Manifestation of dimensional quantization levels in the nonlinear transmission spectra of semiconductor microcrystals

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(Submitted 19 February 1991)
Pis'ma Zh. Eksp. Teor. Fiz. **53**, No. 6, 301–306 (25 March 1991)

Brightening peaks attributable to transitions between dimensional quantization levels are recorded in the transmission spectra of CdSe microcrystals (80 and 300 K) excited by picosecond light pulses. The dynamics of transmission restoration, which is explained on the basis of a model of discrete level filling in the conduction and valence bands, is investigated.

The dimensional quantization effect in semiconductor microcrystals may produce discrete energy levels associated with quantization of the energy of exciton translational motion (in comparatively large microcrystals) or the energy of electron and hole motion (in microcrystals of small radius).[1,2] The broadening of these levels due to the deviations in microcrystal size and shape makes it difficult to observe their associated discrete spectral structure by ordinary linear spectroscopic techniques.

In the present letter we present the results of an experimental study of the restoration dynamics of the transmission spectra of CdSe microcrystals (80 and 300 K) after excitation by a powerful ultrashort light pulse (USP). A structure determined by the dimensional quantization levels of the electrons and holes that is not found in the transmission spectra of unexcited samples is recorded.

Doped CdSe glass samples containing microcrystals up to 10 nm in radius were analyzed. The samples were excited by second harmonic USP pulses produced by a self-mode-locked neodymium laser (YAD:Nd^{3+}). The individual pump pulses ranged from 20 ps to 25 ps in duration with energy $w \leqslant 0.2$ mJ. The excitation radiation was focused onto a spot 0.5–1 mm in diameter with the central section of this spot probed by a "white" light beam obtained by irradiating a cell containing heavy water by a 1.06 μm laser USP. The delay line permitted tuning of the probe pulse delay over a range of 0–3 ns relative to the excitation pulse. The probe radiation (before and after the sample) was recorded by means of two monochannel OVA-284 spectrum analyzers with USP pump energy selection accurate to $\pm$ 10%. The differential transmission spectra $DT(\lambda) = [T(\lambda) - T_0(\lambda)]/(T_0(\lambda))$ were recorded during the experiments [$T(\lambda)$ and $T_0(\lambda)$ are the transmission spectra of an excited and unexcited sample, respectively].

The excitation pulse produced strong bleaching on the short- $\pm$ wavelength side of the absorption edge of the sample (Fig. 1a). The spectral range in which bleaching was observed narrowed with increasing delay Δt; in this case, the short-wavelength edge of the $DT(\lambda)$ spectrum shifted toward lower energies, while the long-wavelength

