Analysis of the temperature dependence of the luminescence spectra of liquid-crystal nanocomposites with a cadmium selenide quantum dots

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Abstract. A theoretical model is proposed for describing the interaction of excitons with phonons and defect states in semiconductor nanocrystals. On the basis of this model, numerical simulation was performed and experimental data on the temperature dependence of the absorption and fluorescence spectra of cadmium selenide quantum dots in liquid crystal solid solutions of cadmium caprylate was discussed.

1. Introduction
Nanocomposites which combine the properties of semiconductor nanocrystals and the material of a solid matrix are widely used in various fields of modern science and technology. Using materials with semiconductor colloidal quantum dots, efficient and economical light-emitting devices are produced (e.g., Samsung's QD-LED technology), as well as various luminescent coatings and labels, and spectral devices [1]. Among the current developments, one can emphasized the search for new gain media for laser generation, sources of nonclassical light for quantum optics and informatics, elements for photovoltaic devices and nanoelectronics. For example, the modeling of collective processes in a dense ensemble of preliminary excited quantum dots demonstrates the possibility of forming short pulses of an electromagnetic field with an extra wide spectrum [2]. In addition, fluorescent labels and markers based on semiconductor quantum dots are highly demanded in biology, medicine, and various diagnostic methods as multiparameter nanosensors, since their spectral properties (e.g., luminescence kinetics) are essentially determined by the parameters of the local field, depend on the thermodynamic parameters of the system and external fields (see, e.g., [3]). In particular, quantum dots are used as temperature sensors [4]. For practical use of nanocomposite materials, a detailed study of their photophysical properties and spectral-luminescent characteristics is necessary. One of the important problems in this area is the investigation of the nature of the fluorescence blinking of single quantum dots [5, 6]. To use semiconductor nanocrystals as temperature sensors, a fundamental study of the dynamical processes that determine the photophysical properties of quantum dots and their relationship to sample temperature is necessary.

The temperature dependences of the absorption and fluorescence spectra of various quantum dots, including CdSe, CdS, InAs, etc., placed in crystalline solutions, have been investigated experimentally...
in a number of papers (see, e.g., [7-10]). Therefore, it is of interest to obtain a theoretical model describing the interaction of excitons with phonons and defect states in nanocrystals that would allow one to analyze the redistribution of the intensity in the fluorescence spectra of cadmium selenide (CdSe) quantum dots in liquid crystal solutions of cadmium caprylate (CdC$_8$) with a temperature change from 77 K to 300 K.

2. Theoretical model
Conjugate absorption and luminescence spectra of liquid crystal solutions of cadmium caprylate with 1.8 nm and 2.3 nm cadmium selenide quantum dots in a wide range of temperatures have been experimentally investigated in [10-12]. Two exciton maxima were observed in the absorption spectra of samples with 2.3 nm cadmium selenide quantum dots (see Fig. 1).

![Figure 1](image1)

**Figure 1.** Fluorescence (solid curve), absorption (bold curve) and fluorescence excitation (dotted curve) spectra of samples with 1.8 nm (left image) and 2.3 nm (right image) CdSe quantum dots in the temperature range 77-300 K.

![Figure 2](image2)

**Figure 2.** Scheme of energy levels and quantum transitions for the system under study.

To describe the quantum states and transitions in the samples, the energy scheme shown in Fig. 2 was proposed. In the scheme, $\theta$ denotes the ground state of the crystal with a population $\rho_0$ corresponding to the Fermi energy. The figure shows only the electron states, the states of the holes correspond to energy levels are symmetric to the energy levels of the electrons relative to the ground level. In the
absence of excitation $\rho_0 = 1$. $I$ and 2 denote two exciton states with populations $\rho_1, \rho_2$ correspondingly. The absorption of external electromagnetic radiation originates from the ground state 0 into exciton states 1, 2 with absorption coefficients (transition rates) $K_1^\delta$, $K_2^\delta$ which explains the occurrence of a broad inhomogeneously broadened absorption band with two exciton maxima.

The radiation from states 1 and 2 is due to spontaneous transitions with a rate $T_1^{-1}$ ($T_i$ is the eigen lifetime of the exciton state), and induced transitions with the rates $K_1^\gamma$, $K_2^\gamma$ correspondingly. These transitions form a luminescence band with two maxima. Such absorption and luminescence bands are observed for a sample with 2.3 nm quantum dots. For a sample with 1.8 nm quantum dots only one maximum corresponding to the interband recombination of the e-h pair in the luminescence band [12] and four exciton maxima in the absorption band were detected. An explanation of this effect will be given below.

