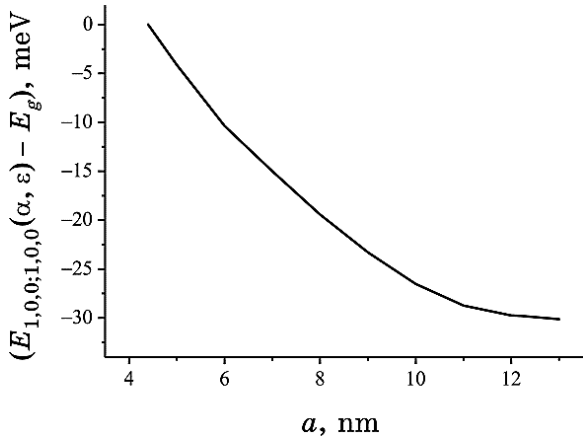

Fig. 1. Energy of a ground state of the exciton, $E_{1,0,0;1,0,0}(a,\varepsilon)$ (10), as function of radius a of the quantum dot of the zinc selenide, where E_g is a band gap of zinc selenide.

exciton $E_{1,0,0;1,0,0}(a)$ are valid only for values of the exciton energy, which are governed by the inequality: $E_{1,0,0;1,0,0}(a) - E_g^0 << \Delta V(a)$, where $\Delta V(a)$ is a depth of the potential well of the electron in the quantum dot. For a wide class of the semiconducting A_2B_6 QDs in size range of $a \geq a_{ex}^0$, the value of $\Delta V(a)$ is of 2.3–2.5 eV [5, 6].

The Coulomb attraction between the electron and the hole within the unlimited semiconductor volume facilitates' formation of an exciton with large radius. In Hamiltonian of the exciton $H(r_e, r_h, a)$ (6), which moves in a volume of the QD, the Coulomb attraction $V_{eh}(r)$ (7) is also reinforced by a certain effective attraction between the electron and the hole caused by the repulsion of the electron $V_{ee'}(r_e, a)$ (4) and the hole $V_{hh'}(r_h, a)$ (3) from their own images (see Fig. 1). Under this conditions, energy of the effective repulsion between the electron and the hole described by terms $V_{eh'}(r_e, r_h, a)$ and $V_{he'}(r_e, r_h, a)$ (5), which are inducing an attraction of quasi-particles to the surface of the QD (to the 'foreign' images), will be less than the energy of additional effective attraction [5–9].

As a result, with decreasing of the QD radius $a < a_{ex}^0$, the value of the additional effective attraction between the electron and the hole will increase $\propto a^{-1}$ [5–9]. This effective polarization attraction leads to the fact that the exciton moves in the volume of the QD with an effective mass $\mu = \mu(a)$, which is greater than the mass of the exciton μ_0 in the bulk crystal with a dielectric constant ε_2. With an increase of the QD radius $a > a_{ex}^0$, the effective attraction between the electron and the hole will decrease $\propto a^{-1}$. Starting with some values of the QD radius a, which is equal to a_c, the energy of such effective attraction between the electron and the hole is become smaller when compared with the binding energy of the volumetric exciton [5, 6]:

$$E_{ex} = Ry_{ex} = \frac{\hbar^2}{2\mu_0 \left(a_{ex}^0\right)^2}. \qquad (11)$$

The volumetric exciton in the QD was meant as the exciton whose structure (reduced effective mass, Bohr radius, and binding energy) is not differ from the exciton in the QD in an unlimited semiconductor material. Consequently, the volumetric exciton will appears only at the QD size of $a > a_{ex}^0$. Moreover, the formation of the volumetric exciton has a threshold character, and it is only possible in the QD whereas its size exceeds a certain value of critical radius of QD $a > a_{ex}^0$ [5, 6]. The behaviour of $\mu(a)$ indicates that, with an increase in radius of the QD $a > a_{ex}^0$, the effective mass of the exciton $\mu = \mu(a)$ decreases and, at the critical radius of the QD (*i.e.*, $a_c = 3.90$, $a_{ex}^0 \approx 12.2$ nm), reaches the value of the effective mass of the exciton $\mu_0 = 0.137 m_0$ in a bulk crystal of ZnSe. Thus, the volu-

metric exciton occurs in QDs of the zinc selenide when the radius of QD reaches $a \geq a_c \cong 3.90$, $a_{ex}^0 \approx 12.2$ nm.

