

Nonlinear optical properties of semiconductor microcrystals

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The absorption edge of CdSe and CdSSe microcrystals has been observed to undergo a significant short-wavelength shift (of more than 30 meV) during excitation by light pulses at the second harmonic from a Nd:YAG laser. An optical-nonlinearity mechanism is proposed. This mechanism involves the filling of levels in the energy spectrum of a spatially bounded multiexciton system in microcrystals with a size comparable to the exciton radius.

Considerable interest has recently been shown in the search for and study of dynamic nonlinearities in semiconductor systems of reduced dimensionality.^{1,2} Some unusually strong nonlinear effects were recently observed in quasi-2D GaAs-AlGaAs structures.³ In the present letter we report the first experimental observation of a

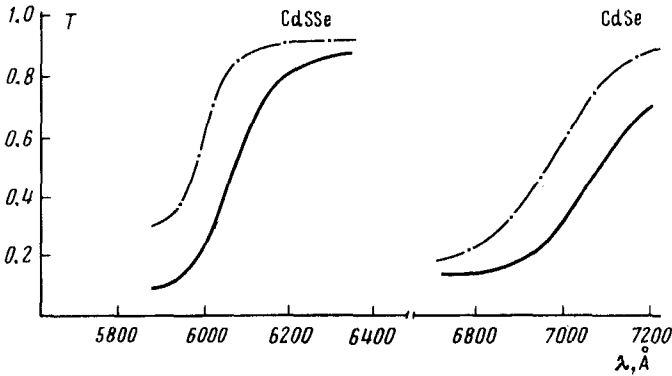


FIG. 1. Transmission spectra of CdSe ($T = 300$ K) and CdSSe ($T = 80$ K) microcrystallites. The size of the microcrystallites is $a \approx 120$ Å. Solid lines—without excitation; dot-dashed lines—excitation by light at a wavelength $\lambda = 532$ nm with a power density $P \approx 2$ MW/cm².

nonlinearity in the optical absorption of quasi-0D structures consisting of semiconductor microcrystallites dispersed in a transparent dielectric matrix.

The CdSe and CdSSe microcrystallites were grown in a matrix of an oxide glass through a diffusion-controlled phase decomposition of a supersaturated solution.⁴ The size of the microcrystallites was $a \approx 120$ Å. Samples of this glass with a thickness of 1–2 mm were excited by light pulses at the second harmonic from a quasi-cw Nd:YAG laser ($\lambda = 532$ nm; pulse length of 100 ns; repetition frequency of 1 kHz). They were synchronously probed with broad-band light from a cell holding an organic dye solution. The cell was pumped with part of the laser beam.

Figure 1 shows transmission spectra of the CdSe and CdSSe microcrystallites measured in the absence of excitation and at the time of excitation by a laser pulse. We see that the laser excitation causes the absorption edge to shift in the short-wavelength direction, both at liquid-nitrogen temperature and at room temperature. This shift could not be a consequence of the heating of the microcrystallites by the laser pulse, since the absorption edge should shift down the energy scale with a temperature rise.

To study the dynamics of the bleaching near the absorption edge, we probed samples containing CdSe with the cw beam from a krypton laser ($\lambda = 6764$ Å) and excited it with pulses at the second harmonic of the Nd:YAG laser ($\tau = 100$ ns). At the time of the application of the exciting pulses we detected an increase in the transmission at the frequency of the krypton laser. The shape of the light pulses from the krypton laser, which were transmitted through the samples, reproduced the shape of the pump pulses. The lifetime of the bleached state thus does not exceed 100 ns.

Figure 2 shows the transmission of the CdSe microcrystallites at the wavelength $\lambda = 6764$ Å as a function of the pump density according to measurements taken at $T = 80$ K. We see that a significant bleaching is achieved at a comparatively low power density of the pump beam, $P \leq 1$ MW/cm².

The nonlinearity mechanisms which have been discussed⁵ for II-VI single crystals

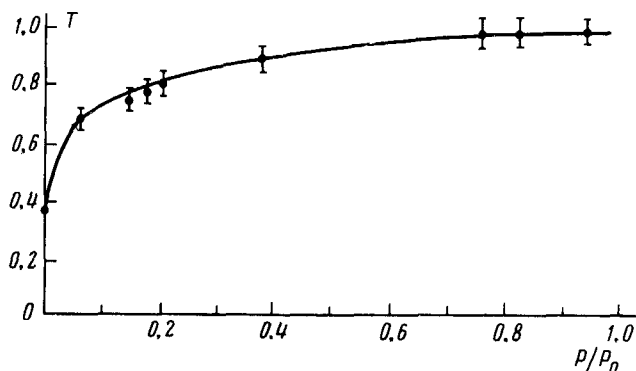


FIG. 2. Transmission of CdSe microcrystallites at the wavelength $\lambda = 6764 \text{ \AA}$ versus the power density of the exciting light ($P_0 = 5 \text{ MW/cm}^2$).

cannot explain the short-wavelength (!) shift of the absorption edge observed in these microcrystallites, which reaches 35 meV. The observed effect might be related to particular features of the energy spectrum of a multiexciton system which arises during intense excitation and which is spatially bounded by the dimensions of the microcrystallite. In microcrystallites with a radius a comparable to the exciton radius r_{exc} (for CdSe, $x_{\text{exc}} \cong 60 \text{ \AA}$) the shift of the absorption edge should occur even during excitation of the second electron-hole pair.

