Excitons States in Semiconductor Quantum Dots

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Abstract: It was found that within the band gap of the quantum dot of zinc selenide appears a zone of exciton states, located at the bottom of the conduction band. It has been shown that a decrease in the band gap width in this nanosystems 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 base state of an exciton from the radius of QD was obtained using a modified method of the effective mass.

Keywords: exciton states, quantum dot, quantum-dimensional level

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1. INTRODUCTION

The solid state technology developments leads to the production of the quasi-zero-dimensional nanostructures, which are a semiconductor quantum dots (QDs) of spherical shape with a radius \( a \approx 1-10 \) nm and grown in the transparent dielectric (or semiconductor) matrix [1-10]. 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 listed characteristics lead to the fact that the phenomenon of spatial size quantization of charge carriers plays an important role in the optical and electro-optical processes in these nanosystems [8-16].

Optical and electro-optical properties of those quasi zero-dimensional nanostructures are largely determined by the energy spectrum of a spatially bounded electron-hole pair (exciton) [1-16]. The energy spectrum of charge carriers in the QD, since the size \( a \) of the Bohr order radius of the electron \( a_e \), or hole \( a_h \), and less, is fully discrete [1-9]; therefore those QDs are called "superatoms" [9]. In these conditions the effect of a spherical surface of interface (QD - dielectric matrix) can cause the size quantization of the energy spectrum of the electron and hole in the QD, which is associated with a purely spatial limitation of the field quantization [1-7], and polarization interaction of charge carriers with the surface of the QD [11-16].

The majority of theoretical models for calculation of energy spectra of quasi particles in QDs utilize an approximation of effective mass as applicable for QDs on the analogy to bulk single crystals [11-14]. The problem of applicability of the effective mass approximation to description of the semiconductor QD remains unsolved [15-22].

Recently [15], a novel modified method of the effective mass approximation was suggested to describe the exciton energy spectrum in semiconductor QDs with radii \( a = a_{ex}^0 \) (\( a_{ex}^0 \) – the exciton Bohr radius in the semiconductor material of the bulk volume of QDs.). Was shown, that in the framework of QD model in which QD was simulated by limitlessly deep potential well the effective masse approximation is liable in description of exciton with QD with radii \( a \) comparable with the Bohr radius of exciton \( a_{ex}^0 \), considering that an adduced effective mass of exciton \( \mu = \mu(a) \) is a function of radius \( a \) of QD.

The optical properties of the samples containing of QDs of zinc selenide placed in air was reported earlier [23]. The average radii 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, was detected the decrease of the band gap (\( E_g \approx (2.61 - 2.68) \) eV) in comparison with the band gap for bulk single crystal of zinc selenide (\( E_g^0 = 2.7 \) eV). The mechanism of such of decreasing in the band gap of zinc selenide QDs is not clear yet.
Therefore, in this paper we showed that a decrease in the band gap within such a nanosystem detected under the experimental conditions [23], 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 was obtained utilizing the variational method in a context of the modified effective mass approximation [15]. It was found that in the band gap of QDs of zinc selenide appears a zone of exciton states which is located at the bottom of the conduction band.

2. **THE VARIATIONAL CALCULATION OF THE ENERGY OF THE BASE STATE OF AN EXCITON IN THE QUANTUM DOT**

A simple model of a quasizero-dimensional system, a neutral spherical semiconductor QD of radius \(a\), which contain a semiconductor material in the bulk with a dielectric constant \(\varepsilon_2\), surrounded by a media with dielectric permittivity \(\varepsilon_1\). was considered. Within the volume of the described QD an electron (\(e\)) and hole (\(h\)) with the effective masses \(m_e\) and \(m_h\) (\(r_e\) and \(r_h\) - distance of electron and hole from the center of the QD) are moving (Fig. 1.). Assuming that the electron and hole bands were parabolic, the characteristic quantities for the problem \(a_e, a_h, a_{ex}^0\)

\[
a_e = \frac{\varepsilon_2 \hbar^2}{m_e e^2}, \quad a_h = \frac{\varepsilon_2 \hbar^2}{m_h e^2}, \quad a_{ex}^0 = \frac{\varepsilon_2 \hbar^2}{\mu_0 e^2}
\]

- are the Bohr radii of the electron, hole, and exciton correspondingly in a semiconductor with the permittivity \(\varepsilon_2\) (\(e\) is the electron charge, and \(\mu_0 = m_e m_h / (m_e + m_h)\) is the modified exciton effective mass).