Transitions from state 2 to the ground state are also possible through a series of intermediate defect states. Such transitions lead to an additional decay of level 2 with a total rate $G$. They form wide intense bands in the red region of the fluorescence spectrum. In the model, we neglect transitions between the exciton states 1 and 2. Such transitions was not experimentally observed in the spectra and are unlikely because of low volume concentration of excitons in the sample. These transitions can be further taken into account in the theory, but they have virtually no effect on the final conclusions.

The system of balance equations for the scheme shown in Fig. 2, can be written as:

$$\dot{\rho}_0 = -(K_1^\delta + K_2^\delta)\rho_0 + \left(K_1^\epsilon + \frac{1}{T_1}\right)\rho_1 + \left(K_2^\epsilon + \frac{1}{T_1}\right)\rho_2 + G\rho_3,$$

$$\dot{\rho}_1 = K_1^\delta \rho_0 - \left(K_1^\epsilon + \frac{1}{T_1}\right)\rho_1,$$

$$\dot{\rho}_2 = K_2^\delta \rho_0 - \left(K_2^\epsilon + \frac{1}{T_1}\right)\rho_2 - G\rho_2,$$

$$\dot{\rho}_3 = G\rho_2 - G\rho_3.$$  \hspace{1cm} (1)

Putting all derivatives with respect to time in the (1) equal to zero, one can find the steady-state solution:

$$\rho_0 = \frac{1}{1 + K_1^\delta \Gamma_1 + K_2^\delta \Gamma_2 \left(1 + \frac{G}{\gamma}\right)},$$

$$\rho_1 = \frac{K_1^\epsilon \Gamma_1}{1 + K_1^\delta \Gamma_1 + K_2^\delta \Gamma_2 \left(1 + \frac{G}{\gamma}\right)},$$

$$\rho_2 = \frac{K_2^\epsilon \Gamma_2 \left(1 + \frac{G}{\gamma}\right)}{1 + K_1^\delta \Gamma_1 + K_2^\delta \Gamma_2 \left(1 + \frac{G}{\gamma}\right)},$$

$$\rho_3 = \frac{\frac{G}{\gamma}K_2^\delta \Gamma_2}{1 + K_1^\delta \Gamma_1 + K_2^\delta \Gamma_2 \left(1 + \frac{G}{\gamma}\right)}.$$  \hspace{1cm} (2)

here $\Gamma_1 = K_1^\epsilon + \frac{1}{T_1}$, $\Gamma_2 = K_2^\epsilon + \frac{1}{T_1} + G$.

If pumping is performed only at the 0$\leftrightarrow$I transition, i.e. $K_2^\delta = 0$, then we obtain a model of a two-level atom. The interaction of a two-level atom with external electromagnetic radiation can be described using a system of optical Bloch equations [13, 14]. From such equations one can proceed to the balance equations for the populations of states of a two-level atom [14]. The system (1) is a generalization of such a system of equations for the case of the presence of two exciton states and defect levels. In this case the zero-phonon line of the Lorentz profile in Bloch’s theory is an inhomogeneously broadened exciton maximum. Comparison with a two-level atom is justified, since for quantum dots spectroscopic phenomena specific of a two-level atom are observed [15-17]. In particular, exciton resonance absorption lines with the Lorentz profile are observed [15]. But there are differences. As can be seen from Fig. 1, the emission and absorption bands are not resonant. Therefore, for the transition rate, the upper indices e (radiation) and g (absorption) are introduced.

Suppose that the pump is only on the 0$\leftrightarrow$I transition, and, as is done in the Bloch theory

$$K_1^\gamma = K_1^\delta = K_1 = 2\chi^2 \frac{y_1}{\Delta_1^2 + (y_1)^2},$$

we find that the shape of the absorption band is described by the Lorentz profile

$$\rho_1(\Delta_1, t \to \infty) = I_1^\delta(\Delta_1) = 2\chi^2 \frac{\Gamma_1 y_1}{\Delta_1^2 + (y_1)^2 + 4\chi^2(y_1)}.$$  \hspace{1cm} (3)
with a half-width $\Delta_{1/2} = 2\gamma_1$. \hfill (6)