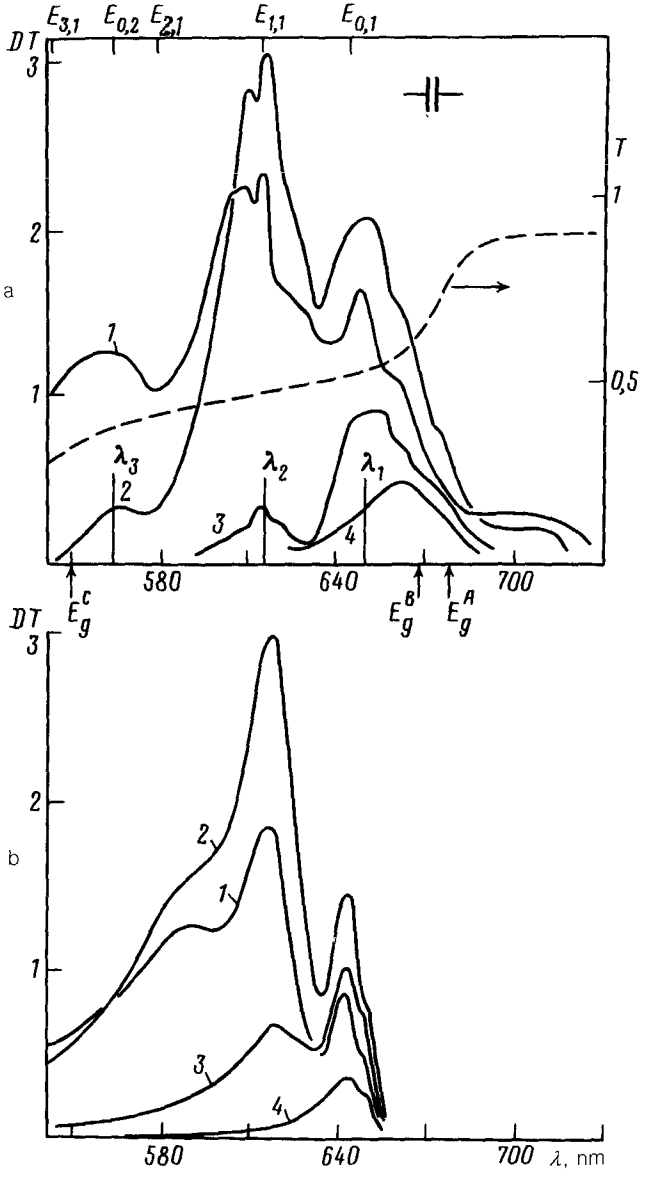

FIG. 1. Measured (a) and calculated (b) differential transmission spectra of the CdSe microcrystals (at 80 K) (the dashed line represents the transmission spectrum of an unexcited sample): a—$w = 0.12$ mJ; $\Delta t = 0$(*1*), 66 ps (*2*), 1 ns (*3*), 2 ns (*4*); b—$T_e = 500$ K (*1*), 80 K (*2, 3, 4*); N = 12 (*1,2*), 4 (*3*), 1 (*4*).

edge remained virtually fixed. Bleaching peaks with maxima at $\lambda_1 = 649$, $\lambda_2 = 616$, and $\lambda_3 = 563$ nm were easily resolved in the $DT(\lambda)$ spectra (no such peaks were observed in the transmission spectra of unexcited samples; Fig. 1a). A strong gain, approximately equal to the absorption coefficient of an unexcited sample, was record-

ed near the λ_1 and λ_2 bands. The dynamics of bleaching relaxation near the λ_1, λ_2, and λ_3 bands differed significantly. The λ_3 band vanished nearly entirely from the $DT(\lambda)$ spectra in the first 70 seconds after the USP excitation pulse, while the λ_2 band grew in amplitude during this period and only later decayed in a time of approximately 2 ns. The longest-lived peak of λ_1 persisted in the $DT(\lambda)$ spectra through maximum delays, $\Delta t = 3$ ns.

The spectral position of the λ_1, λ_2, and λ_3 peaks and the dynamics of their decay make it possible to attribute the bleaching observed in this case to filling of the dimensional quantization levels of the electrons and holes by photoexcited carriers. The position of the absorption peaks, which are attributable to the transitions between the dimensional quantization levels in the valence band and the conduction band, is given by[1] $E_{l,n} = E_g + \hbar^2 \varphi_{l,n}^2/(2m_r R^2)$, where E_g is the bandgap, $m_r = m_e m_h/(m_e + m_h)$ (m_e and m_h are the effective masses of the carriers), R is the microcrystal radius, and $\varphi_{l,n}$ is the nth root of the Bessel function $J_{l+1/2}$. For $R = 5$–6 nm the energies of the first two transitions, $E_{0,1}$ and $E_{1,1}$ are virtually identical to the position of the λ_1 and λ_2 peaks (Fig. 1a). The λ_3 peak lies in the vicinity of the transitions of energies $E_{2,1}$, $E_{0,2}$, $E_{3,1}$.