Within the studied in this work simple model of quasi-zero system, the interaction energy of the electron (\(e\)) and the hole (\(h\)), which are in the volume of QDs in points of \(r_e\) and \(r_h\), with the polarization field induced by those quasiparticles, is written as follows [24]:

\[
U(r_e, r_h, a) = -\frac{\varepsilon_2}{2(\varepsilon_2 + \varepsilon_1)a} \int_0^\infty dy \frac{\varepsilon(y - (a^2/r_h))}{|r_e - y(r_h/r_e)|} - \frac{\varepsilon(y - (a^2/r_e))}{|r_h - y(r_e/r_h)|},
\]

Where the parameter \(\beta = (\varepsilon_2 - \varepsilon_1)/(\varepsilon_2 + \varepsilon_1)\), angle \(\theta = r_e, r_h\), and a \(\Theta(x)\) – is the Heaviside function.

The energy of the polarization interaction \(U(r_e, r_h, a)\) (2) with a relative permittivity \(\varepsilon = (\varepsilon_2 / \varepsilon_1) \approx 1\) can be represented as the algebraic sum of the energies of the interaction of an electron and a hole with “their” \(V_{hh}(r_h, a), V_{ee}(r_e, a)\) and “strangers” \(V_{eh}(r_e, r_h, a) = V_{he}(r_e, r_h, a)\), respectively [24 - 27] (Figure 1):

\[
U(r_e, r_h, a) = V_{hh}(r_h, a) + V_{ee}(r_e, a) + V_{eh}(r_e, r_h, a) + V_{he}(r_e, r_h, a),
\]

where

\[
V_{hh}(r_h, a) = \frac{\varepsilon^2}{2\varepsilon_2 a} \left( \frac{a}{a^2 - r_h^2} + \frac{\varepsilon_2}{\varepsilon_1} \right),
\]

\[
V_{ee}(r_e, a) = \frac{\varepsilon^2}{2\varepsilon_2 a} \left( \frac{\varepsilon}{a^2 - r_e^2} + \frac{\varepsilon_2}{\varepsilon_1} \right),
\]

\[
V_{eh}(r_e, r_h, a) = V_{he}(r_e, r_h, a) = -\frac{\varepsilon^2 \beta}{2\varepsilon_2 a} \frac{a}{[(r_e r_h/a)^2 - 2r_e r_h \cos \theta + a^2]^{1/2}}.
\]
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Within the studied simple model of quasi-zero structures in the framework of the noted above approximations, as well as in 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 center of the QD, the Hamiltonian of the exciton moving in volume QD, transforms in to [15]:

\[
H(r_e, r_h, a) = -\frac{\hbar^2}{2m_e} \left( \frac{\partial^2}{\partial r_e^2} + \frac{2}{r_e} \frac{\partial}{\partial r_e} + \frac{r_e^2 - r_h^2 + r_e^2}{r_e r_h} \frac{\partial^2}{\partial r_h^2} + \frac{\partial^2}{\partial \theta_e \partial \theta_h} \right) - \frac{\hbar^2}{2m_h} \left( \frac{\partial^2}{\partial r_h^2} + \frac{2}{r_h} \frac{\partial}{\partial r_h} + \frac{r_h^2 - r_e^2 + r_e^2}{r_e r_h} \frac{\partial^2}{\partial \theta_h \partial \theta_e} \right) - \frac{\hbar^2}{2\mu_o} \left( \frac{\partial^2}{\partial \theta_e^2} + \frac{2}{r} \frac{\partial}{\partial \theta_e} \right) + V_{eh}(r) + U(r_e, r_h, a) + V(r_e, r_h) + E_0^g(7)
\]

Where the first three terms are the operators of the kinetic energy of electron, hole and excitons, \( E_0^g \) – band gap in the unlimited semiconductor with dielectric permittivity \( \varepsilon_2 \).