In formulas (5-6) $\Delta_1 = \Omega_1 - \omega_I$ – is the difference between the frequency of excitonic excitation and the frequency of electromagnetic radiation (detuning), $\chi = (\vec{d} \vec{E})/\hbar$ – is the Rabi frequency, $\vec{d}$ – is the transition dipole moment, $\vec{E}$ – is the electric field. The value of $\gamma_1$ determines the half-width of the inhomogeneously broadened absorption maximum. Similar results one can obtain for the case of pumping at the $0 \rightarrow 2$ transition and $G = 0$, i.e. there are no intermediate defect states. In the case of simultaneous pumping of two transitions, two exciton maxima appear in the absorption spectrum. Thus, if $K^g_1 \neq 0$ ($K^g_2 = 0$) and $K^g_1 = K^e_1 = K_1$, then we have a model of a two-level atom. In this case, the absorption and luminescence bands are resonant to each other and have a Lorentz profile. In our case, the absorption and luminescence lines are not resonant to each other, i.e. there is a Stokes shift [18].

Figure 3. Calculated luminescence bands (solid curve) and experimental data (points) [10-12] for a sample with a) 1.8 nm and b) 2.3 nm quantum dots at 77.3 K and 300 K (on the left). Modeling the redistribution of intensity in the luminescence spectrum for a sample with 2.3 nm quantum dots for different values of $GT_1$ and $G/g$: a) 0, 0; b) 0.5, 0.5; c) 1, 1; d) 3, 3; e) 3, 1 (on the right).

The results of a numerical calculation of the absorption and luminescence bands for 1.8 nm and 2.3 nm CdSe quantum dots at two different temperatures are shown in Fig. 3. The half-width of the inhomogeneous luminescence band for a sample with 1.8 nm quantum dots was $0.5 \times 10^{14}$ s$^{-1}$ and $0.4 \times 10^{15}$ s$^{-1}$ at temperatures of 77.3 K and 300 K correspondingly. The luminescence bands for a sample with 2.3 nm quantum dots of size at given temperatures are represented by the sum of two Lorentzians with half-widths $(0.5 \times 10^{14})$ s$^{-1}$. Calculation for a sample with 1.8 nm quantum dots at 77.3 K indicates that the luminescence band contains one exciton maximum, while the absorption band contains two exciton maxima. The absorption band is described by Lorentz profiles with a half-width of $0.5 \times 10^{14}$ s$^{-1}$ and $0.8 \times 10^{14}$ s$^{-1}$.

The obtained values indicate a strong inhomogeneous broadening of spectra, which is practically independent on temperature. We associate it with the distribution of quantum dots sizes. The width of homogeneous luminescence bands depends strongly on temperature, but against a background of strong inhomogeneous broadening, this effect is practically not manifested. In this case, the integral intensity
of the luminescence bands and the redistribution of the intensity between the luminescence maxima are noticeably manifested with a simultaneous increase in the intensity of broad bands in the red spectral region, which are associated with the defect states of the nanocrystals. These effects can be explained on the basis of the proposed balance equations (1) due to the temperature variation of the corresponding transition rates and changes in the level populations. The temperature increase leads to a significant increase in the value of $G$ and an increase in the probability of transitions from the exciton level to the defect states. Consequently this leads to a decrease of the stationary values of the population of the exciton states and an increase of the population of the defect states.

Consider the effects of redistribution of intensity in the lines of luminescence. The luminescence band is proportional to the sum of the populations of the exciton states:

$$I^e(\omega) \propto \rho_1 + \rho_2 = \frac{K_1^g / \Gamma_1 + K_2^g / \Gamma_2}{1 + K_1^g / \Gamma_1 + K_2^g / \Gamma_2 (1 + G/G)}.$$  \hspace{1cm} (7)

In accordance with (7) and the scheme in Fig. 2, two exciton maxima should be observed in the luminescence band. Since $K_1^g \approx K_2^g$ the ratio of the intensities of the luminescence maxima

$$I_2^e(\omega)/I_1^e(\omega) \sim \rho_2/\rho_1 \sim \Gamma_1/\Gamma_2$$  \hspace{1cm} (8)

Consider the case when fast transitions from the second exciton state to defective intermediate states play an important role. In this case, the population of the second exciton state $\rho_2$ decreases, according to (2c), and the second exciton maximum in the luminescence band disappears. Wide intense fluorescence bands are observed in the red region of the spectrum. Physically, this means that, in spite of the fact that the absorption band of the second exciton continues to exist and the level 2 is intensely populated, radiative and nonradiative transitions to intermediate states practically instantaneously occur from it. In this case, the population $\rho_2$ can be much larger than the population $\rho_1$ due to the factor $G/g$ in the formula (2d). Such a situation was observed experimentally for a sample with 1.8 nm CdSe quantum dots [10-12]. Here we observe four exciton maxima in absorption band and one exciton maximum in luminescence band. If $G/g$ is small then there are two exciton luminescence maxima in the fluorescence spectrum, along with wide intense lines in the red region. Such a situation was observed for 2.3 nm CdSe quantum dots.

