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An estimate of shape-distribution of small CdS particles with luminescence spectra

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Abstract. The luminescence spectra of CdS particles obtained by sedimentation method are studied. The comparison of measured and calculated photoluminescence spectra was used as the base of the method defining the shape distribution of the particles. For this purpose one can use the symmetry rule for absorption and luminescence spectra. Absorption spectra were calculated via dissipative function in terms of local field theory. The experimental spectra of the photoluminescence were measured during the process of sedimentation in the CdS nano-composite powder. The modification of luminescence spectra detected during sedimentation time is associated with changing the dimension and shape distributions of CdS suspension. As a result, the particles shape distribution was estimated for sizes less then 1 μm.

PACS. 61.46.Df Nanoparticles – 78.67.Bf Nanocrystals and nanoparticles

1 Introduction

The development of nano-technologies requires the effective methods to control the parameters of nano-systems. There are numerous methods, which are used for this purpose, such as electron microscopy [1], X-ray [2] and optical spectroscopy [3], etc. Optical methods are the most demanded in characterization of nano-composites. The widely used optical methods such as luminescence and absorption spectroscopy allow studying of numerous characteristics of materials. However, the standard approaches to luminescent and absorption spectroscopy become invalid for nano-composites. This is because, as it is known, optical properties depend on both the dimension and shape of nano-particles [4–6]. Moreover, one needs to measure the extremely weak signals. Then, the methods of these signals analysis should allow discriminating the usable parts of the signals. This means that the role of theoretical modeling increases. Theoretical approaches have to take into account the essentially inhomogeneity and shape dependence of the system under consideration. Photoluminescence is a simple, sensitive, non-destructive technique [7]. In particular, photoluminescence is used to study physical properties of semiconductors [8]. Due to its high sensitivity, this method does enable to study dilute solutions, composite materials with small contents of emitted component, etc. The bulk CdS crystals concern to a class of crystal-phosphorus with a high quantum yield of the luminescence [9]. The CdS films are widely used as a component of solar devices [10]. The usage of CdS nano-particles as luminescent markers in modern biology is widely discussed as well [11]. Thus, the obtaining of composites based on CdS nano-crystallites in a neutral matrix is perspective for the development of new technologies.

The dependence of absorption and luminescence spectra on the shape and dimension of particles [5,6,12] needs to separate the particles both on the shape and on the dimension. The sedimentation method could allow succeed in it. In the case of submicron particles the dependence on shape is prevalence. Then, one should separate the heavy particles, which dimensions are sufficiently large. The sedimentation of the small particles suspension in the non-polar liquid can lead to the remaining of particles which are mainly characterized by the same shape and linear dimensions in fixed cross-section of the sell. Then, the small particles with the approximately same dimensions will be prevalent in the layer of suspension in the system under consideration (see Fig. 1). Then, the luminescence spectra will mainly depend on shape distribution of the particles. We can use this fact for definition of shape distribution in this work.

2 The separation of nano-particles by dimension and sharp with sedimentation method

To obtain nano-particles of definite shape and dimension one can use the sedimentation method, the main idea of

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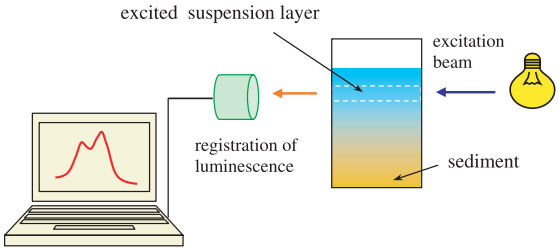

Fig. 1. Set-up of experiment. Suspension of CdS nano-particles is form sediment in the quartz cell. The fixed layer of the suspension (marked by white dash lines) is radiated by excitation ultra-violet beam. Detecting system detects the luminescence spectrum.

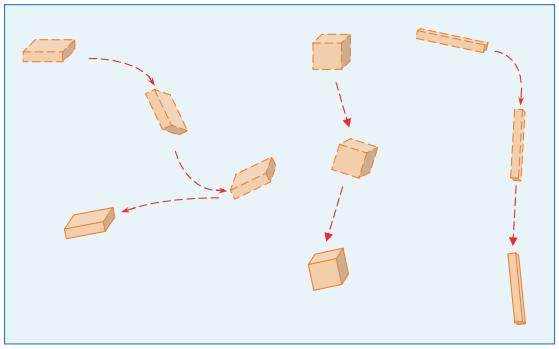

Fig. 2. The drowing of plate-like, cube-like and stick-like particles.

