Exciton luminescence of ideal solid solutions (the $Zn_xCd_{1-x}Se$ system with $0<x<1$)

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The concentration dependence and temperature dependence of the exciton emission spectra of $Zn_xCd_{1-x}Se$ have been studied. The results indicate that processes which occur through excitons trapped by large-scale composition fluctuations are very effective. The results also indicate that the state density of the bottom of the band is continuous. These results are of general interest for ideal solid solutions.

The semiconductor solid solutions $Zn_xCd_{1-x}Se$ form at arbitrary compositions, and their electronic characteristics (the width of the band gap, and the energy of the valence-band splitting) vary smoothly with the composition. Such solid solutions fall in the category of disordered systems, in which the disorder is related to composition fluctuations because of the statistical distribution of substituent atoms among sites in the corresponding sublattice (ideal solid solutions). For II-VI solid solutions of semiconductors the large radius of the exciton makes an interaction with large-scale composition fluctuations the most likely interaction, with the result that excitons are trapped. This trapping leads to the formation of a tail on the density of trapped exciton states and also a scattering of untrapped exciton states.[1,2] In these solid solutions, the fluctuational disorder causes a concentration-dependent broadening of the exciton reflection spectra[3] and of the emission lines of exciton complexes.[4] It also gives rise to a new mechanism for the emission of trapped excition states at low temperatures.[5]

In the present study we have established some general features of the radiative recombination involving excitons in ideal solid solutions by working from measurements of the optical spectra of $Zn_xCd_{1-x}Se$ $(0<x<1)$ crystals. The results are important in connection with the use of $Zn_xCd_{1-x}Se$ solutions as laser active media which emit over the entire visible range.[6]

The $Zn_xCd_{1-x}Se$ crystals were grown by a free-growth method[6] and exhibited one of several structures: a cubic structure $(0.7<x<1.0)$, a hexagonal structure $(0<x<0.5)$, or an intermediate structure $(0.5<x<0.7)$.[7] The reflection and emission spectra were studied by a photoelectric method. The luminescence spectra were excited by the line at $\lambda = 441.6$ nm of a He–Cd laser and the line at $\lambda = 514.5$ nm of an Ar laser.

The emission spectra of the ZnSe crystal $(x = 1)$ and the CdSe crystal $(x = 0)$ are dominated at $T = 2$ K by the lines I_2 and I_1 of exciton complexes of excitons which

are bound to neutral donors and acceptors. The intrinsic exciton luminescence of these crystals is very weak, and the corresponding narrow line is in the region of the dispersive reflection curve (Fig. 1). Emission lines of the exciton complexes are also found in the spectra of $Zn_xCd_{1-x}Se$ crystals.[6,8] As x increases, these lines become noticeably broader and come to form a single broad band $I_{1,2}$, which (because of the different ratios of the intensities of lines I_2 and I_1 in different crystals) may vary substantially in shape and position (Fig. 1). The rapid broadening of the emission lines of exciton complexes with the concentration x is seen in the spectra of these solid solutions of semiconductors in the fluctuational nature of the inhomogeneous blurring of these states.[4]

The most important changes in the emission spectrum of the $Zn_xCd_{1-x}Se$ crystals occur in the exciton part of the spectrum. The longest-wavelength corresponding emission line I_L, exhibits the following behavior. First, it flares up markedly with increasing degree of disorder (as x is varied). While at small values of x (or of $1-x$ it is less intense than the emission lines of exciton complexes, at intermediate compositions x the line I_L dominates the luminescence spectrum at 2 K (Fig. 1). Second, the position of this line is in the region of the dispersive structure of a reflection line (nea

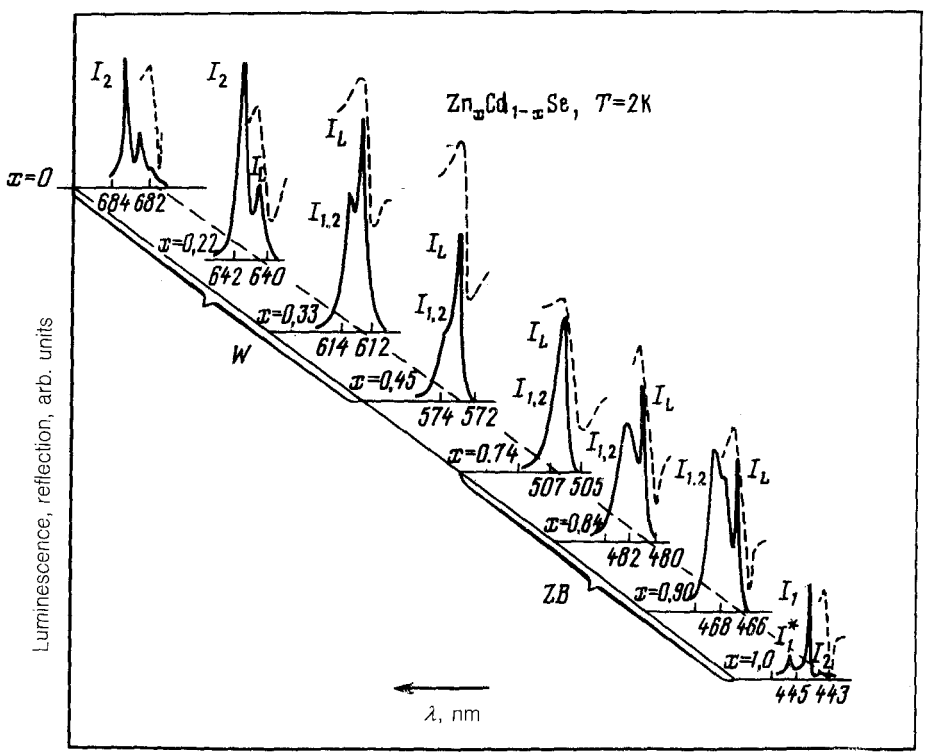

FIG. 1. Luminescence spectra (solid lines) and reflection spectra (dashed line) of $Zn_xCd_{1-x}Se$ solid solutions ($0<x<1$) at $T=2$ K. I_L—Emission line of excitons trapped by large-scale composition fluctuations; $I_{1,2}$—lines of exciton complexes.