In the Hamiltonian \( H(r_e, r_h, a) \) (7) the energy of polarization interaction \( U(r_e, r_h, a) \) is determined by formulas (3) - (6) and the energy of the Coulomb interaction between the electron and the hole \( V_{eh}(r) \) is described by the formula:

\[
V_{eh}(r) = -\frac{\hbar^2}{\varepsilon_2 r}.
\]  
(8)

In the Hamiltonian the exciton potential (7)

\[
V(r_e, r_h) = \begin{cases} 
0, & r_e, r_h \leq a \\
\infty, & r_e, r_h > a
\end{cases}
\]  
(9)

Describes a motion of quasiparticles in the QD volume via model of the infinitely deep potential well.

The variation radial wave function of the base state of an exciton (1 s - electron states and 1 s - hole state) in the QD with radius \( a \) can be written as follows [15]:

\[
\psi_0(r_e, r_h, r) = A \exp \left( -\frac{\mu(a)}{\mu_0} \cdot \frac{r}{a^0} \right) \frac{\sin(\pi r_e/a)}{r_e} \frac{\sin(\pi r_h/a)}{r_h} \frac{a^2}{a^2 - r_e^2} \frac{a^2}{a^2 - r_h^2} \frac{r}{a} \frac{|r_e - (a/r_h)^2 r_h|}{a}.
\]

(10)

Herein the \( A \) coefficient was conditioned by the exciton wave function normalization (10)

\[
\int_0^a r_e dr_e \int_0^a r_h dr_h \int_0^{r_e + r_h} \frac{\psi_0^2(r_e, r_h, r)}{r} dr = 1,
\]

and the reduced mass of the exciton \( \mu(a) \) is a variational parameter.

To determine the energy of the base state of the exciton \( E_{1,0,0,1,0,0}(a) \) in the variational method for the QD radius \( a \) in the base state of the exciton \( (n_e = 1, l_e = m_e = 0; n_h = 1, l_h = m_h = 0 \) where \( n_e, l_e, m_e \) and \( n_h, l_h, m_h \) - principal, orbital and magnetic quantum numbers of the electron and a hole, respectively) was performed via minimization the function \( E_{1,0,0,1,0,0}(a, \mu(a)) \) (11)

\[
\frac{\partial E_{1,0,0,1,0,0}(a, \mu(a))}{\partial \mu(a)} \equiv F(\mu(a), a) = 0
\]

(12)

Without writing an unwieldy expression for the first derivative of the functional \( (\partial E_{1,0,0,1,0,0}(a, \mu(a)) / \partial \mu(a)) \equiv F(\mu(a), a) \) the numerical solution of the equation \( F(\mu(a), a) = 0 \) is shown in a Table 1. Table 1 shows that the solution of this equation is a function of \( \mu(a) \), which insignificantly and monotonically changes in the range:
0.29 ≤ (μ(a)/m₀) ≤ 0.137

While the radius α of the QD changes in the area:

4A ≤ α ≤ 19,4 nm

(where m₀—is the mass of the electron in a vacuum).

Via substituting the values of the variational parameter μ(a) (13) from the Table 1 with corresponding values of radius α of the QD in interval (14) into the functional $E_{1,0,0;1,0,0}(a, μ(a))$ (11), the energy of the base state of exciton $E_{1,0,0;1,0,0}(a)$ (11) was obtained as a function of radius of QD.

