

# Optical properties of semiconductor clusters in a polymer matrix

A. E. Varfolomeev, A. V. Volkov, D. Yu. Godovskii,  
D. F. Zaretskii, Yu. A. Malov, and M. A. Moskvina

*Russian Science Center "Kurchatov Institute," 123182 Moscow, Russia  
M. V. Lomonosov Moscow State University, 119899 Moscow, Russia*

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The optical properties of CdS semiconductor nanocrystals (clusters) in a polymer matrix were studied. It was found that the band gap of CdS semiconductor clusters depends on their concentration in the polymer. The mechanisms giving rise to this effect were discussed. © 1995 American Institute of Physics.

Polymer compositions with  $\sim 1$ -nm ultradispersed semiconductor particles (or clusters) as a filler are promising as new conducting, photosensitive, magnetic, catalytic, and other materials which combine the properties of a polymer medium and a semiconductor filler.<sup>1,2</sup> The advantage of such media lies in the fact that it is possible to obtain both systems with low concentrations of noninteracting nanoparticles in a polymer matrix and systems with high concentrations of interacting particles. This makes it possible to study the cooperative properties of such systems as a function of the cluster concentration. In the present study we have focused principally on the analysis of the optical properties of CdS clusters in a polymer matrix as a function of the concentration of the clusters.

Water-gelling film polymer compositions (membranes) were obtained by the procedure described in Ref. 3. Polymer films based on polyamide were used as an initial matrix to obtain polymer–CdS compositions. The polymer film was treated in a CdI<sub>2</sub> solution and then in a Na<sub>2</sub>S solution. In some cases the polymer film was subjected to uniaxial stretching in ethanol or dioxane in order to change the size of the micropores. The CdS content in the films was determined by the method of thermogravimetric analysis according to the residue remaining after the samples were burned in a "Mettler TA-4000" apparatus. Examinations under a microscope showed that the experimental samples of the polymer–CdS compositions have a layered structure. A bright yellow CdS-containing layer of polymer is present near the surface of the polymer film; the center of the film is colorless and does not contain a significant amount of CdS. For a total thickness of the polymer film of about 100  $\mu\text{m}$  the typical thickness of the CdS-containing layer was about 10  $\mu\text{m}$ . Because of the layered structure of the samples, we present the data on the volume concentration of CdS for the CdS-containing layer of the polymer film. For the CdS content in the experimental samples ranging from 0.5 to 90% by weight, the volume content of CdS in the CdS-containing layer of the composite film was equal to 0.001–0.3 of the volume of the given layer.

X-Ray reflections characteristic of hexagonal crystalline CdS were recorded at 52°, 44°, 26.5°, and 24° in the diffraction patterns of the polymer–CdS compositions. In

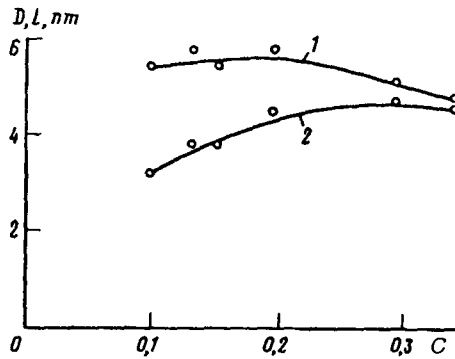


FIG. 1. Average cluster size  $D$  (1) and average intercluster distance  $L$  (2) as functions of the volume fraction of CdS.

the samples that were subjected to stretching in order to change the size of the pores in the polymer by more than an order of magnitude, the intensity of the x-ray reflection at  $24^\circ$  was higher and the position of the reflection was slightly shifted relative to the value  $24.8^\circ$ , which corresponds to the reflection from the (100) plane of hexagonal CdS. The particle sizes in this direction, which were estimated from the half-width of this reflection, are found to be 1.5–2 times greater than for the other reflections. This behavior can be explained by the appearance of texture of CdS nanocrystals, where the crystallites grow in uniaxially deformed pores of the polymer with a predominant crystallographic orientation [100] and assume the form of pores.