The absorption spectra of excited and unexcited microcrystals were calculated in order to analyze the results obtained here. The contributions of the ten lower dimensional quantization levels were summed, with allowance for the A, B, and C subbands of the valence band. The size distribution function of the microcrystals $P(u)$ ($u = R/\overline{R}$; $\overline{R}$ is the average radius of the microcrystals) derived by Lifshitz and Slizov[3] was employed to describe the inhomogeneous broadening of the absorption band which is attributable to an isolated transition. The final expression for the absorption coefficient is

$$K(\hbar\omega) = G \sum_i f_i \sum_l \sum_n (1 - n_{l,n}^e - n_{i,l,n}^h) \int_0^\infty P(u)\delta(\hbar\omega - E_{l,n}^i)du,$$

where $E_{l,n}^i = E_g^i + \hbar^2 \varphi_{l,n}^2/(2m_r R^2)$ (E_g^i is the bandgap associated with the ith valence subband), f_i are the polarization-averaged oscillator strengths, $n_{l,n}^e$ and $n_{i,l,n}^h$ are the level occupation numbers, G is a constant proportional to the squared matrix element modulus of the dipole moment. The occupation numbers were found by assuming a quasiequilibrium Fermi energy distribution with a certain electron temperature T_e. The total number of electron–hole (EH) pairs in the single crystal (N) was estimated on the basis of the measured transmittance at the pump wavelength and the bulk semiconductor concentration in the glass ($\sim 1\%$). It was approximately 10 for $w = 0.12$ mJ and $R = 5$–6 nm. Bleaching (amplification) peaks associated with the first two dimensional quantization levels were clearly visible in the calculated $DT(\lambda)$ spectra (Fig. 1b). The position of these peaks matched the value measured experimentally for $\overline{R} = 5$ nm, which is consistent with previous simple estimated for R.

The time evolution of the dynamics $\Delta K = K_0 - K$ near the bands λ_1, λ_2, and λ_3 was investigated in order to determine the relaxation characteristics of the ED system. Within the framework of the level filling model this quantity is proportional to the total number of carriers in the states attributable to this transition.

The fast relaxation of the λ_3 peak [characteristic time $\tau = -\Delta K(d(\Delta K)/dt)^{-1} = 60$ ps] observed in the initial stage ($\Delta t < 70$ ps) and the insignificant growth in amplitude of bands λ_2 and λ_3 (Fig. 2) can be attributed to the cooling of carriers that accompany their transition from the higher to the lower states (see spectra 1 and 2 in Figs. 1a and 1b). The subsequent behavior of the system ($\Delta t > 70$ ps) appears to be due to carrier recombination (spectra 3 and 4 in Figs. 1a and 1b) during which the λ_2 peak vanishes (the characteristic time τ for this process increased from 300 to 700 ps with increasing Δt) and partial relaxation of the longest-lived band λ_1 was observed; the value of ΔK for this band decayed nearly exponentially with a characteristic time of approximately 2 ns.

The nonexponential decrease in the number of EH pairs registered in the initial decay stage can be attributed to the Auger recombination[4] or to the effect of the induced processes. Scattering of the enhanced radiation along the edges of the crystal was visually evident at excitation levels as low as $w > 20$ μJ. A comparatively narrow enhanced luminescence peak appeared in the luminescence spectra at the top of the broad spontaneous emission band (see the inset in Fig. 2).

The USP pump pulse was also found to cause significant bleaching of the samples at 300 K (Fig. 3). The maximum value of DT in this case was slightly less than unity, while the induced bleaching relaxation time was less than 40 ps. The peaks associated