Table 1. Values of the variational parameter μ(a) as function of radius α of the QD zink selenide

<table>
<thead>
<tr>
<th>(S)</th>
<th>a(nm)</th>
<th>(μ (a)/m₀)</th>
</tr>
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<tbody>
<tr>
<td>2.0 (0.54)</td>
<td>0.292</td>
<td></td>
</tr>
<tr>
<td>2.3 (0.62)</td>
<td>0.263</td>
<td></td>
</tr>
<tr>
<td>2.6 (0.70)</td>
<td>0.243</td>
<td></td>
</tr>
<tr>
<td>3.0 (0.81)</td>
<td>0.228</td>
<td></td>
</tr>
<tr>
<td>3.5 (0.94)</td>
<td>0.216</td>
<td></td>
</tr>
<tr>
<td>4.0 (1.08)</td>
<td>0.206</td>
<td></td>
</tr>
<tr>
<td>4.5 (1.21)</td>
<td>0.197</td>
<td></td>
</tr>
<tr>
<td>5.0 (1.35)</td>
<td>0.188</td>
<td></td>
</tr>
<tr>
<td>6.0 (1.62)</td>
<td>0.174</td>
<td></td>
</tr>
<tr>
<td>7.0 (1.88)</td>
<td>0.162</td>
<td></td>
</tr>
<tr>
<td>8.0 (2.15)</td>
<td>0.152</td>
<td></td>
</tr>
<tr>
<td>10.0 (2.7)</td>
<td>0.140</td>
<td></td>
</tr>
<tr>
<td>12.0 (3.23)</td>
<td>0.135</td>
<td></td>
</tr>
<tr>
<td>14.5 (3.9)</td>
<td>0.132</td>
<td></td>
</tr>
</tbody>
</table>

The values of the function $μ(a)$ (13) and the results of the variational calculation of the base state of the exciton energy $E_{1,0,0;1,0,0}(a)$ (11) in the QD, which radius is determined by the inequality (14), were obtained under experimental conditions [23]. The results of the variational calculation of the base state of the exciton energy $E_{1,0,0;1,0,0}(a)$ (11) of the QD with radius α are shown in Fig. 2.

The obtained values of the energy of the base state of the exciton $E_{1,0,0;1,0,0}(a)$ are valid only for values of the exciton energy which are governed by the inequality: $(E_{1,0,0;1,0,0}(a) - E^0_{g}) ≪ ΔV(a)$, where $ΔV(a)$ is a depth of the potential well of the electron in the quantum dot. For a wide class of semiconductor $A_2B_6$ QDs in size range of $α ≥ a^0_{ex}$, the value of the $ΔV(a)$ is $(2.3 - 2.5)$ eV [7].

The Coulomb attraction between the electron and the hole within the unlimited semiconductor volume facilitates formation of an exciton with large radius. In the Hamiltonian of the exciton $H(\mathbf{r}_e, \mathbf{r}_h, α)$ (7), which moves in a volume of the QD, the Coulomb attraction $V_{eh}(\mathbf{r})$ (8) is also reinforced by a certain effective attraction between the electron and a hole caused by the repulsion of the electron $V_{ee'}(\mathbf{r}_e, α)$ (5) and a hole $V_{hh'}(\mathbf{r}_h, α)$ (4) from their own images (see. Fig. 1). Under this conditions energy of the effective repulsion between the electron and a hole, described by terms $V_{eh'}(\mathbf{r}_e, \mathbf{r}_h, α)$ and $V_{he'}(\mathbf{r}_e, \mathbf{r}_h, α)$ (6) which are inducing an attraction of quasiparticles to the surface of the QD (to the "foreign" images, Fig. 1) will be less than the energy of additional effective attraction [11].

As a result, with decreasing of the QD radius $α < a^0_{ex}$ the value of the additional effective attraction between the electron and a hole will increase $~ α^{-1}$ [11]. This effective polarization attraction leads to the fact that the exciton moves in the volume of the QD with an effective mass $μ = μ(α)$ 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 $α > a^0_{ex}$ the effective attraction between the electron and a hole will decrease $~ α^{-1}$. Starting with some values of the QD radius $α$ which is equal to $a_ε$, the energy of such effective attraction between the electron and a hole is become smaller when compared with the binding energy of the, volumetric exciton [11,15-16]

$$E_{ex} = R_y_{ex} = \frac{\hbar^2}{2μ_0(a_{ex}^0)^2}$$
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Such as the volumetric exciton in a QD was meant the exciton whose structure (reduced effective mass, the Bohr radius, and the 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 \( a > a_{ex}^0 \) [11, 15-16].