Figure 1 displays the dependences of energies $E_{1,0,0;1,0,0}(a,\varepsilon)$ (10) of the base state of exciton in nanosystems containing of zinc selenide QDs with radius a and shows that bound states of the electron–hole pair occur near to the spherical surface of the QD starting with the critical radius of QD $a \geq a_c^{(1)} = 4.4$ nm. The states of the electron–hole pair, starting with radius of the QD $a \geq a_c^{(1)}$, are in the region of negative energies (measured from the top limit of the band gap E_g of a bulk crystal of zinc selenide), which corresponds to a bound state of the electron and the hole. In this case, the energy of the Coulomb interaction $V_{eh}(r)$ (8) between the electron and the hole and the polarization interaction energy $U(r_e,r_h,r,a,\varepsilon)$ (3) for the electron and the hole with section of the spherical surface (QD–dielectric matrix interaction) are prevail over the dimensional quantization energy of the electron and the hole in nanosystems. With an increase in the radius a of the QD, an increase of energy of the base state of the exciton $E_{1,0,0;1,0,0}(a,\varepsilon)$ (10) was observed. Starting with radius of the QD of $a \geq a_c \cong 3,90$, $a_{ex}^0 \approx 12.2$ nm, the values (10) of energy of the base state of the exciton approaches asymptotically to the value of the binding energy of the volumetric exciton ($E_{ex} = 28.41$ meV) (11) (see Fig. 1).

3. SPECTROSCOPY OF EXCITON STATES IN QUANTUM DOTS

From results of the variational calculation of the base state of an exciton $E_{1,0,0;1,0,0}(a,\varepsilon)$ (10) in nanosystems, which contain QDs of the zinc selenide with change of an average radii a of QD in interval $a \geq a_c^{(1)} = 4.4$ nm, it is follows that, in the band gap of such QDs, a zone of the exciton mode with width of

$$\Delta E_{ex} = E_{ex} = 28.41 \text{ meV} \tag{12}$$

appears and is located under the bottom of the conductive zone.

The optical properties of the samples of zinc selenide containing QDs located in air (with dielectric permeability $\varepsilon_2 = 8.1$ and an effective mass of the electron and the hole $(m_e/m_0) = 0.17$ and $(m_h/m_0) = 0.7$, respectively, where m_0 is a mass of free electron) was reported earlier [7]. For interpretation of the experimental results [12], let us assume that the QDs have a spherical shape. The average radius of those QDs is in the range

$$\bar{a} \approx 14 - 21 \text{ nm}. \tag{13}$$

At low experimental concentrations of QDs ($x = 0.003\%$ and

$x = 0.03\%$) [12], the mutual interactions of QDs are nonsignificant. The optical properties of these samples were defined by energy spectra of the electron and the hole, which are localized near the spherical surface of the singular QDs immersed in air. At such low concentrations of QDs, whereas optical properties are characterized by optical properties of the singular QD in air, a narrowing of the band gap zone were detected,

$$E_g \approx 2.61\text{–}2.68 \text{ eV}, \tag{14}$$

comparing to the zinc selenide single-crystal band-gap energy (*i.e.*, $E_g^0 = 2.7$ eV).