Estimates of the sizes of the CdS clusters from measurements of the half-width of the x-ray reflection at  $44^\circ$  (Ref. 4) and the intercluster distance computed on the basis of these estimates are shown in Fig. 1 as functions of the volume fraction of CdS in the CdS-containing layer of the polymer film. As the concentration of CdS in the composition increases, the size of the particles tends to increase. The average intercluster distance at high concentrations is found to be of the same order of magnitude as the sizes of the clusters. Large particles consisting of clusters can appear at the maximum CdS concentrations.

The methods developed for synthesizing film polymer compositions with a filler in the form of ultradispersed CdS semiconductor particles thus make it possible to obtain particle sizes  $\approx 50 \text{ \AA}$  in a wide range of concentrations.

Investigations in the UV and visible regions of the spectrum were performed on a SF-46 spectrophotometer. The absorption coefficient was determined from the measured transition spectra taking into account absorption in the polymer. For polymer–CdS compositions the absorption edge is strongly smeared and in contrast to a continuous semiconductor the absorption increases gradually over an interval of several tenths of an electron volt. The photon energies corresponding to direct allowed transitions in the case of parabolic bands satisfy the relation<sup>5</sup>

$$k(\omega)\hbar\omega = \text{const}(\hbar\omega - E_g)^{1/2}. \quad (1)$$

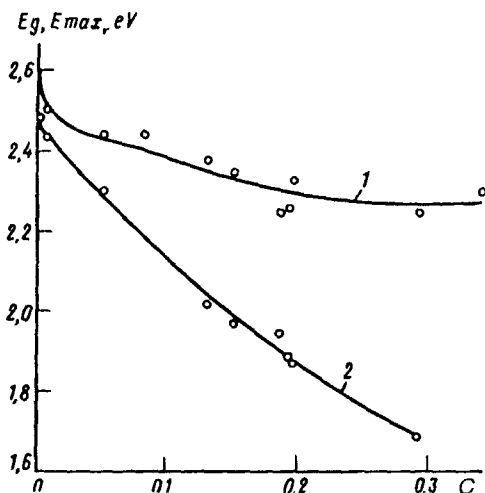


FIG. 2. Optical band gap  $E_g$  (1) and position  $E_{\max}$  (2) of the maximum of the luminescence spectrum as functions of the volume fraction of CdS.

The band gap  $E_g$  can then be determined from the function  $(k(\omega) \hbar \omega)^{1/2}$  versus  $\hbar \omega$ . This procedure for determining the optical band gap gives values which are approximately the same for the "onset" of absorption.<sup>2</sup> The band gap  $E_g$  was determined in a similar manner for all experimental samples with different CdS concentrations (Fig. 2). For low concentrations ( $<0.8\%$ ) the band gap  $E_g$  for clusters is greater than the band gap in the bulk of CdS ( $\approx 2.5$  eV). The quantum-size effect for electrons and holes, which is associated with the finite dimensions of the clusters, apparently plays a role in this phenomenon.<sup>1,2</sup> At high CdS concentrations ( $>10\%$ ) it was found that as the volume concentration increases,  $E_g$  decreases substantially compared to continuous CdS.

The maximum of the absorption coefficient for a sample with the minimum CdS concentration (0.1%) was recorded at 5 eV. This maximum could correspond to a  $E_1$  transition (in the nomenclature of Ref. 6) for hexagonal CdS, taking into account a 0.1 eV shift due to the quantum-size effect.

The luminescence spectra of CdS clusters in a polymer matrix at room and liquid-nitrogen temperatures were also investigated. The luminescence spectrum was excited by the 406 nm line of a DRSH-500 mercury lamp. The luminescence spectrum was obtained with a MDR-23 monochromator and a FÉU-79 photomultiplier. The spectrum has the form of a wide, structureless band. The position of the maximum of the luminescence band shifts in the direction of low energies as the volume concentration of CdS increases, just as for the optical band gap (Fig. 2). For the maximum volume concentrations the maximum of the luminescence spectrum corresponds to energies which are 0.7 eV smaller than the band gap in a bulk semiconductor. The maximum shift of the luminescence spectrum thus depends strongly on the concentration of CdS clusters.

