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Interband absorption of semiconductor quantum dots

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ABSTRACT

A theory of the interband absorption of cadmium sulfide quantum dots developed under conditions when the polarization interaction of an electron and a hole with the surface of a quantum dots is importance. A comparison of the theory and experiment is used to determine the average radii $\overline{a}$ *of cadmium sulfide quantum dots dispersed in a jelly matric.*

Keywords: interband absorption, nanocrystals, polarization and Coulomb interaction, electron, hole, exciton, quantum dots.
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INTRODUCTION

Recently extensively studied the optical properties of semiconductor quasi-zero-dimensional structures, which are semiconductor nanocrystals (called quantum dots (QDs)) spherical with radii $a \approx 1 \div 10\ nm$, grown in transparent dielectric (semiconductor) environments [1 – 7]. The fact that the size of *a* QDs is comparable with de Broglie wavelength of the electron (hole) or (and) of Bohr radius leads to the fact that the phenomenon of spatial size quantization of charge carriers play a dominant role in the optical [1 – 10] and electrooptical [11-13] processes in such nanosystems.

When studied the optical properties of QDs is necessary, as in the evaluation of their radii *a* as well as in setting their size depending on the conditions and time of storage QDs. For QDs, which were grown in a transparent dielectric matrix is used for such purposes by transmission electron microscopy with high resolution [1, 2], methods of Raman scattering [2 – 4] and small angle X–ray scattering [2, 5 – 7]. Using the above methods is limited such drawbacks, as appropriate, in some cases, a special sample preparation for measurement, control and inability to express etc. In addition, microscopic methods nanosystems give an error in determining the size of *a* QDs least $(2 \div 3)\ nm$. This error is caused by fluctuations in the structure of the matrix, which submerged semiconductor QDs [1 – 7].

Optical methods allow to basically determine the mean radius of *a* QDs (the absorption spectra) [1 – 7, 13 – 16], the life time of nonequilibrium electrons (with fading kinetics of luminescence bands) [17], composition (with Raman spectra) [2 – 4, 18]. The use of optical methods is limited to their lack of sensitivity. To investigate quasi-zero-dimensional semiconductor systems by optical methods requires that executed the ratio [1 – 4]:

$$KD \approx 1,$$

where *K* – the coefficient line light absorption, *D* – diameter of the QDs, which has the order of the exciton Bohr radius in a single crystal, that is $D \approx a_{ex}$. In connection with this experiment mainly studied quasi-zero-dimensional structures containing a large collection of QDs. The presence of QDs size dispersion can determine only the mean values of optical parameters, which can be attributed to the QDs–range $a = \overline{a}$ [1 – 7, 13 – 16].

QDs of *CdS* was obtained in [17] by chemical synthesis using as a stabilizer of an aqueous solution of gelatin. Choice of gelatin as a stabilizing agent was due to the following factors: gelatin is non-toxic substance and gelatin emulsion is widely used in photographic materials produced [7]. In addition, it should be noted that gelatin refers to polymers containing highly polar groups, amide, amine, carboxyl [7]. These groups have complexing properties towards transition metal ions and therefore may play a role in shaping the properties of the interface QDs – matrix, as well as radiative processes in the QDs.

Interband absorption spectra synthesized of [17] QDs CdS showed quantum effect, which manifests itself in the "blue" shift of the absorption threshold. Thus, in [17] studied the frequency dependence $\omega(\overline{a})$ of the spectrum peaks interband light absorption QD CdS, the average radius $\overline{a}$ of the QDs.

In this paper, using new optical theory method determined the average values of the radii *a* of CdS QDs, which are in satisfactory agreement with the size QDs, which investigated experimentally [17].

MATERIALS AND METHODS

Interband absorption of quantum dots

In [8 – 10] studied the model quasi-zero-dimensional nanosystems – spherical QDs radius *a* on the dielectric constant ε_2 immersed in a dielectric medium with dielectric constant ε_1. In this volume moved QDs electron *e* and hole *h* with effective masses m_e and m_h under (r_e and r_h – distance electron and hole from the center QD), and dielectric permittivity QDs and matrix significantly different (that is $\varepsilon_2 >> \varepsilon_1$). It was assumed also that the band electron and hole QDs had a parabolic shape.

Typical quasi-zero-dimensional nanosystems is of size (a, a_e, a_h i a_{ex}): where

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

Bohr radius of the electron, hole and exciton, respectively, in an infinite semiconductor with dielectric constant ε_2 (*e* – electron charge, $\mu = m_e m_h /(m_e + m_h)$ – reduced effective mass of the exciton) The fact that all the characteristic dimensions of the system quasi-zero-dimensional

$$a, a_e, a_h, a_{ex} >> d \tag{2}$$

much larger interatomic *d*, makes it possible to consider the motion of electrons and holes in the QDs effective mass approximation [13, 14].