The redistribution of the intensity in the luminescence spectra is shown on the right-hand side of Fig. 3. The product $GT_i$ significantly influences the intensity distribution between two exciton luminescence bands. An increase in the values of the ratio $G/g$ leads to a total decrease in the intensity of the two bands of exciton luminescence (Fig. 3 d, e), and an increase in the intensity of the fluorescence bands in the red region of the spectrum associated with transitions to the intermediate states $\lambda$.

Thus, it is shown that the redistribution of the intensity in the fluorescence spectra for a system whose quantum states are depicted in Fig. 2, is completely determined by two parameters $GT_i$ and $G/g$.

### 3. Results and discussion

In Fig. 2 and in the system of equations (1), we did not take into account the decays of the exciton state $I$ into defect states, since the luminescence corresponding to the $1 \rightarrow 0$ transition is observed for all temperatures and for two types of samples. Transitions from the exciton level $I$ to defect states are less likely than similar transitions from level 2. They can be easily taken into account in theory and do not affect its basic positions.

In the model we used a level scheme with two exciton states (Fig. 2). It can also be extended to a greater number of exciton states. Four maxima in the absorption band for a sample with 1.8 nm quantum dots are associated with four exciton states. The luminescence lines corresponding to the decay of the three exciton states, in our case, are suppressed by transitions to defect states. The exciton luminescence band consists of a single maximum.

Fig. 3 shows the displacement of the exciton luminescence bands in the red spectral region with temperature increasing. This displacement can be due to the manifestation of exciton-phonon interaction. In the first approximation, phonons can be described by a set of independent linear
oscillators. In this case, for high temperatures \((kT \gg h\nu)\), the width of the phonon zone located near the ground state of the crystal increases linearly with temperature, i.e.

\[
\Delta E_{ph} \propto k\Delta T.
\]  

(9)

Transitions from the exciton states 1 and 2 (Fig. 2) are carried out to the upper region of the phonon zone, which is near the Fermi level. Accordingly, the luminescence line is shifted to the red side by an amount proportional to \(\Delta E_{ph}\). The effect of the size of the sample under investigation on this shift and crystal lattice defects can be taken into account by introducing the parameter \(\alpha\), which in our approximation does not depend on the temperature \(T\).

Taking into account these remarks we obtain the following temperature dependence of the luminescence energy:

\[
E = E_0 - \alpha kT,
\]

(10)

where \(E_0\) corresponds to the energy at some fixed temperature \(T_0\) (in our case, 70 K).

\[\text{Figure 4. Experimental data [10-12] (points) and result of calculation (solid lines) for the temperature dependence of the position of the luminescence bands: a) luminescence spectrum for a sample with 1.8 nm quantum dots (}\alpha = 3.13, E_0 = 2.79\text{ eV), b) two luminescence maxima for a sample with 2.3 nm quantum dots (}\alpha = 3.84, E_0 = 2.5\text{ eV, }\alpha = 2.82, E_0 = 2.33\text{ eV).}\]

The result of calculation of the position of the luminescence bands maxima according to (10) with the corresponding parameters \(E_0\) and \(\alpha\) for samples with 1.8 nm and 2.3 nm quantum dots is shown in Fig. 4 together with the experimental data.

4. Conclusion

It is shown that the simulation of \(K_{eg}\) functions by Lorentz profiles, allows one to describe the shape of inhomogeneously broadened absorption bands and exciton luminescence bands. The introduction of two or more exciton states into the scheme of the levels of the system under study makes it possible, on the basis of the balance equations and the assumption of the Lorentz profile of the exciton band, to describe the redistribution of the radiation intensity in the exciton luminescence spectra with a change in the temperature and size of the quantum dots of the sample. These equations can be generalized to study the effects of blinking fluorescence of single semiconductor nanocrystals [19]. It is shown that the effect of phonons on the dynamics of the system under study leads to a shift of the bands of exciton luminescence to the red spectral region with increasing temperature. The numerical calculation of the temperature dependence of the luminescence spectra in the framework of the proposed model is consistent with the experimental results.
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