which consists in settling out the nano-crystallite powder by gravity [13–16]. Obviously the heavy particles have to settle more quickly. Then the heavy particles will not be presented at fixed cross-section of the cell at appointed time. Due to hydrodynamic properties the particles characterized by stick-like and cub-like shapes have to settle more quickly than the plate-like particles (see, Fig. 2) of the same weight. Taking into account these circumstances we can suppose that differences of luminescence of the particles from appointed cross-section of the sedimentation column are caused by different shapes of the particles. The process of sedimentation was performed by the next steps. The first step consisted in dust preparation. Particularly, high cleanliness and milled in an agate mortar powder of CdS was intermixed with alcohol for homogeneous suspension. The next step was the settling of the suspension. For 60–120 min heavy fractions of CdS powder settled on the bottom of the cell. As a result, the suspension of submicron dimensions particles was obtained. As the water is a dipole medium, the electrostatic interaction between the water and crystallites can lead to the meshing of particles with each other, and aggregates of the particles could arise. As a result, the spectrum of luminescence can disfigure. Therefore the study should be carried out in non-polar liquid, for example, in alcohol. For this case the sedimentation happens much faster. Then, the process of experimental measurements should be carried out during not long time. This fact leads to the request for use of the automatic high sensitive experimental equipment for the registration of weak signals from luminescent particles.

To make sure that the sedimentation process allows us to obtain sufficiently homogeneous on the weight suspension we simulated numerically this process, where the initial distribution of particles obtained by a mechanical refinement was supposed as Gaussian, with the average of distribution of the dimension $R_0 = 0.35\ \mu$m [17], namely it was supposed as $N_i^0 = \left(N_0/\sigma\sqrt{2\pi}\right)\cdot\exp\left[-(R-R_0)^2/\sigma^2\right]$, with σ dispersion of particle distribution over size. Then, the concentration of particles with the average dimension R_0 at the height h is described by equation

$$N_i(h,t) = N_i^0 \cdot \left(\frac{sign\,(h - x_i) + 1}{2}\right), \qquad (1)$$

where $x_i = U_i t$ is the depth at which the particle falls for time t. To obtain the velocity U_i we have written the motion equation for the particle with the radius R_i in the form

$$\rho V_i g = 6\pi\rho_\nu \nu R_i U_i + \rho_v g V_i, \qquad (2)$$

where $V_i = (4/3)\pi R_i^3$ is the volume of particle with the radius R_i , ρ_ν and v are the density and viscosity of solvent and g is the acceleration of gravity. Solving equations (1) and (2) one obtains the number of particles with the radius R which are situated at the h depth of the sell

$$N(R,h,t) = \frac{N_0}{2\sigma\sqrt{2\pi}} e^{-(R-R_0)^2/\sigma^2} \cdot sign\,(h - (2/9)R^2 g\left((\rho-\rho_v)/\rho_v\nu\right)t), \qquad (3)$$

where normalization factor is

$$N_0 = 3M/(4\pi\rho I), \qquad (4)$$

with M the mass of the particle and $I = \int_0^\infty \zeta e^{-(\zeta/R_0-1)^2} d\zeta$.

This dependence of particles distribution on time is shown in Figure 3. One can see that the particles, which remain in the suspension after 8 h of sedimentation, will be less than 0.2 μm. Then, it could be supposed that investigated suspension consists of nano-particles which luminescent properties are defined by its shapes. The study of suspension with optical microscopy has given us an additional corroboration of nano-dimension of the particles under consideration. Indeed in Figure 4 one can see that the dimensions of the particles in the suspension are about or less than 0.1 μm. Due to the crystalline lattice of CdS (we used CdS crystals with a zincblend lattice), the grinding of CdS crystals will lead to obtaining the powder characterized by the rectangular shape particles with different ratios between the edges (it is well visible at the AFM image). Then, one can suppose that three types of the shape of the particles will form the suspension after sedimentation — cube-like, plate-like and stick-like. Taking into account that absorption and luminescence spectra of the particles depend on the particles shape, one can estimate the shape distribution of the particles in the suspension using the experimentally obtained luminescence spectra.