In the investigated model within the above approximations exciton in QDs Hamiltonian has the form [8 – 10]

$$H(r_e,r_h,a)=-\frac{\hbar^2}{2m_e}\Delta_e-\frac{\hbar^2}{2m_h}\Delta_h+E_g+V_e(r_e,a)+V_h(r_h,a)+V_{eh}(r_e,r_h)+ \\ +U(r_e,r_h,a), \tag{3}$$

where the first two terms determine the kinetic energy of the electron and hole; E_g – band gap in an infinite semiconductor with dielectric constant – ε_2; $V_{eh}(r_e,r_h)$ the energy of the Coulomb interaction between electrons and holes; $U(r_e,r_h,a)$ – energy polarization interaction of electrons and holes with a spherical interface between QD – dielectric medium, $V_e(r_e,a)$ and $V_h(r_h,a)$ – the height of the potential barrier for electrons and holes in the QD value of which depends on the radius of a QDs [18].

Based on the papers [8 – 10], in the framework of a simple model quasi-zero-dimensional system, we obtain the energy spectrum of an exciton in a spherical QDs in the approximation in which the QDs for electrons and holes, which moved to its volume, is infinitely deep spherical a potential hole. The radius of *a* QDs cramped conditions

$$a_h << a \le a_e \approx a_{ex} \tag{4}$$

in the performance of which in the potential energy of the Hamiltonian (3) polarization interaction $U(r_e,r_h,a)$ played a dominant role.

Performing the condition (4) use the adiabatic approximation, assuming the kinetic energy of the electron maximum value and considering the last two terms in the Hamiltonian $H(r_e,r_h,a)$ (3), together with the operator not adiabatic by perturbation theory. Using only the first order perturbation theory, we obtain the energy spectrum of an exciton $E^{n_h,l_h,m_h=0}_{n_e,l_e=0,m_e=0}(\bar{S})$ in state (n_e, $l_e=0$, $m_e=0$; n_h, l_h, $m_h=0$, where n_e,l_e,m_e and n_h,l_h,m_h – radial, orbital and magnetic quantum number of electrons and holes, respectively), the QDs radius $\bar{S}$ in the following form [8 - 10]:

$$E^{n_h,l_h,0}_{n_e,0,0}(\bar{S})=E_g+T^e_{n_e,l_e=0}(\bar{S})+\bar{V}^{n_e,0,0}_{ee'}(\bar{S})+\lambda^{n_h,l_h,0}_{n_e,0,0}(\bar{S}), \tag{5}$$

where $T^e_{n_e,0}(\bar{S})$ – the kinetic energy of an electron in an infinitely deep spherical hole QDs, which was described by the energy levels of an electron moving in a spherical pit of infinite depth

$$E^e_{nl}(\bar{a})=T^e_{nl}(\bar{a})=\frac{\hbar^2}{2m_e a^2}(\varphi^e_{nl})^2, \tag{6}$$

where φ_{nl} – the roots of Bessel functions $J_{1+\frac{1}{2}}(\phi_{nl})=0$.

The dimension $\bar{V}^{n_e,0,0}_{ee'}(\bar{S})$ is the average value of the interaction energy of the electron with its own images on the wave function infinitely deep spherical QDs, which is determined by the equation:

$$\bar{V}^{n_e,0,0}_{ee'}(\bar{S})=\frac{Z_{n_e,0}}{\bar{S}},\ Z_{n_e,0}=\frac{\varepsilon_2}{\varepsilon_1}+2\int_0^1\frac{dx\sin^2(\pi n_e x)}{1-x^2}. \tag{7}$$

In the equation (5) $\lambda^{n_h,l_h,0}_{n_e,0,0}(\bar{S})$ is a spectrum hole oscillator types:

$$\lambda^{t_h}_{n_e,0,0}(\bar{S}) = \frac{P_{n_e,0}}{\bar{S}} + \omega(\bar{S},n_e)\,(t_h + \frac{3}{2}), \tag{8}$$

$$P_{n_e,0} = 2Ci(2\pi n_e) - 2ln(2\pi n_e) - 2\gamma + (\varepsilon_2/\varepsilon_1) - 1, \tag{9}$$

where *Ci(y)* – integral cosine $\gamma = 0{,}577$ – const of Euler.

In the spectrum holes (8) $\omega(\bar{S},n_e)$ is the oscillation frequency holes

$$\omega(\bar{S},n_e) = 2(1 + \frac{2}{3}\pi^2 n_e^2)^{1/2}\bar{S}^{-3/2} \tag{10}$$

the adiabatic electronic potential QDs. Here $t_h = 2n_h + l_h = 0,1,2,...$ – the principal quantum number of holes, $\bar{S} = (\bar{a}/a_h)$ – dimensionless radius QDs ($\bar{a}$ – mean radius QDs). Energy in equations (5) – (10) is measured in units $Ry = \left(\hbar^2 / 2m_h a_h^2\right)$.

