

# Kinetics of the formation of localized excitons in the solid solution $\text{CdS}_{1-x}\text{Se}_x$

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(Submitted 27 November 1986; resubmitted 11 March 1987)

*Pis'ma Zh. Eksp. Teor. Fiz.* **45**, No. 8, 391–393 (25 April 1987)

The kinetics of the luminescence of localization excitons in the solid solution  $\text{CdS}_{1-x}\text{Se}_x$  has been studied with picosecond time resolution at liquid-helium temperatures with resonant and nonresonant excitation. The frequency of the exciting light strongly influences the luminescence kinetics.

The photoluminescence spectra of  $\text{CdS}_{1-x}\text{Se}_x$  solid solutions at liquid-helium temperatures correspond to an emission by excitons which are localized at fluctuations of the potential relief.<sup>1,2</sup> Studies of the luminescence kinetics in the nanosecond and subnanosecond ranges have revealed a dispersion of the lifetime of localized excitons and have established the existence of a spectral diffusion over an inhomogeneously broadened luminescence band.<sup>3,4</sup> The energy conversions can be studied in detail by the method of picosecond spectrochronography,<sup>5</sup> which is capable of a spectral-temporal analysis of the secondary emission with a Fourier-limit resolution.<sup>6</sup>

In this letter we report a study with a picosecond time resolution of the kinetics of various parts of the photoluminescence band of  $\text{CdS}_{1-x}\text{Se}_x$  samples with  $x = 5\%$ ,  $14\%$ , and  $60\%$  and of the dependence of the kinetics on the frequency of the exciting light. The single-crystal wafers are immersed in liquid helium and excited in the  $E_{\perp c}$  polarization by a train of pulses from a synchronously pumped dye (coumarin-102) laser. The length of the pulses is 3 ps; the repetition frequency is about 80 MHz; and the energy in the pulse does not exceed 0.1 nJ. To study the kinetics of the luminescence, we use either a double monochromator with subtraction of dispersion (resolution of 0.15 nm) by means of a streak camera, which is swept at the pulse repetition frequency (the dynamic range is at least two orders of magnitude; the instrumental response time is 10 ps), or the method of time-correlated photon counting (resolution of 300 ps). The free sweep interval ( $\cong 12$  ns) makes it possible to reliably analyze the shape of the photoluminescence pulse with a time scale  $\tau \leq 2$  ns through the use of the streak camera or  $\tau \leq 4$  ns in the photon-counting method.

The primary result of this study is that the photoluminescence kinetics is governed by the frequency of the exciting light. Let us examine the most important features of this dependence.

1. Figure 1 shows the photoluminescence spectrum of a sample of the solid solutions  $\text{CdS}_{1-x}\text{Se}_x$  with  $x = 0.14$  at  $T = 4.2$  K with cw excitation in the region of delocalized states ( $\hbar\omega_{exc} = 2.602$ ). The logarithmic scale clearly reveals the existence of a hot tail on the photoluminescence band and also some faint lines of resonant

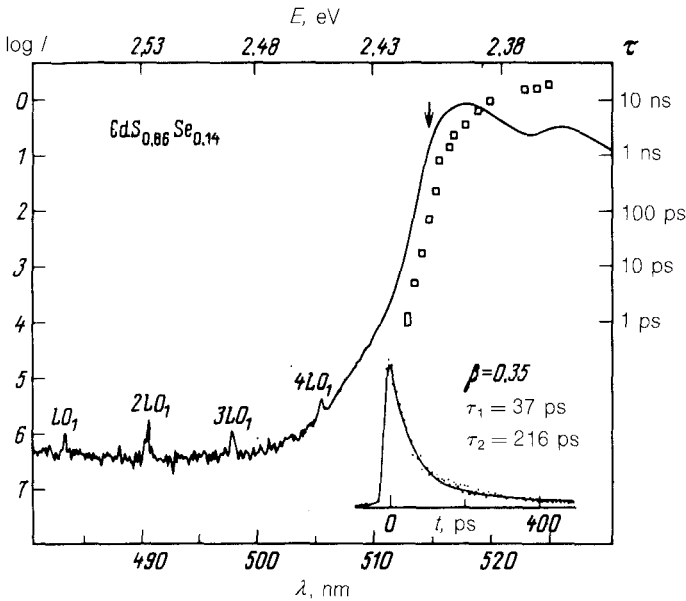


FIG. 1. Photoluminescence spectrum of a  $\text{CdS}_{0.86}\text{Se}_{0.14}$  sample in logarithmic scale (solid line; scale at the left). The small rectangles show the effective luminescence decay time (scale at the right). The inset shows the photoluminescence kinetics of the state marked by the arrow, with excitation at 2.460 eV. Points—experimental; line—description by a two-exponential law with the specified parameter values.

