Exciton Self-Trapping in ZnSe-ZnTe Alloys

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The low-intensity luminescence of $ZnSe_{1-x}Te_x$ with $x = 1\%$ exhibits several unusual features which are attributed to the occurrence of efficient exciton self-trapping induced by Te atoms. This type of exciton localization is strikingly different from that observed in other II-VI or III-V mixed crystals.

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The problem of carrier localization in solids is attracting renewed attention, especially in view of its relevance for transport phenomena in systems of reduced dimensionality. Excitons are particularly well suited for such studies because useful information about their mobility can be obtained directly from the luminescence due to their recombination. The case of excitons subject to the weak random potential present in a semiconductor alloy has been studied recently in several III-V or II-VI compound mixtures.[1-3] The experimental results have been interpreted in the framework of a virtual-crystal model[4] based on the Mott-Anderson localization theory.[5] In this model, the compositional disorder is considered to lead to statistically distributed fluctuations of an average potential, which in the ideal case of an infinite exciton lifetime introduces a sharp boundary between localized and mobile excitons. Here most excitons which are trapped in potential valleys may be viewed as nearly free (or weakly localized) in the sense that deep potential valleys are statistically improbable so that a small activation energy can raise a majority of them to the mobility edge. The spectroscopic signature of this model is a rather narrow, inhomogeneously broadened exciton absorption line. The emission line is also narrow and at low temperatures is usually located on the low-energy tail of the absorption as a consequence of thermalization and because weakly localized excitons have a larger radiative recombination probability.[6] Furthermore, resonant excitation into the localized states usually produces significant fluorescence-line-narrowing effects. In a recent development, the vertical transport in GaAs superlattices with randomness in barrier thickness[7] or the in-plane transport of GaAs quantum wells with random fluctuations in well thickness[8] has also been discussed along these lines.

The purpose of this Letter is to present experimental evidence in a particular solid solution of II-VI compounds in which this type of description proves totally inadequate. On the other hand, by adoption of another point of view, developed mainly by Toyozawa and coworkers,[9] it is possible to explain the observed results described below. In this second model, applied so far only to Frenkel excitons in alkali halides,[10,11] the combined action of the potential fluctuations and of the lattice vibrations leads to an unstable situation such that excitons separate into either free or strongly localized states. The key difference with the previous model is the fact that a strong localization occurs even if the localized and propagating excitons have nearly the same internal energy. This behavior reflects the presence of a potential barrier of elastic energy separating mobile and localized excitons. This second model, which can be viewed as an exciton self-trapping triggered by alloy potential fluctuations, predicts a sharp absorption line (corresponding to the creation of free excitons) but a broad Gaussian emission band with a large Stokes shift, corresponding to the decay of relaxed (localized) excitons.

The system that we have investigated is an anion-mixed ZnSe-ZnTe semiconductor bulk crystal. Taken separately, both ZnSe and ZnTe exhibit the sharp exciton absorption and emission lines typical of delocalized Wannier excitons. However, as shown by Reznitsky *et al.*,[12] significant changes appear in the low-temperature luminescence of this alloy, even for a small concentration x of Te.

Figure 1 shows emission spectra of a single crystal $ZnSe_{1-x}Te_x$ with $x = 1\%$ obtained under optical excitation by a weak cw He-Cd laser (excitation photon energy $= 3.814$ eV) as a function of lattice temperature. Also shown in the figure is the measured absorption edge of the same sample. We wish to point out several remarkable features in this luminescence. First, while the absorption edge remains sharp, as expected for free-exciton creation, the alloy luminescence is dominated at low temperature by a new broad emission S_1 with a Stokes shift (>100 meV) which is much larger than the exciton binding energy E_x of either ZnSe or ZnTe. Also, the radiative efficiency of this emission band S_1 exceeds that of

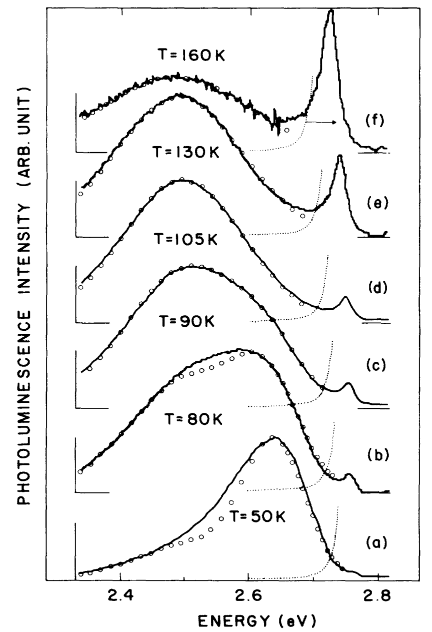

FIG. 1. Photoluminescence of a $ZnSe_{1-x}Te_x$ alloy sample ($x = 1\%$) excited with a cw He-Cd laser (incident power $= 1.2$ mW, photon energy $\hbar\omega = 3.814$ eV, spot diameter on sample surface $\phi \simeq 100$ μm) recorded at different temperatures. Also shown is the low-energy absorption edge of the same sample (dotted lines). The broad luminescence is fitted with the sum of two Gaussians S_1 and S_2 (open circles) of the following relative weights S_1/S_2: (a) 3.33, (b) 0.68, (c) 0.26, (d) 0.17, and (e),(f) 0.