![Fig1. Schematic representation of an exciton within the spherical QD of a semiconductor. Radius-vectors \( r_e \) and \( r_h \) define the distance of the electron (e) and a hole (h) from the center of the QD with radius a. Charges of image \( e'=(a/r_e)e \) and \( h'=(a/r_h)h \) are located at the distances \( r'_e=(a^2/r_e) \) and \( r'_h=(a^2/r_h) \) from the center of the QD and representing the point charge images of the electron and hole.](image)

![Fig2. Energy of a base state of the exciton \( E_{1,0,0;1,0,0}(a) \) (11) as function of radius \( a \) of the quantum dot of the zinc selenide, where \( E_g \) is a band gap of zinc selenide.](image)

Table 1 shows the numerical value of the \( \mu = \mu(a) \) function. 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 \( (a_c = 3.90, \ a_{ex}^0 \approx 12.2 \text{ nm}) \) reaches the value of the effective mass of the exciton \( \mu_0 = 0.137m_0 \) in bulk crystal of ZnSe (Table 1). Thus, the volumetric exciton occurs in QDs of the zinc selenide when the radius of QD reaches \( a \geq a_c \approx 3.90 \ a_{ex}^0 \approx 12.2 \text{ nm} \).

Figure 2 which displays an dependences of energies \( E_{1,0,0;1,0,0}(a, \epsilon) \) (11) of the base state of exciton in nanosystems containing of zinc selenide QDs with radius \( a \) 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 \( a \geq a_{c}^{(1)} \approx 4.4 \text{ nm} \). 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 a hole. In this case, the energy of the Coulomb interaction \( V_{eh}(r) \) (8) between the electron and a hole, and the polarization interaction energy \( U(r_e,r_h,\epsilon) \) (3) for the electron and a hole with section of the spherical surface (QD – dielectric matrix interaction) is prevail over the dimensional quantization energy of the electron and a hole in nanosystems.
With an increase in the radius \( \alpha \) of the QD an increase of energy of the base state of the exciton \( E_{1,0,0,1,0,0}(a, \varepsilon) \) (11) was observed. Starting with radius of the QD of \( a \geq a_c \approx 3,90 \text{nm} \) the values (11) of energy of the base state of the exciton approaches asymptotically to the value of the binding energy of the volumetric exciton \( E_{\text{ex}} = 28.41 \text{meV} \) (15) (Fig. 2).

Thus, the energy dependence of the base state of an exciton \( E_{1,0,0,1,0,0}(a, \varepsilon) \) (11) of the radius of the QD (14) was obtained by using a variational method in a framework of the modified method of the effective mass (Fig 2). Was shown that with an increase in radius \( \alpha \) of the QD starting with radius of QD \( a \geq a_c \approx 3,90 \text{nm} \) a volumetric exciton occurs in the bulk of QD with binding energy (15) equal \( E_{\text{ex}} = 28.41 \text{meV} \). When the radius \( a \) of the QD is increasing \( (a \geq a_c) \) the base state of the exciton energy \( E_{\text{ex}}(a) \) (11) is approaching asymptotically to the value of the binding energy of the volumetric exciton \( E_{\text{ex}} = 28.41 \text{meV} \) (15) (Fig. 2).

3. SPECTROSCOPY OF EXCITON STATES IN QUANTUM DOTS

From results of the variational calculation of the base state of an exciton (11) in nanosystem which contain QDs of the zinc selenide with change of an average radii \( \alpha \) of QD in interval (14) is follows that in the band gap of such QDs appears a zone of the exciton mode with width of:

\[
\Delta E_{\text{ex}} = E_{\text{ex}} - 28.41 \text{meV},
\]

located under the bottom of the conductive zone.

