

# Localized excitons and migration of their energy in semiconducting solid solutions

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The first experimental proof of a tail of localized exciton states in the band gap of solid solutions is reported. Evidence of a migration of the energy of these states has been obtained.

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In substitutional semiconducting solutions, concentration fluctuations give the lattice a random charge image, with wells capable of localizing free carriers and excitons. The localized exciton states are distributed continuously on the long-wave side of the bottom of the  $k=0$  band and form a tail on the state-density function.<sup>1,2</sup> The broadening of exciton states, which results from this mechanism in  $A^{II}B^{VI}$  solid solutions, can be seen in their exciton reflection (or absorption) spectra.<sup>3</sup>

In the present experiments we have obtained, by a direct method, experimental confirmation that localized exciton states exist in semiconducting solid solutions, and we have also obtained spectroscopic evidence of a migration of their energy. These results were obtained by analyzing the luminescence spectra of  $Zn_xCd_{1-x}S$  crystals and their dependence on the temperature and concentration of the solid solution.

The luminescence spectra of the solid solutions were studied with a He-Cd laser with  $\lambda = 441.6$  nm over the concentration interval  $0 < x < 0.12$ . At low temperatures ( $T < 30$  K) the predominant features in the  $Zn_xCd_{1-x}S$  emission spectra are luminescence lines of bound excitons,  $I_1$  (a complex consisting of a neutral acceptor and an exciton) and  $I_2$  (a neutral donor and an exciton), and a phonon repetition of  $I_1$  (Ref. 4).

A detailed study of these spectra revealed a new luminescence line ( $I_L$ ), at the shortest wavelength, with several characteristic features. 1) Its spectral position at  $T = 2$  K is between the line  $I_2$  (corresponding to an exciton complex) and the exciton resonant frequency  $A$  (the line  $A$  is not found in the luminescence spectra of these samples<sup>4</sup>; the position of this resonance was determined from the exciton reflection spectra<sup>3</sup>). The distance from this new line to  $I_2$  depends on the concentration of the solid solution.<sup>1</sup> For samples with  $x = 0.11$ , for example, this distance is 4 meV, while for samples with low concentrations ( $x = 0.03$ ) it is 6 meV, and  $I_L$  essentially coincides with line  $A$  (Fig. 1). 2) The line  $I_L$  is very asymmetric, with a steep slope on the short-wave side and a gentler slope on the long-wave side. The width of this line increases with increasing  $x$  (Fig. 1). 3) The shape, half-width, and peak position of the line  $I_L$  all change substantially as the temperature of the crystal is changed. As the temperature is raised, the  $I_L$  peak begins at  $T = 2$  K to shift gradually in the short-wave direction; this shift continues until the peak coincides with line  $A$ , the resonant frequency of the exciton. At the



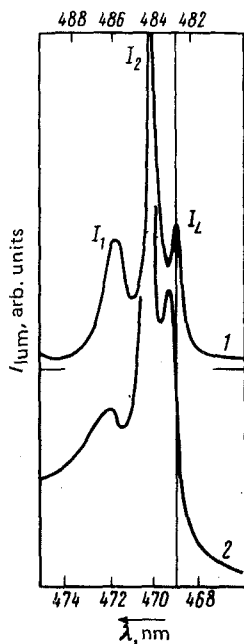


FIG. 1. Dependence of the relative position of the emission line  $I_L$ , which corresponds to localized excitons, on the concentration of the  $\text{Zn}_x\text{Cd}_{1-x}\text{S}$  solid solution. 1— $x=0.03$ , upper  $\lambda$  scale; 2— $x=0.11$ , lower  $\lambda$  scale.  $T=2$  K.

same time, the line broadens and changes in shape, becoming more symmetric (Fig. 2). Over the temperature interval  $45 < T < 77$  K the lines corresponding to the exciton complexes disappear from the spectrum of the solution  $\text{Zn}_{0.11}\text{Cd}_{0.89}\text{S}$ , and these spectra are dominated by the "free"-exciton luminescence line  $A$  and its phonon repetitions,  $A = 1$  LO and  $A = 2$  LO (Ref. 7).