The luminescence spectra were measured in the experiment, set-up of which is shown in Figure 1. The photoluminescence was excited by the xenon lamp of wavelength

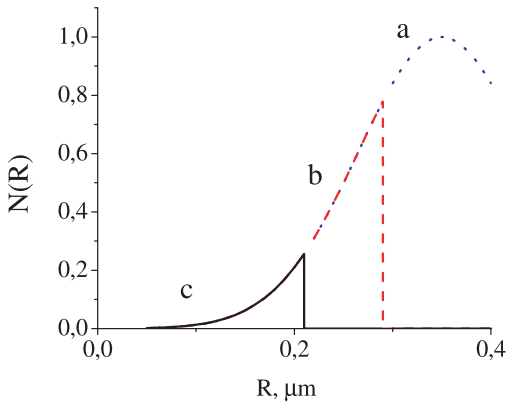

Fig. 3. Particle size distribution: (a) at the initial moment, (b) after 4 h, (c) after 8 h.

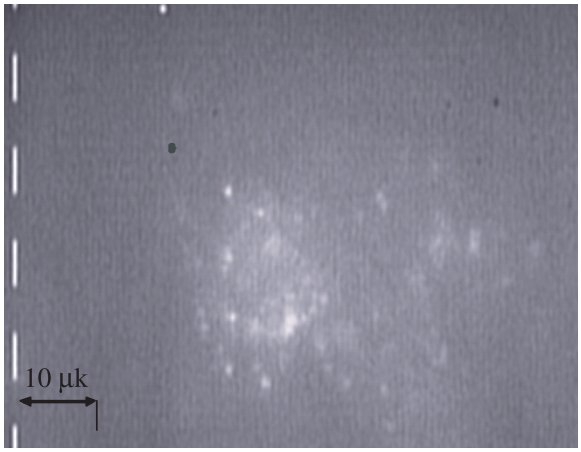

Fig. 4. Image of particle, make on optical microscope. Particles size are defined less or 1 μm.

$\lambda = 337$ nm, which was focused at the upper part of the sell. The luminescence spectra were detected every 15 min during 10 h. In the course of time the luminescence spectra varied. The evolution of the spectrum measured after 15 min, 3 h and 6 h is shown at Figure 5. The first spectrum measured after 15 min sedimentation (curve *a*) has the bell-shaped profile, with the peak at frequency 18 000 s m^{-1}. It has wide, weakly structured profile that corresponds to a spectrum of a bulk material. Spectrum measured after 3 h has peak at frequency 2.23 eV, and also additional, weakly expressed peak centered at 2.04 eV (curve *b* in Fig. 5). The occurrence of this peak can be connected with the increase of the relative number of plate-like particles in the cross-section of the suspension. After the lapse of 6 h, the spectrum has two pronounced peaks (at 2.23 eV and 2.04 eV). This means that the stabilization of the shape distribution in the suspension took place. One should note that in this case, the intensity of radiation is weaker as compared with the previous cases, because the amount of emitting particles decreased.

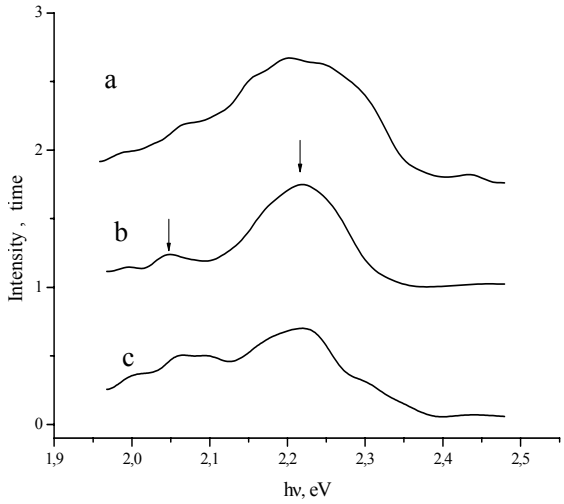

Fig. 5. Photolumioescence spectra after 15 min (a), 3 h (b) and 6 h (c), sedimentation in spirit.

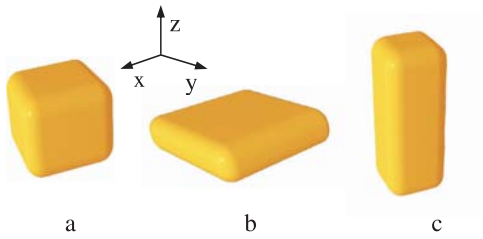

Fig. 6. Model of nano-particles under consideration (a) cube-like; (b) plate-like; (c) stick-like.