The half-width of the luminescence band as a function of the volume concentration of CdS is shown in Fig. 3. The half-width is equal to about 1 eV for low concentrations

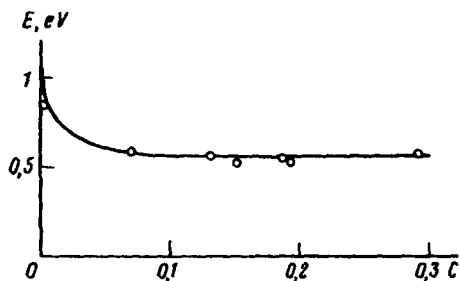


FIG. 3. Half-width  $\Delta E_{1/2}$ (eV) of the luminescence line as a function of the volume fraction of CdS.

and at high concentrations it drops to 0.5 eV, and then remains constant. At the maximum of the luminescence spectrum the intensity decreases markedly as the concentration of the CdS nanocrystals increases (Fig. 4); i.e., concentration quenching of the luminescence is observed. At the liquid-nitrogen temperature the maximum of the luminescence shifts in the direction of high energies by  $\approx 0.1$  eV. The shape of the spectrum and the intensity of the luminescence do not change substantially. This result shows that traps and impurities do not play a dominant role in the displacement of the maximum of the luminescence spectrum.

Let us now discuss the results. The decrease in the band gap with increasing CdS concentration could be attributed to the influence of the electric dipole-dipole interaction. Similarly, the concentration quenching of luminescence can be explained by transfer of the electronic excitation energy from one cluster to another as a result of the dipole-dipole interaction.

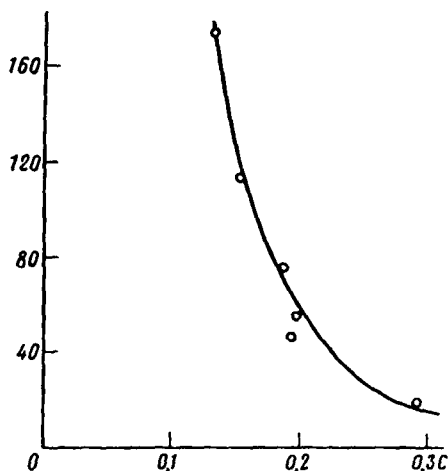


FIG. 4. Luminescence intensity  $I$  at the maximum as a function of the volume fraction of CdS.

The field produced in a dielectric medium with a dielectric constant  $\epsilon_2$  by a cluster with dipole moment  $d$  is given by the relation

$$\mathbf{E} = \frac{3(\mathbf{R} \cdot \mathbf{d})\mathbf{R} - d\mathbf{R}^2}{\epsilon_2 R^5}, \quad (2)$$

where  $\mathbf{R}$  is the distance from the center of the cluster. We assume that the clusters are insulators with a dielectric constant  $\epsilon_1$ . The dipole moment of such a cluster in a medium with  $\epsilon_2$  is then determined by the relation<sup>7</sup>

$$\mathbf{d} = \frac{3\epsilon_2}{2\epsilon_2 + \epsilon_1} e\mathbf{r}, \quad (3)$$

where  $\mathbf{r}$  is the radius vector, and  $e$  is the charge. We now estimate the field produced inside a cluster as a result of the interaction of the cluster with another cluster. The result is

$$|\mathbf{E}| \cong \frac{6\epsilon_2 ea}{(2\epsilon_2 + \epsilon_1)\epsilon_2 R^3}, \quad (4)$$

where  $a$  is the radius of the cluster. If  $\epsilon_1 \gg \epsilon_2$ , then

$$|\mathbf{E}| \cong \frac{6ea}{\epsilon_1 R^3}. \quad (5)$$

For  $\epsilon_1 \approx 9$  and  $2a \approx R \approx 10^{-7}$  cm the relation (5) gives the following estimate for the field:

$$|\mathbf{E}| \cong 0.5 \times 10^7 \text{ V/cm}. \quad (6)$$

This estimate shows that for high concentrations the electric field inside a cluster can be strong enough to decrease the band gap (Franz–Keldysh effect). If clusters have impurity centers, then as the clusters penetrate into the dielectric matrix, they can become ionized. An electric field will then arise around a charged cluster. This field can also affect the band gap of the nearest clusters.

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