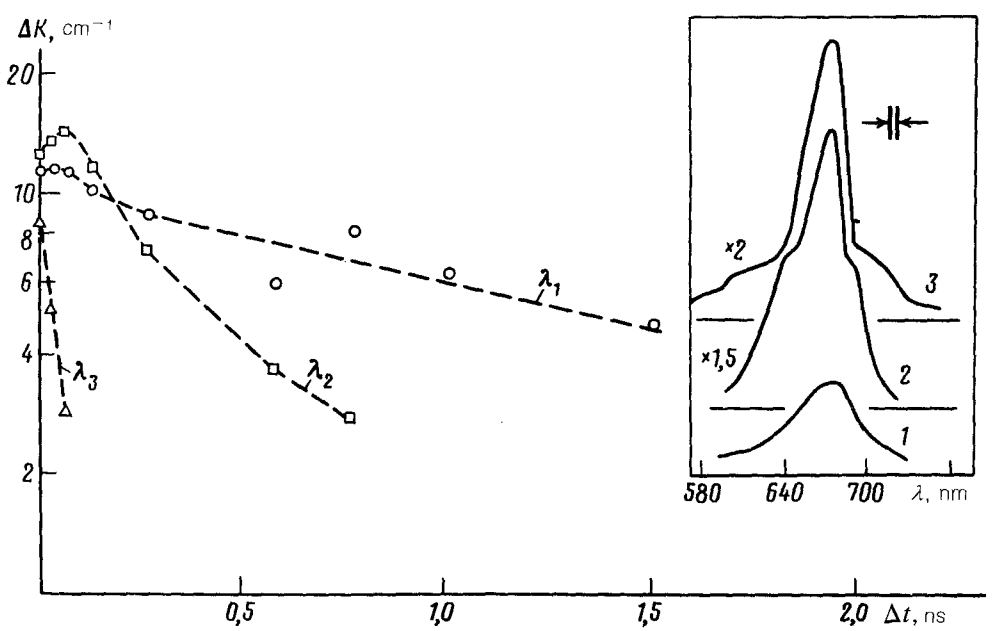

FIG. 2. Behavioral dynamics of $\Delta K(\lambda)$ in the vicinity of bands λ_1, λ_2, and λ_3 with increasing delay Δt. The inset shows the luminescence spectra of the CdSe microcrystals (80 K) for $w = 0.01$ mJ (*1*), 0.042 mJ (*2*), 0.12 mJ (*3*).

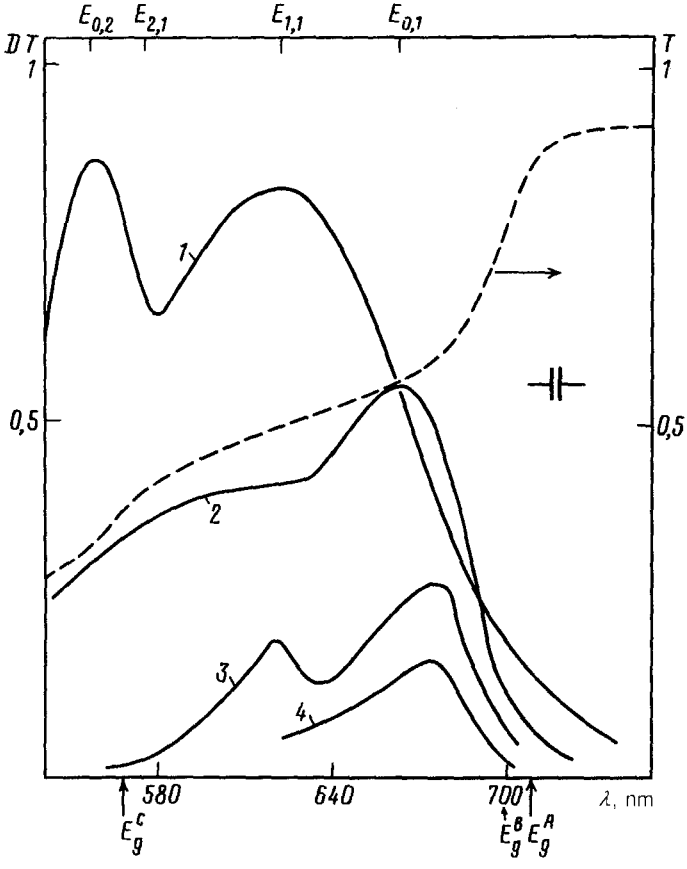

FIG. 3. Differential transmission spectra of CdSe microcrystals (at 300 K) for $w = 0.056$ mJ and $\Delta t = 0$ (*1*), 13 ps (*2*), 27 ps (*3*), 40 ps (*4*) (the dashed line represents the transmission spectrum of an unexcited sample).

with the dimensional quantization levels were clearly distinguishable in the $DT(\lambda)$ spectrum, as in the case of liquid-nitrogen temperatures.

We wish to thank A. I. Ekimov for graciously providing the samples.

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Translated by Kevin S. Hendzel