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EXCITON MOBILITY EDGE IN $CdS_{1-x}Se_x$ SOLID SOLUTIONS

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Low temperature emission spectra of localized excitons in $CdS_{1-x}Se_x$ solid solutions under the monochromatic excitation with tunable laser have been studied. It has been found that the luminescence of localized excitons has a high degree of linear polarization with respect to the polarization direction of exciting light. This polarization reflects the "hidden" anisotropy of macroscopically isotropic localized exciton system and strongly depends on the frequency of exciting light. Study of this dependence has permitted for the first time a determination of position of the "mobility edge" for exciton migration in disordered semiconductor solid solution.

Semiconductor solid solutions represent a new type of crystals with variable band-gap controlled by composition. A characteristic feature of such systems is the possibility of exciton localization in the random potential wells formed by composition fluctuations. Such localization has been theoretically predicted by Baranovski and Efros[1] and observed experimentally by Lai and Klein[2] for indirect excitons in $GaAs_{1-x}P_x$. Localized states form the exponential tail of the exciton band spreading into the forbidden gap.

It has been shown recently[3,4] that the radiative recombination in direct-gap solid solutions $CdS_{1-x}Se_x$ at liquid helium temperatures is dominated by the luminescence of localized excitons over the entire range of composition. The corresponding emission band has very high intensity. High probability of localized exciton emission has two easily understandable reasons. First of all, fast localization of photo-excited electron-hole pairs or excitons hinders the energy migration in mixed crystals and thus prevents nonradiative recombination through the deep centers. As a result, no impurity emission can be detected in $CdS_{1-x}Se_x$ at helium temperatures[5]. Secondly, the additional increase of radiative probability is connected with the absence of nonradiative Auger recombination for the two-particle localized excitons.

The problem of energy migration in semiconductor solid solutions is of special interest. In the gross features the energy spectra of mixed crystals strongly resemble those of the parent compounds and are only slightly modified by the presence of localized states. Fig. 1 sketches the distribution of exciton potential energy along the spatial coordinate and the energy dependence of exciton density of states in a semiconductor solid solution. At high energies, exceeding by far the amplitude of potential fluctuations, the excitons in mixed crystals propagate almost freely. The random fluctuating potential causes only additional exciton scattering. At lower energies

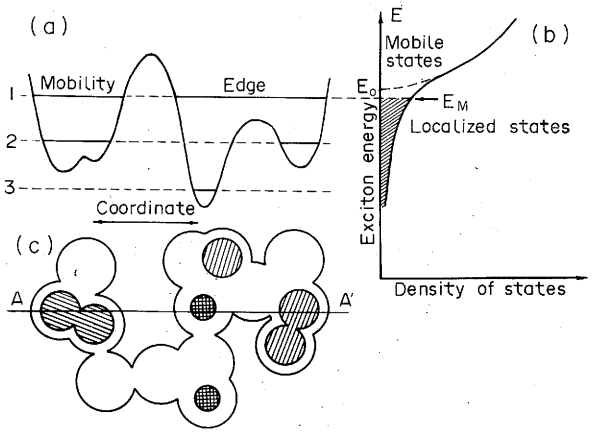

Fig. 1.
a - schematic representation of exciton potential energy dependence on coordinate in semiconductor solid solution.
b - energy dependence of exciton density of states. Arrow E_M indicates the effective mobility edge separating localized and mobile exciton states.
c - equipotential cross-section of the random potential of curve "a" which is in fact a potential relief along AA' line. Open, shaded and cross-hatched areas correspond to the energy levels 1, 2 and 3. Exciton states are delocalized at level 1, partly overlapped at level 2 and completely separated at level 3 (see text).

the excitons are localized and completely immobile. Such coexistence of localized and delocalized excitations in the same spectrum is closely related to the problem of Anderson localization in nonuniformly broadened spectra[6]. However, the large spatial extent of exciton states in semiconductors and the fast energy relaxation for the band-like exciton states bring forth some essential differences between the real system of excitons and idealized Anderson model. Nevertheless, a characteristic energy, separating the localized and delocalized states, can be expected for the excitons in mixed crystals. This energy can be identified with the "mobility edge" in the Mott - Anderson localization model.