3 Modeling of luminescence spectra

The basic aim of these experimental and theoretical investigations is to separate the CdS powder by particular size and shape. Since CdS material has good luminescent properties, luminescence of nano-particles can be observed during the sedimentation process even at small concentrations of a powder. Luminescence properties of nano-particles are strongly termed by their size and shape, which make it possible to estimate the sizes and shapes of particles by comparing theoretical and experimental luminescence spectra of dilute suspension. To estimate the luminescence spectra we used the symmetry of luminescence and absorption spectra principle.

There are a lot of methods for describing absorption properties of nonaparticles. For example, one can point the works performed by Fuchs method [18,19]. The absorption properties of electron near dielectric surfaces were analyzed by boundary element method in [20,21]. The local field distribution in the nano-particle system can be calculated with widely used method of discrete-dipole approximation [22,23]. In most cases the methods of calculation of electrodynamical properties of nano-systems are based on direct solution of Maxwell's equations. We could use these methods for calculating absorption spectra, but solution of Maxwell's equations in the case of different rectangular particles is very complicated, and derived result usually

is not analytic, however it is very important for our numerical method. Discrete-dipole approximation method is not opportune for spherical or ellipsoidal form particles. Due to this we appeal to method of local-field distribution calculation, this method allows us to obtain analytically the effective susceptibility, which is the important characteristic of the system. The effective susceptibility method for calculation of local field distribution in the system of nano-particles was developed in [24–26]. The main idea of the method consists in calculation of dissipation function of the system which can be written via effective susceptibility. The method allows us to obtain analytical solution of the Lippmann-Schwinger equation for the local field in arbitrary point of the system via effective susceptibility. This is completely analytical method which allows us to describe particles with different form. In the present work this method was used for calculation of effective susceptibilities (and it automatically means — dissipative function) for rectangular-shape particles.

The absorption spectra were calculated in the frame of local-field approach using near-field approximation. It was supposed that particles in suspension have plate-like, cube-like and stick-like shape. To calculate the absorption spectra we estimated the dissipative function of the system taking into account its dilution. The term dissipative function used for the energy absorbed by the unit of volume of the system per unit of time can be presented in the form

$$Q = n\overline{\langle(\vec{J}+\vec{J}^*)(\vec{E}+\vec{E}^*)\rangle}, \tag{5}$$

with $\vec{J}(\vec{R})$ local current inside a particle, $\vec{E}(\vec{R})$ local field, and n concentration of the particles in the suspension. The next designation used in equation (5): $\langle ... \rangle$ is the averaging over the volumes of the particles, $\overline{(...)}$ means the time averaging.

The particle is described by the effective susceptibility [26]

$$\mathrm{X}_{ij}(\vec{R},\omega) = \chi(\omega) P_{ij}(\vec{R},\omega), \tag{6}$$

where $\chi(\omega)$ is the electric linear response of the material of particle (the linear response on the total field), and

$$P_{ij}(\vec{R},\omega) = \left[\delta_{ji} - \int\limits_V d\vec{R}' G_{ji}(\vec{R},\vec{R}',\omega)\chi(\omega)\right]^{-1} \tag{7}$$

is the factor, which describes the local-field correction. Here $G_{ij}(\vec{R},\vec{R}',\omega)$ is electrodynamic Green function (photon propagator) [27] which describes the field propagation from point $\vec{R}'$ to point $\vec{R}$. Integration in equation (7) is over volume of the particle. Then, the dissipative function can be written in the form

$$Q = 2\omega n I_0 \mathrm{Im}(\chi(\omega)) \frac{1}{V} \int\limits_V d\vec{R} \cdot \left|\vec{\vec{P}}(\vec{R},\omega)\right|^2 \vec{e}\cdot\vec{e}, \tag{8}$$

with I_0 intensity and $\vec{e}$ polarization vector of external radiating field. The using of linear response method allows us to calculate analytically the local field correction factor for the simple shape of the particles in the frame of near-field approximation. It leads to essential simplification of numerical calculations. Namely, one only needs to calculate the final equation [Eq. (8)] defining the absorption profile. To calculate the local field correction factor in the near-field approximation we used the photon propagator in the form

$$\vec{\vec{G}}(\vec{R},\vec{R}',\omega) = \frac{1}{4\pi}\left[\frac{c^2}{\omega^2\cdot R_s^3}\vec{\vec{U}} - \frac{3c^2}{\omega^2\cdot R_s^3}\vec{e}_R\vec{e}_R\right], \tag{9}$$