Analysis of characteristics 1)–3) of the  $I_L$  emission line in the spectra of the  $\text{Zn}_x\text{Cd}_{1-x}\text{S}$  solid solutions leads to the conclusion that this line results from localized electron states.<sup>2)</sup> We also conclude that the energy of these states migrates along a non-uniform contour which is formed by an ensemble of states with different exciton-localization energies in the disordered crystal lattice. In accordance with the theoretical predictions of Baranovskii and Ėfros,<sup>2</sup> the tail of the localized exciton state density lies on the long-wave side of the bottom of the exciton band. We evaluated the decay of this tail from the characteristic localization energy  $E_0$ ; it depends on the concentration of the solid solution. From the position of the line  $I_L$ , on the long-wave side of the exciton resonance  $A$ , we can determine  $E_0$  and its  $x$  dependence (at  $x=0.11$ , we have  $E_0=2$  meV, and at  $x=0.03$  we have  $E_0 < 0.5$  meV; Fig. 1). These results on  $E_0$  correspond well to estimates of  $E_0$  obtained from data on the concentration broadening of the exciton-reflection lines of these crystals (2.6 meV and 0.05 meV, respectively).<sup>3</sup>

The substantial length of the localized exciton state tail allows us to take up the energy migration mechanism. This process, which operates in the direction which would establish a thermodynamic-equilibrium energy distribution of the excitations, leads to a lowering of the energy at low temperatures, which leads in turn to a Stokes shift of the luminescence spectrum with respect to the absorption (or reflection) spectrum of these crystals. Evidence for this mechanism comes from characteristics 1)–3) of the emission



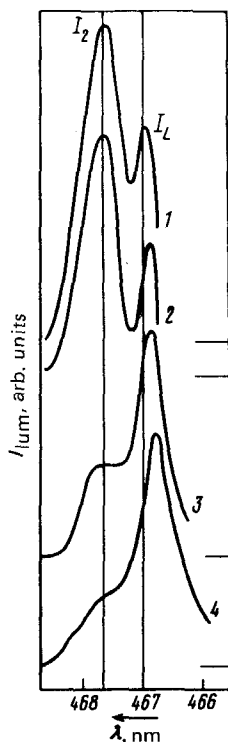


FIG. 2. Temperature dependence of the relative position of the localized-exciton luminescence peak  $I_L$  of  $\text{Zn}_{0.11}\text{Cd}_{0.89}\text{S}$  crystals. 1, 2, 3, 4— $T = 6, 20, 30$ , and  $45$  K, respectively. The scale (in nanometers) corresponds to the lower spectrum.

spectra of the solid solutions. For example, the elongated long-wave wing of the  $I_L$  line at low temperatures reflects the behavior of the localized exciton state density; all the states on the long-wave side of the peak are filled ( $T = 2$  K). As the crystal temperature is raised, the energy migration along the nonuniform contour of localized exciton states draws states of progressively higher energy into the luminescence process because of the interaction among these states; the result is a short-wave shift of the peak (Fig. 2), which continues until states at the bottom of the exciton band have come into play (at  $T > 30$  K).

This study has yielded the first experimental demonstration of a tail on the localized exciton state density in the band gap of semiconducting solid solutions. These experimental results show that the length of this tail depends on the concentration of the solid solution, and they show that the energy distribution is continuous with a transition to the bottom of the exciton band, in agreement with the theory of Ref. 2. The interaction between localized electron states is accompanied by a migration of their excitations.

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<sup>1)</sup>The line  $I_2$  can be used as a reference point for determining the relative position of the new line  $I_L$  (and also the position of the exciton resonance) in the spectra of different samples. The reason is that the binding energies ( $E_i$ ) of the exciton complexes  $I_2$  are approximately equal in the original CdS and ZnS crystals (6 and 8–9 meV, respectively<sup>5,6</sup>), and for samples with  $0 < x < 0.12$  the binding energies  $E_i$  should not be greatly different from  $E_i$  for CdS (6–6.3 meV).



<sup>2)</sup>We should point out that there is an analogy between localized and bound excitons in semiconducting crystals. For all these states, according to the Rashba model,<sup>8</sup> the oscillator strengths are typically huge, so that the localized exciton states may effectively appear in the luminescence spectra of solid solutions.

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