The optical properties of the samples of zink selenide containing QDs located in air (with dielectrical permeability \( \varepsilon_2 = 8.1 \) and an effective mass of the electorone and a hole \( (m_e/m_0) = 0,17 \) and \( (m_h/m_0) = 0,7 \) where \( m_0 \) is a mass of the free electron) was reported earlier [23]. For interpretation of the experimental results [23] assume that the QD have a spherical shape. The average radius of those QDs is in the range:

\[
\bar{a} \approx (14 - 21) \text{nm}.
\]

At low experimental concentrations of QDs \( (x = 0,003\% \) and \( x = 0,03\%) \) [23] the mutual interactions of QDs is nonsignificant. The optical properties of these samples were defined by energetic spectra of the electron and a hole which localized near to 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 were detected a narrowing of the band gap zone:

\[
E_g \approx (2,61 - 2,68) \text{eV},
\]

comparing to the zinc selenide single crystal band gap energy \( (E_g^0 = 2.7 \text{eV}) \).

In [23] 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\(_2\)SeO\(_3\), 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 confirms the cubic phase of the zinc selenide (ZnSe (JCPDS 37-1463)) with crystallite size of about 27 nm (Fig. 3.).

For samples treated by ammonium hydroxide which partially dissolve ZnSe particles aggregates and the size of crystallite increase up to \( \sim 42 \text{nm} \). A width of the band gap zone was determined via transforming the spectra into Kubelka-Munk coordinates. A width of the band gap for synthesized semiconductor ZnSe is \( E_g = (2,61 - 2,68) \text{eV} \) and \( E_g^0 = 2,56 \text{eV} \) for ammonia treated sample (Fig. 4). A width of the band gap for samples is narrower than for bulk of zinc selenide \( (E_g^0 = 2.7\text{eV}) \) by:

\[
\Delta E_g = (E_g - E_g^0) \approx (20 - 90) \text{meV}
\]
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The exciton mode zone $\Delta E_{ex}$ reaches a maximal width (16) starting from radius $a$ of QDs $a \geq a_c \approx 12.2$ nm which lesser than the average radius $a$ if QDs from interval (17) in research reported earlier [23]. Therefore in regards to (16) and (19) the narrowing in the width of band gap comparing to the same in bulk crystal of ZnSe for value (19) is conditioned by transfer of the non-equilibrium electron from quantum size level within the valance zone of the QD to the level of the exciton mode with width $\Delta E_{ex}$ (16). The electron transition within the zone of exciton mode invokes the significant absorption of irradiation in a visible and near infrared wavelengths, and causes a significant blurring of the absorption edge which is experimentally observed [23]. The origin of the band gap value ($E_g = 2.56$ eV) [23] 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 research.

4. CONCLUSION

This research is dedicated to development of the theory of exciton states in the quantum dot of the semiconductor in conditions where polarizing interaction of the electron and a hole with the spherical surface of interface (quantum dot – dielectric matrix) have a predominant character. The dependence of the energy of a base state of an exciton from the radius of QD was obtained using a modified method of the effective mass. Was shown that with an increase in radius and starting from certain critical radius of the QD ($a \geq a_c$) the exciton appears in the volume. Was found that the energy of a base state approaches to the value of the volumetric exciton asymptotically with an increase of radius $a$ of the QD. Appearance of the zone of exciton modes under bottom of the conductive band in the band gap of the QD of zinc selenide was demonstrated. Established, that the narrowing of the band gap in this nanosystem is conditioned by transition of non-equilibrium electron from quantum-size level into valence zone of the QD to the level of the exciton mode.

![Fig3. Diffraction patterns: 1 – ammonia treated ZnSe, and 2 – pristine ZnSe.](image1)

![Fig4. Reflection spectra in Kybelka-Munk coordinates: 1 – ammonia treated ZnSe, and 2 – pristine ZnSe.](image2)
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