Raman scattering. The effective decay times of the emission  $\tau_{\text{eff}}$ , determined at the  $1/e$  level, are shown in this figure.

The decrease in the intensity of the steady-state photoluminescence and the decrease in the effective decay time in the hot tail occur essentially in parallel. The observation of times in the range 1–100 ns indicates that the decay of the emission in the short-wave part of the band is determined by fast processes of a relaxation of excitation energy near the bottom of the free-exciton band and a tunneling migration away from shallow localized states.

The kinetics of the emission in various parts of the photoluminescence band in the case of nonresonant excitation is clearly nonexponential, in agreement with the results of Ref. 4. The decay curves of the photoluminescence of sufficiently shallow localized states can be approximated well by the sum of the two exponential functions:  $I = I_0[\exp(-t/\tau_1) + \beta \exp(-t/\tau_2)]$  (see the example in the inset in Fig. 1). It turns out that the parameters  $\tau_1$ ,  $\tau_2$ , and  $\beta$  are not characteristics of exclusively the state under study; they increase with increasing frequency of the exciting light.

2. The photoluminescence decay curves take their simplest shape in the case of resonant excitation. The shape of the photoluminescence pulse at a minimal frequency deviation between the excitation and the measurement (2 meV under our conditions) can be described in practice by a single exponential function over two orders of magnitude of the intensity. The characteristic decay times measured with nearly resonant

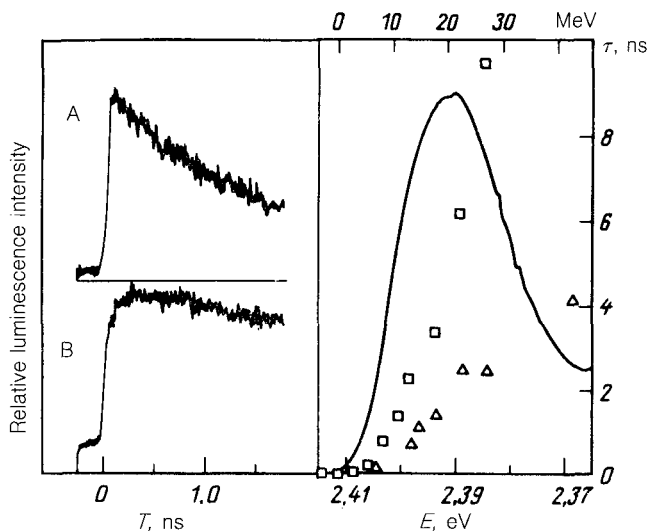


FIG. 2. Lifetime of excitons with various localization energies in a  $\text{CdS}_{0.14}\text{Se}_{0.86}$  samples for the cases of nearly resonant excitation (triangle) and effective photoluminescence decay times in the case of nonresonant excitation (2.460 eV; squares). Solid line—steady-state photoluminescence spectrum; upper scale—exciton localization energy. Shown at the left is the photoluminescence kinetics of the state with an energy of 2.396 eV during excitation by photons with (A) 2.398 eV and (B) 2.460 eV.

excitation increase monotonically with increasing exciton localization energy (as shown by the triangles in Fig. 2). Shown for comparison in Fig. 2 are the effective decay times  $\tau_{\text{eff}}$  of the photoluminescence pulse during interband excitation at 2.460 eV. These times also increase with increasing localization energy, reaching values on the order of 10 ns, i.e., values two or three times the decay times in the case of resonant excitation. Furthermore, in the case of nonresonant excitation we can clearly see in the luminescence pulse regions of an increase, with time scales ranging to 1–2 ns. Figure 2 compares the kinetics of the photoluminescence decay at the frequency 2.396 eV for the cases of essentially resonant and nonresonant excitation (curves A and B, respectively). These changes in the decay curves with increasing frequency of the exciting light occur gradually; i.e., no threshold in the exciton mobility or in the interband transitions can be seen directly in the kinetics.

3. The presence of regions of growth which are substantially broader than the length of the exciting pulse, reflects the filling of deep states by a tunneling migration from shallower localized states. The slowing of the decay kinetics with increasing frequency of the exciting light apparently reflects the complex kinetics of the formation of localized excitons from free electrons and holes. Another possibility is that recombination processes which are not excited resonantly are manifested in the emission in the case of interband excitation. One such process is the tunneling radiative recombination of holes localized by potential fluctuations of the solid solution with impurity (donor) states of electrons.

In samples of other compositions which we studied in these experiments we observed a similar dependence of the photoluminescence kinetics on the frequency of the exciting light. The behavior which we have observed may evidently be common to a longer list of disordered materials.

We wish to thank P. M. Saari for support and interest.

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Translated by Dave Parsons