Let us consider the formation energy of the second electron-hole pair in a microcrystallite in the case in which the hole mass is much greater than the electron mass: $m_h \gg m_e$. As has been shown previously, the interaction with an electron results in the localization of a hole at the center of a microcrystallite over the entire size region $a \lesssim 3r_{\text{exc}}$ (Refs. 6 and 7). This effect corresponds to a minimum energy of the system. The same energetically preferred configuration of the second electron-hole pair cannot be achieved because of the Coulomb repulsion of the holes. Its excitation thus requires additional energy.

To find a quantitative estimate of this effect, it is convenient to work with microcrystallites with a size $a < r_{\text{exc}}$, since in this case the energy of the size quantization of the electrons, $\sim \hbar^2/m_e a^2$, is much greater than the energy of the Coulomb interaction of electrons with holes and with each other: $e^2/\kappa a$, where κ is the permittivity of the semiconductor. In this case, two electrons in the lower quantum-size level create, by virtue of their Coulomb field, an adiabatic potential which acts on the holes⁸:

$$V(r_h) = - \frac{e^2}{\pi \kappa a} \int \frac{d^3 r \text{Sin}^2(\pi r/a)}{r^2 |\vec{r}_h - \vec{r}|} = - \frac{2e^2}{\kappa a} \left[1 - \frac{\text{Sin} 2\pi x_h}{2\pi x_h} + \text{Cin}(2\pi) - \text{Cin}(2\pi x_h) \right], \quad (1)$$

where $x_h = r_h/a$, and $\text{Cin}(x)$ is the integral cosine. This potential has a minimum at the center of this sphere, and one of the holes may localize at it.¹⁾ In this case the binding energy of the hole is twice that of a single electron-hole pair,⁶ $E_{1h} \approx -2.4(e^2/$

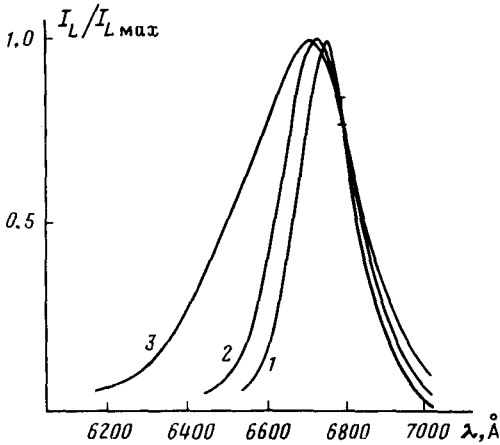


FIG. 3. Luminescence spectra of CdSe microcrystallites during excitation by light with $\lambda = 532$ nm at various power densities: 1— $P_{\text{excit}} \approx 150$ kW/cm²; 2— $P_{\text{excit}} \approx 350$ kW/cm²; 3— $P_{\text{excit}} \approx 5$ MW/cm² ($T = 300$ K).

κa). The energy of the second hole is now determined both by potential (1) and by the Coulomb potential of the first hole, localized at the center of the microcrystallite, $e^2/\kappa r_h$. This quantity reaches a minimum at $r_h = 0.5a$; this minimum value is $E_{2h} \approx -1.6e^2/\kappa a$. On the other hand, the energy of the electrostatic repulsion of two electrons in the first quantum-size level is $E_e \approx 1.8e^2/\kappa a$. As a result, we find that the minimum additional energy required for the excitation of a second electron-hole pair is $\Delta = E_{2h} + E_e \approx 0.2e^2/\kappa a$.

An even greater energy of the exciting photon is required for producing a third electron-hole pair in microcrystallites with a/r_{exc} . In this case, the Pauli principle states that a third electron cannot occupy that $1s$ lower quantum-size level, while the next level, a $1p$ level, is separated by a distance $(\hbar^2/2m_e a^2)(\phi^2 - \pi^2)$, where⁸ $\phi \approx 4.5$. This circumstance should result in an even greater shift of the absorption edge in the short-wavelength direction.

This nonlinearity mechanism, involving the filling of the levels of a spatially bounded multiexciton system, should also be manifested in the luminescence spectra of microcrystallites. Indeed, we see in Fig. 3 that an increase in the pump intensity leads to a broadening of the recombination-radiation band, because of a shift of the short-wavelength edge, while the long-wavelength edge remains essentially unchanged.

In summary, glass samples activated with semiconductor microcrystallites demonstrate a pronounced nonlinearity in optical properties and constitute a promising system for studying nonlinear effects in semiconductor systems with reduced dimensionality.

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¹) Here and below, we are ignoring the motion of the hole, assuming that its mass is infinite ($m_h \rightarrow \infty$).

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