The aim of the present paper was to find the spectroscopic manifestation of the exciton mobility edge in the $CdS_{1-x}Se_x$ semiconductor solid solutions. We have shown that this characteristic energy can be determined by the study of dependence of the degree of polarization of localized exciton luminescence on the frequency of exciting light.

We have studied the luminescence of wurtzite $CdS_{1-x}Se_x$ single crystals (symmetry C_{6V}^4) with chemically polished or natural faces normal to the optical axis c . The samples were directly immersed into the pumped liquid helium (T = 2 K) and were excited with polarized light from either low power pulsed Coumarin 152 or cw Rhodamin 6G dye lasers. Both excitation and observation were performed along c-axis in backscattering orientation. Polarization degree (PD) of emitted light was calculated as

$$\rho = (I_{\parallel} - I_{\perp})/(I_{\parallel} + I_{\perp})$$

Here $I_{\parallel}$ and $I_{\perp}$ are the luminescence intensities with polarization, respectively, parallel or perpendicular to that of exciting light. Two methods were used for the measurement of PD . In the first method $I_{\parallel}$ and $I_{\perp}$ were recorded successively with the aid of optical multichannel analyser OMA-2 and then processed digitally with built-in microprocessors. In the other method a two-channel photon counting registration was used. The digital data were also processed with a mini-computer.

The luminescence spectra of $CdS_{1-x}Se_x$ with x = 0.1 are shown on Fig. 2 . Curve 1 shows the luminescence at band-gap excitation. The most intense high energy band in this spectrum corresponds to the resonant luminescence of localized excitons, all other bands being its phonon repetitions[3] . At these excitation conditions the luminescence is nonpolarized which indicates a complete loss of polarization memory during the process of exciton localization. Curves 2 and 3 represent the exciton reflection spectra of the same sample taken in polarizations E c and E c , respectively.

At resonant monochromatic excitation the emission spectrum exhibits a characteristic narrowing (curve 4) due to the selective excitation of localized excitons with certain energies[3,4].

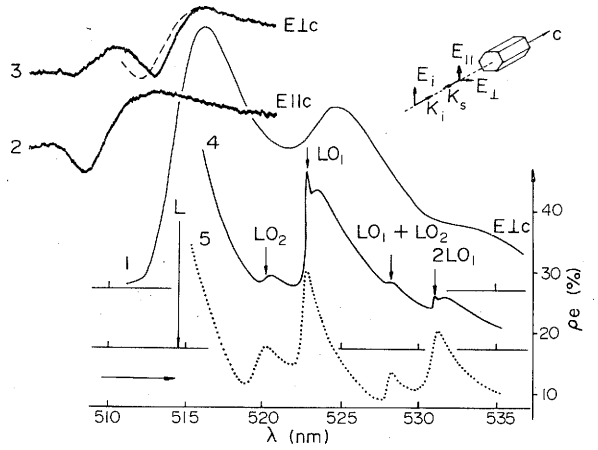

Fig. 2.
Experimental results for $CdS_{0.9}Se_{0.1}$ sample at T = 2 K. 1 - luminescence spectrum at band-gap excitation, 2 and 3 - reflection spectra in E c and E c polarizations, respectively. Dashed curve shows corrected n = 1A (E ⊥ c) relfection line, assuming equal line-widths for n = 1A and n = 1B excitons. 4 - emission spectrum at monochromatic excitation with 514.5 nm Ar^+ laser line (shows by arrow L). 5 - polarization degree ρ_l of emission spectrum 4, as measured in configuration shown by the insert.

Pronounced phonon structure of this spectrum reflects a two-mode behaviour of LO phonons in $CdS_{1-x}Se_x$. At resonant excitation with linearly polarized light the luminescence of localized excitons has rather high positive PD in respect to polarization direction of exciting light (curve 5). PD is maximum near the exciting laser line and smoothly decreases along the band contour. Similar spectral dependence of PD is also observed for all phonon repetitions.

Localized excitons in $CdS_{1-x}Se_x$ are derived from the lowest n = 1A (Γ_5) exciton state which can be represented by two degenerate dipoles in E c plane[7]. In principle, under the resonant excitation with polarized light the optical orientation or optical alignment can be acheived for this state[8] showing up, respectively, in circular or linear polarization of luminescence. Both orientation and alignment are observable at the same condition $\tau_s \gg \tau_e$, where τ_s is the spin relaxation time and τ_e is the total life-time of exciton. If the linear

polarization of luminescence were due to the optical alignment, the circular polarization should be also observed. However, at circularly polarized resonant excitation the luminescence of localized excitons does not show any polarization. The linear polarization of luminescence is also not affected by the longitudinal magnetic field $H \parallel c$, which should be the case for the optical alignment [9]. So we have concluded that the linear polarization of luminescence observed in our experiments is not connected with the dynamical effect of optical alignment but is a result of "hidden" anisotropy in the macroscopically isotropic system of localized excitons.