The resulting exciton energy spectrum (5) is applicable only for weakly excited states of the exciton $(n_e,0,0;t_h)$, for which the inequality

$$E^{t_h}_{n_e,0,0}(\bar{S}) - E_g << \Delta V(\bar{S}), \tag{11}$$

where $\Delta V(\bar{S})$ – the depth of the potential well for electrons in the QDs (eg in QD *CdS* in size (4) the value of $\Delta V = 2{,}3...2{,}5$ eV [18]).

When interband light absorption QDs radius $\bar{S}$, containing in its direct band bulk semiconductor material, the QDs must be traceable series of discrete lines with frequency [8 - 10]:

$$\omega^{n_h,l_h,m_h}_{n_e,l_e,m_e}(\bar{S}) = E^{n_h,l_h,m_h}_{n_e,l_e,m_e}(\bar{S}) = E_g + T^{e}_{n_e,l_e}(\bar{S}) + \bar{V}_{ee'}(\bar{S}) + \lambda^{n_h,l_h,m_h}_{n_e,l_e,m_e}(\bar{S}) \tag{12}$$

It follows from equations (5) – (10), (12), the absorption threshold QDs radius $\bar{S}$ is the frequency of light $\omega^{t_h=0}_{n_e=1,l_e=0;m_e=0}(\bar{S})$ that is [8-10]:

$$\omega^{t_h=0}_{n_e=1,l_e=0;m_e=0}(\bar{S}) = E_g + \left(\frac{m_e}{m_h}\right)\frac{\pi^2}{\bar{S}^2} + \frac{1}{\bar{S}}(Z_{1,0} + P_{1.0}) + \frac{3}{2}\omega(\bar{S},n_e=1), \tag{13}$$

Thus the light absorption threshold QDs cause transition of holes equidistantly level $|t_h = 0> = |n_h = 0,\ l_h = 0, m_h = 0>$ to a lower level of size quantization of electron $|t_h = 1> = |n_e = 1, l_e = 0,\ m_e = 0>$.

Comparison of theory with experiment

In [17] experimentally investigated CdS QDs with average radius $\bar{a}$ is not exceeded $(5 \div 7)$nm. As a first approximation, assume has spherical QDs. Dimensions of QDs $\bar{a}$ is comparable with the value of the exciton Bohr radius $a_{ex} \approx 2{,}5\,nm$ in a single crystal CdS. Therefore, the frequency dependence $\omega(\bar{a})$ of interband absorption peaks in the spectrum of light QDs CdS, the radius of the $\bar{a}$ QDs, which was obtained in [17] can be described by equation (10).

In [8-10] it was shown that the main contribution to the formation threshold interband light absorption QDs CdS dimensions which satisfy the condition (4), allows spectral line hole, which is

due to the transition of holes equidistantly level $|t_h = 0>$ to a lower level of size quantization of electron $|t_h = 1>=| \ n_e = 1, \ l_e = 0, \ m_e = 0>$.

To determine the average radius $\overline{a}$ of QDs CdS apply new optical method. Its essence is as follows. Comparing the absorption threshold $\omega^0_{1,0,0}(\overline{a})$ (13) light QDs radius $\overline{a}$ with the experimental absorption peaks provisions $\left(0{,}13 \le \left(E(\overline{a}) - E_g\right) \le 0{,}5\right)$ eV in QDs CdS, which were obtained in [17], we define the average radius $\overline{a}$ of QDs (*Table1*). From the results given in the table 1, it follows that the change of the absorption peaks provisions from 0.13 to 0.332 eV mean radius $\overline{a}$ of QD CdS, due to quantum effects, reduced from 5.7 to 2.5 nm.

Thus, found the values mean radius QDs CdS $2.5 \le \overline{a} \le 5.7$ nm are in good agreement with the size QDs, which in [17] studied experimentally $\overline{a} \le (5 \div 7)$ nm. As for the range of energy absorption $\left(0.332 \le \left(E(\overline{a}) - E_g\right) \le 0.5\right)$ eV, which was investigated in an experiment [17], in the framework of our proposed theory [13], which is built only for the size of QDs $\overline{a} \approx a_{ex}$, the interval energy can not be explained. In contrast, by transmission microscopy [1, 2], we proposed a new optical method allowed us to determine the average radius of the QDs CdS less than the value of $\overline{a} \le (5 \div 7)$ nm.

Table1 **.** The dependence of the exciton energy spectrum $\left(E^0_{1,0,0}(\overline{a}) - E_g\right)$ (13) of the mean radius $\overline{a}$ of QDs CdS.

$\left(E^0_{1,0}(\overline{a}) - E_g\right)$ (*eV*)	*a* (*nm*)
0.13	5.7
0.20	4.1
0.226	3.5
0.263	3.0
0.332	2.5

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