In Ref. [12], nanodimensional particles of the zinc selenide were synthesized via hydrothermal method; 4 mmol of $ZnSO_4$ was dissolved in DI water, and then, the ammonia hydroxide was added until complete dissolution of sediment of the zinc hydroxide. Then, a sodium selenide (Na_2SeO_3, 4 mmol in DI water) was added. The solution of hydrazine sulphate of pH 8–9 (adjusted by NaOH) was added to the reaction at the vigorous stirring. Resulting mixture was placed into the Teflon lined autoclave and kept at 433 K for 24 hours. Precipitate was washed with DI water and, therefore, dried at 333 K. Results of XRD confirm the cubic phase of the zinc selenide (ZnSe (JCPDS 37-1463)) with crystallite size of about 27 nm (see Fig. 2).

For samples treated by ammonium hydroxide, which are partially dissolve ZnSe, particles aggregate, and the size of crystallite increases up to $\cong 42$ nm. A width of the band gap zone is determined via transforming the spectra into the Kubelka–Munk coordinates. A width of the band gap for synthesized semiconductor ZnSe is

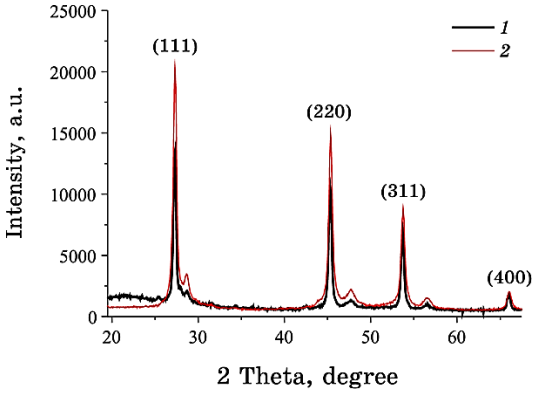

Fig. 2. Diffraction patterns for *1*—ammonia treated ZnSe and *2*—pristine ZnSe.

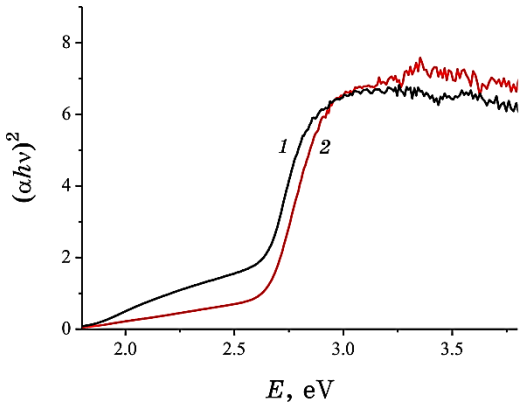

Fig. 3. Reflection spectra in the Kubelka–Munk coordinates for *1*—ammonia treated ZnSe and *2*—pristine ZnSe.

$E_g = 2.61–2.68$ eV, and $E_g = 2.56$ eV for ammonia-treated sample (see Fig. 3). A width of the band gap for samples is narrower than for bulk of zinc selenide ($E_g^0 = 2.7$eV) by

$$\Delta E_g = E_g - E_g^0 \approx 20–90 \text{ meV}. \qquad (15)$$

The exciton mode zone ΔE_{ex} reaches a maximal width (12) starting from radius a of QDs, $a \geq a_c \cong 12.2$ nm< which is lesser than the average radius a of QDs from interval (13) in research reported earlier [12]. Therefore, in regards to (14) and (15), the narrowing in the width of band gap comparing to the same in bulk crystal of ZnSe for value (15) is conditioned by transfer of the non-equilibrium electron from quantum size level within the valence zone of the QD to the level of the exciton mode with width ΔE_{ex} (12). The electron transition within the zone of the exciton mode invokes the significant absorption of irradiation in visible and near-infrared wavelengths and causes a significant blurring of the absorption edge, which is experimentally observed. The origin of the band gap value ($E_g = 2.56$ eV) [12] in the framework of the considered model of the exciton, which moves in a volume of QD of the zinc selenide, is not clear. The origination of this value needs a further investigation.

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