Quite natural supposition is that the potential wells localizing the excitons do not posess the spherical symmetry. A doubly degenerate exciton state in the anisotropic well will split into two dipole states Γ_X and Γ_Y with orientations determined by the anisotropy axes of the well under consideration. Though the orientation of X and Y axes in different wells is random, under the resonant excitation with linearly polarized light, the luminescence of such a system, as it can be easily shown [10,11], will have PD of 50 % provided three conditions are fulfilled:

1) linear dipole oscillators Γ_X and Γ_Y are independent, i.e. the magnitude of the level splitting is greater than the uniform (natural) width of Γ_X and Γ_Y levels.
2) there is no exciton transfer from the well where it was originally excited to other wells with different anisotropy orientations.
3) there is no energy transfer between X and Y levels within the same well.

No circular polarization of emission can be expected for the system of randomly oriented linear dipoles.

Our experimental results are in good qualitative agreement with the predictions of this phenomenological model. The observed maximum value of PD ($\simeq 35$ %) is also rather close to the theoretical limit.

We have found that the value of PD of localized exciton luminescence strongly depends on the frequency of exciting light. Fig. 3 shows such dependence for the samples with $x = 0.10$ and $x = 0.49$. Experimental points (black circles) represent the maximum values of PD in the region of LO_1 phonon replica at given excitation frequency. Below we shall refer to such dependence as the excitation spectrum of PD. The dashed line through the points is drawn as a guide to the eye. Solid line shows the luminescence spectrum at band-gap excitation. Exciton reflection for the sample with $x = 0.10$ is also presented.

As can be seen from Fig. 3, the emission of localized excitons is polarized only at resonant excitation. Polarization of emission appears when the frequency of exciting light enters the luminescence band. At the same time starts the characteristic narrowing of the emission spectrum shown by curve 4 on Fig. 2. At further lowering of the excitation energy PD of emission first reaches the maximum and then smoothly decreases. At low enough excitation energies the polarization of emission vanishes. However, the emission spectrum in this excitation region retains the characteristic narrowed shape [5]

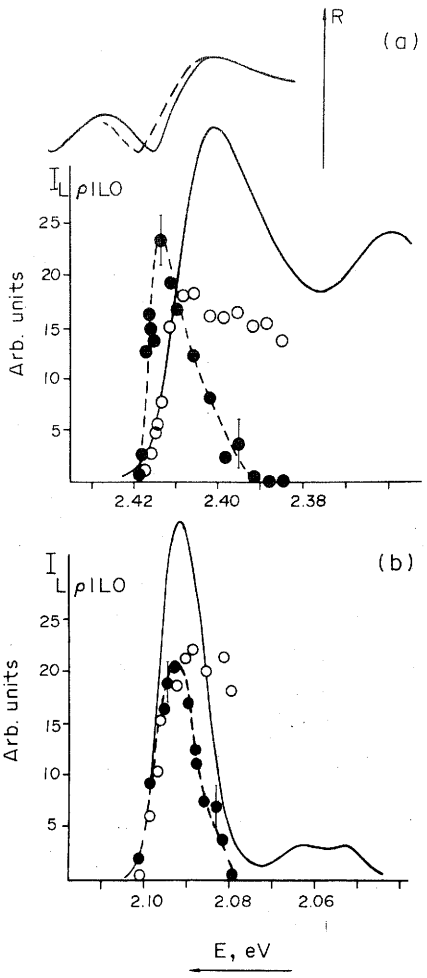

Fig. 3.
Excitation spectra of polarization degree (PD) in $CdS_{1-x}Se_x$ with $x = 0.10$ (a) and $x = 0.49$ (b). Energy scale corresponds to the exciting laser light. Black circles represent the maximum value of PD in LO_1 replica at given excitation. Open circles show energy dependence of narrow LO_1 line intensity in relation to LO_1 wing intensity. Solid lines show the luminescence at band-gap excitation. Reflectivity spectrum for $x = 0.10$ sample is also presented.