with $\vec{\vec{U}}$ unit dyadic, $\vec{R}_s = \vec{R} - \vec{R}'$, $R_s = \left|\vec{R}-\vec{R}'\right|$, $\vec{e}_R = \vec{R}_s/R_s$. Green function $\vec{\vec{G}}_{il}(\vec{R},\vec{R}',\omega)$ has a pole at $\vec{R}' = \vec{R}$, and evaluation of integral in equation (7) becomes nontrivial problem. This problem is well-known and related to the so-called radiation reaction field. The problem can be solved in the frame of scheme proposed by van Bladel [28] and Yaghjan [29]. The main idea of this approach is to introduce the exclusion volume V_δ whose depolarizing properties are accounted for by a special source dyadic [28–30]. Then, when calculating the self-consistent field the following relation should be applied

$$\vec{E}(\vec{R}) = -i\omega\mu_0 \lim_{\delta\to 0} \int\limits_{V-V_\delta} d\vec{R}'\vec{\vec{G}}(\vec{R},\vec{R}')\vec{J}(\vec{R}') - \frac{1}{i\omega\mu_0}\vec{\vec{L}}\cdot\vec{J}(\vec{R}). \tag{10}$$

The polar part of an effective susceptibility depends on electromagnetic interaction between an object and a medium, in this case, the interchanging of a virtual photon with a surrounding medium. In the frame of foregoing scheme, we have calculated the absorption profiles for different cases of the particles shape (Fig. 7). Total absorption profile was defined as the sum of partial profiles caused by the light absorption of the particles for three kinds of the shape

$$I_{abs}^{(t)}(\omega) = f_c I_{abs}^{(c)}(\omega) + f_p I_{abs}^{(p)}(\omega) + f_s I_{abs}^{(s)}(\omega), \tag{11}$$

where f_c, f_p and f_s are the comparative parts in the suspension of cube-like, plate-like and stick-like particles, respectively. $I_{abs}^{(c)}(\omega)$ is the partial absorption profile for cube-like particles, $I_{abs}^{(p)}(\omega)$ is the partial absorption profile for plate-like particles, and $I_{abs}^{(s)}(\omega)$ is the partial absorption profile for stick-like particles [31].

Choosing values of f_c, f_p and f_s in such way that the total absorption profile would have a view similar to any reflected frequency the luminescence spectrum, we obtained for these coefficients $f_c = 0.2$, $f_p = 0.67$ and $f_s = 0.13$. As it is clear, the values f_c, f_p and f_s define the shape distribution of the particles. Total absorption spectrum for obtained shape-distribution of the particles in the suspension is shown at Figure 8. The spectrum of luminescence obtained by reflection relatively any frequency is shown at this figure too. The comparison of the calculated and experimentally obtained luminescence profiles is shown at Figure 9. One can see, that calculated and experimentally obtained profiles are very similar.

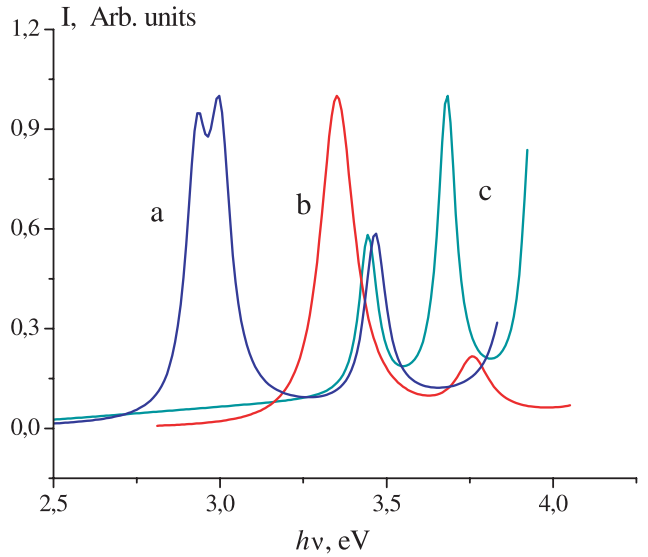

Fig. 7. Absorption spectrum of plate-like (a), cube-like (b) and stick-like (c) particles.

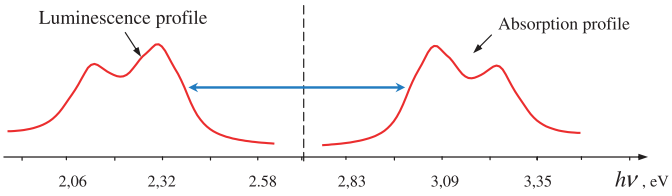

Fig. 8. The construction of luminescence profile as reflection of absorption profile.