the maximum of this structure in Fig. 1), with the implication that it is of an exciton nature. Third, it is fairly narrow, with a half-width of 2–4 meV, which is smaller than the width of the reflection line (smaller than the distance between the maximum and minimum in the reflection structure), which is 5–7 meV for intermediate compositions (Fig. 1). Fourth, the line I_L acquires a smooth broadening as the crystal temperature is raised. In the interval 2–40 K, for example, it broadens by a factor of about two, and its half-width becomes similar to that of the reflection line (Fig. 2). We might note in this connection that for high-quality binary II-VI crystals (e.g., CdS, CdSe, and ZnSe) the exciton luminescence line exhibits a totally different behavior: It fades as the quality of the crystal is degraded, and it exhibits no significant broadening in the temperature interval 2–40 K.

These aspects of the exciton luminescence in the solid solution $Zn_xCd_{1-x}Se$ reflect the particular features of these solutions as disordered systems, and they are evidence of the appearance of a new and effective mechanism for the emission of trapped exciton states at low temperatures and of excitation migration processes. 1. The pronounced intensification of the line I_L with increasing degree of disorder, on the one hand, and the small half-width of this line, on the other, can be explained in a reasonable way by assuming that at low temperatures not all of the states of the band bottom are emptied—only those in the low-energy tail of the density of trapped exciton states, for which the oscillator strength is huge[9] and the density increases exponentially with x (Refs. 1 and 2). 2. The observed temperature-induced broadening of the emission line I_L due to a short-wavelength admixture should be associated with pro-

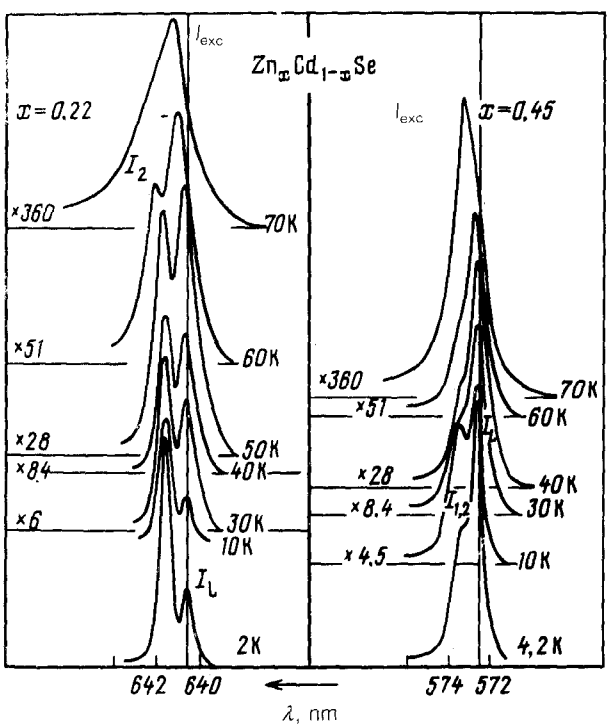

FIG. 2. Emission spectra of $Zn_{0.22}Cd_{0.78}Se$ and $Zn_{0.45}Cd_{0.55}Se$ crystals at various temperatures.

cesses involving a migration of excitations of trapped exciton states (a tunneling of electronic excitations from certain isolated fluctuational wells into deeper neighboring wells, in a process accompanied by the absorption of acoustic lattice phonons[5,10]). The spatial migration is accompanied in this case by a spectral migration. At higher temperatures, at which kT becomes greater than the half-width of the inhomogeneous line of trapped exciton states, emission processes involve untrapped exciton states. At temperatures above 40 K (in the interval 40–70 K), for example, after the dissociation of exciton complexes has been completed, the emission line I_{exc}, which is formed by all states at the bottom of the exciton band, completely dominates the spectrum (Fig. 2). Its intensity is some two orders of magnitude lower than at $T = 2$ K. The reason for the latter circumstance is that the emission is caused primarily by untrapped exciton states, for which radiationless processes become important and for which the oscillator strength is three orders of magnitude lower than for the trapped exciton states.[9] The temperature is accordingly the factor which makes possible a selection of various exciton states in the emission process: At low temperatures, these are trapped exciton states, while at higher temperatures they are primarily untrapped exciton states of the band bottom.

These studies of the concentration dependence and temperature dependence of the emission spectrum of this system of semiconductor solid solutions provide evidence that the emission mechanism involving trapped exciton states is very effective and that there is no energy gap between trapped exciton states and the bottom of the exciton band—i.e., that the distribution of states is continuous. The behavior which has been found here for the exciton luminescence spectrum in $Zn_xCd_{1-x}Se$ crystals ($0 < x < 1$) is very similar to that which has been observed for another system of solid solutions of semiconductors with a cationic substitution ($Zn_xCd_{1-x}S$ with $0 < x < 0.15$; Ref. 5). The indication is that these features of the spectrum are of a general nature. The behavior of the spectrum is direct proof of a fluctuation blurring of the bottom of the exciton band, which is characteristic of ideal solid solutions, according to the theory of Refs. 1 and 2.

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