We have concluded that the sharp drop of PD on the high energy side of the maxima in the excitation spectra of Fig. 3 reflects the onset of mobility in the system of localized excitons. Transfer of excitation from the originally excited dipole state to regions with different anisotropy orientation will completely destroy the polarization of emission. The increase of migration probability at higher excitation energies is favoured by the exponential increase of the exciton state density near the bottom of unperturbed exciton band [1]. Such an increase leads first to a partial overlap of localized exciton wave functions and then, at high enough energies, to the formation of delocalized exciton states.

The high energy border in the excitation spectra of PD corresponds to a 100 % probability of excitation transfer at least to the nearest potential well with deeper localization energy and can be considered as an effective mobility edge for excitons in $CdS_{1-x}Se_x$ solid solutions.

Both in x = 0.10 and x = 0.49 samples exciton mobility edges correspond to the energy of steep intensity increase in the luminescence spectra. This shows that the main contribution to the radiative recombination in $CdS_{1-x}Se_x$ comes from localized states. Mobile or delocalized states have a very short life-time limited by fast localization and do not show up in emission.

It has been found [4,5] that the intensity of sharp LO lines in resonantly excited emission spectra abruptly decreases with the increase of excitation energy in the region of emission origin. Frequency dependence of the sharp LO_1 line intensity for our samples is shown by open circles on Fig. 3 . Cohen and Sturge [4] have argued that vanishing of sharp LO_1 line can serve as a measure of exciton mobility . This statement, though not completely proven, finds some independent spectroscopic confirmation in frequency dependence of LO wing shapes [5]. The critical energy of LO_1 sharp line disappearance closely corresponds to the exciton mobility edge as found from the excitation spectra of PD in Fig. 3 .

Now let us discuss the decrease of polarization in the low-energy part of PD excitation spectra. No exciton migration can be expected for the corresponding excitation energies. On the basis of our phenomenological model we can suppose that the decrease of PD in this case is connected with the decrease of anisotropic part of potential seen by the localized exciton beyond some critical value at which the splitting of X and Y states becomes smaller than the uniform level width. Two possible reasons can account for such decrease of anisotropy :

1) The dependence of potential anisotropy on the localization energy can be a result of interaction between the potential wells. The deepest localization states will have low density and will correspond to the isolated almost isotropic wells with minimum possible dimensions [1]. More shallow wells will have higher density of states and larger dimensions. Due to the partial overlap of such wells we can expect in a certain range of localization energies the formation of highly anisotropic but still separated localization areas. Further increase in density of states and well dimensions will lead to formation of more and more delocalized states. A qualitative illustration of the idea is given in the lower part of Fig.1.

2) At large localization energies the spatial dimensions of deep enough potential fluctuations can become too small to localize the exciton as a whole. However, the situation is possible when only the heavy component of exciton, the hole in the present case, will be localized by deep and small-size fluctuation of the valence band potential [5]. The electron which will be bound to the hole by the Coulomb forces will move outside the fluctuation and average its anisotropy. Such localized exciton will not show an anisotropic splitting whereas more shallow excitons will be localized within the wells as a whole and will suffer the level splitting.

In any case, the problem of explicit symmetry of localized excitons in semiconductor solid solutions deserve more careful theoretical consideration.

The dependence of emission PD on exciton localization energy explains also the spectral dependence of PD in the luminescence spectrum of Fig. 2 (curve 5) taken at fixed excitation frequency. It has been shown [5] that the broad wings of LO replicas are formed by superposition of emission of excitons with different localization energies excited simultaneously through the acoustic absorption side-bands. So at monochromatic excitation the different parts of observed emission wings correspond to the luminescence of excitons with different initial PD of emission. Decrease of PD along the wing contour in some way reflects the dependence of emission PD on the exciton localization energy.

In conclusion, we have used the spectral dependence of polarization degree of exciton luminescence for the experimental detection of the mobility edge for the excitons localized by random potential fluctuations in semiconductor solid solution. We have found that the emission of localized excitons has high degree of linear polarization whereas the onset of the energy migration completely destroys polarization of emission. Position of the exciton mobility edge closely corresponds to the high energy border of the strong exciton luminescence band.

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