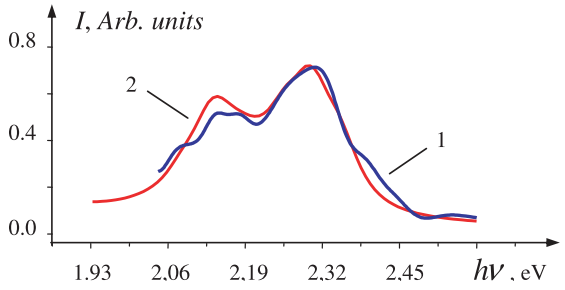

Fig. 9. Measured (1) and calculated (2) luminescence profiles.

This means that obtained shape distribution of the particles is, at least qualitatively veritable. Of course, we have taken into account only three kinds of particle shape, which make strongly worse the result. Moreover, only defined relations between the edge lengths for plate-like and stick-like particles were used. There were $a_z/a_x = 2/3$ for plate-like particles and $a_z/a_x = 5$ for stick-like particles. These values of ratio were chosen taking into account the results of modeling as hydro-dynamical as absorption properties of suspension under consideration. Of course, even remaining in the frame of this simple model, one can essentially improve the results and obtain more adequate distribution function for shape distribution of the suspension. Indeed, if one will take into account not one but two kinds of plate-like particles, the structure of the peak at

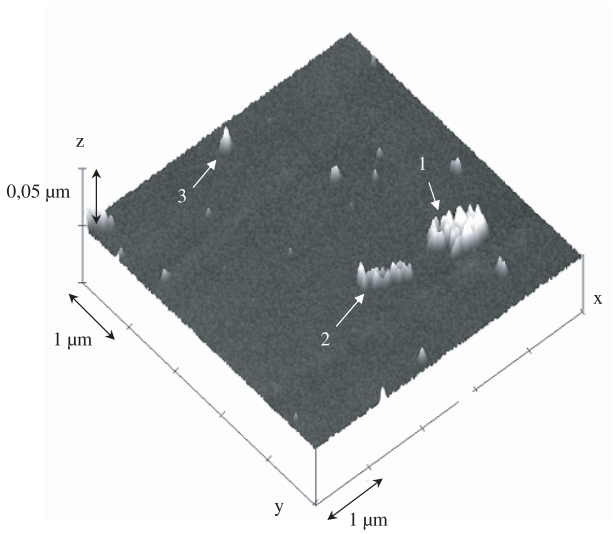

Fig. 10. AFM pattern of the silica surface at which the CdS particles were sedimented.

2.04 eV could be obtained. Nevertheless, proposed scheme demonstrated that even in the simplest cases one can obtain rather good results.

If the speculations used in this paper are correct, then the fixed layer of solution after some hours sedimentation will consist mainly of plate-like particles. In support of this concept we observed the sedimentation of suspension for 6 h. Then we took the probe from layer under consideration and placed it on the surface of silica. The surface, which was prepared by such method was analyzed with the help of AFM. At Figure 10 the AFM image is shown. Here the graduating marks are 1 μm for OX and OY axes and 0.05 μm for OZ axis. As it can be seen, the particle N 1 is characterized by dimensions $1 \times 1 \times 0.025$ $(\mu\text{m})^3$, the particle N 2 is characterized by the dimensions $0.8 \times 0.2 \times 0.025$ $(\mu\text{m})^3$, the particle N 3 is characterized by the dimensions $0.2 \times 0.2 \times 0,025$ $(\mu\text{m})^3$. All particles are similar to the plate-like particles with different ratios between their linear dimensions. This result experimentally confirms our assumptions.

4 Conclusion

The luminescence spectra of small CdS particles, obtained by sedimentation method were measured. The comparison of measured and calculated photoluminescence spectra was used as the base of the method defining the shape distribution of the particles. Then, the simple approach allowing us to estimate the shape distribution of the nano-composites was proposed in this work. For modeling luminescence spectra it was supposed that the luminescent spectrum can be obtained as symmetrically reflected absorption spectrum, which can be calculated in the framework of effective susceptibility concept. Proposed approach was demonstrated for the simple case of nano-composite which is constituted of alcohol suspension

of CdS particles with linear sizes less than 1 μm. The calculation of absorption profile was performed in the simplest model, taking into account only three types of the particle shape — cube-like, plate-like and stick-like. Nevertheless obtained results are reconcilable and give the characteristic features of CdS small particles suspension.

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