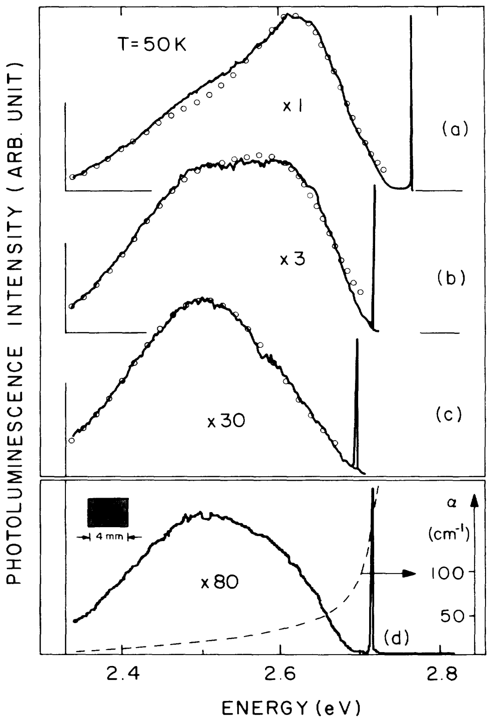

FIG. 2. Photoluminescence of the same sample as in Fig. 1, obtained under selective excitation with a tunable cw dye laser of the same power as in Fig. 1 and detected through a linear polarizer set perpendicular to the incident laser polarization vector. The laser wavelength is also shown. All spectra have been multiplied by the number indicated and have been fitted with two Gaussians (open circles) with respective weights $S_1/S_2 =$ (a) 1.47, (b) 0.52, (c) 0. In (d) the emission spectrum recorded 1 mm away from the excitation spot (diameter $\phi \leq 100$ μm) in the backward detection geometry is shown. Also shown in (d) is the low-energy absorption edge of the sample as measured on a scale expanded by a factor 10 if compared to Fig. 1.

nominally pure ZnSe or ZnTe by several orders of magnitude. Another peculiar feature is the large spectral shift of the emission, from the blue to the green part of the spectrum, occurring within a small temperature range around 80 K [Figs. 1(b) and 1(c)]. This effect corresponds in fact to the appearance of an emission band S_2 at lower energies, the latter growing at the expense of S_1. At still higher temperatures $T > 100$ K, a relative increase of the narrow emission at the position of the free exciton on the high-energy side of S_1 takes place [Figs. 1(d)-1(f)]. A similar spectral change from S_1 to S_2 can also be obtained at *fixed* crystal temperature below $T = 80$ K by resonant excitation of the sample with a cw dye laser. This spectral shift occurs then only if the incident excitation-photon energy is tuned to the low-energy edge of the free-exciton absorption line. This behavior is illustrated in Figs. 2(a)-2(c) for a lattice temperature of $T = 50$ K, but was also observed at the lowest temperature achieved in our experiments ($T = 10$ K). Finally, a pronounced spatial diffusion of the luminescence is observed at sample temperatures $T < 80$ K conferring a striking glow to the entire sample, a few millimeters in size. Emission spectra could be easily detected *macroscopic distances* away from the excitation spot, as shown in Fig. 2(d). Here also, recombination spectra recorded under such conditions differ from those emitted from the directly excited part of the sample, being characterized by a relative growth of S_2. We have also studied samples with larger Te concentration ($x \sim 10\%$). Spectral changes with temperature are less spectacular in these samples, the percentage of emission band corresponding to S_2 being dominant already at lower temperatures.

All these results can be understood in the framework of the model of exciton extrinsic self-trapping.[9] For the sake of simplicity, we will assume in the discussion that excitons become localized by the lattice distortion they induce around single Te (band S_1) or double (nearest-neighbor) Te sites (band S_2) only, and we neglect next-nearest-neighbor interactions or larger Te clusters. One expects then, in the adiabatic approximation, the appearance of two emission bands with Gaussian shapes for the recombination of such self-trapped excitons, a criterion well satisfied for S_2 and to a lesser degree for S_1 as can be seen from line fits shown in Figs. 1 and 2. Self-trapped excitons have higher radiative efficiency than free excitons because of their very large effective translational mass, preventing migration towards nonradiative recombination centers. The spectral changes occurring under band-to-band excitation when the sample temperature is increased above $T \simeq 70$ K [Figs. 1(b)-1(d)] reflect the presence of energy barriers ΔE_1 and ΔE_2 separating free and both types of localized excitons. A corresponding configurational coordinate diagram is shown schematically in Fig. 3. At low temperatures $T < 70$ K, excitons which are created initially free will be captured[13] and subsequently recombine mostly around the more numerous single Te atoms with smaller energy barrier, giving rise to a luminescence dominated by band S_1 (process *a* in Fig. 3). As the temperature is increased, excitons localized at single Te sites are thermally activated back over barrier ΔE_1 (process *b*, Fig. 3) restituting mobile excitons which in turn become increasingly captured at double Te sites (process *c*, Fig. 3), thereby leading to emission S_2. At still higher temperatures, the reverse process (*d*, Fig. 3) over barrier ΔE_2 takes place, explaining the relative increase of free electron-hole recombination as observed in Figs. 1(e) and 1(f). Nonradiative processes now reduce the overall luminescence efficiency.

The fact that all these spectral changes occur over a small temperature interval $k\Delta T < E_x \ll \Delta E$ (Stokes) indicates that the internal energy of the localized excitons is nearly the same as that of free excitons at rest. This conclusion is also reached from an inspection of the position and width of band S_2, making use of the following relation borrowed from the model for intrinsic self-trapping[9]:

$$D^2 \simeq 11 E_R kT, \tag{1}$$

where D is the width (FWHM) of the Gaussian emission band, E_R represents the elastic energy stored in the equilibrium position of the distorted lattice, and T is the lattice temperature. At sample temperatures above $T = 150$ K relation (1) yields a lattice relaxation energy $E_R \sim 250$ meV.[14] This value is comparable to the measured Stokes shift between S_2 and the free exciton. From Fig. 3, it is then apparent that free and trapped excitons must have nearly the same *electronic* energy, despite the large observed Stokes shift.

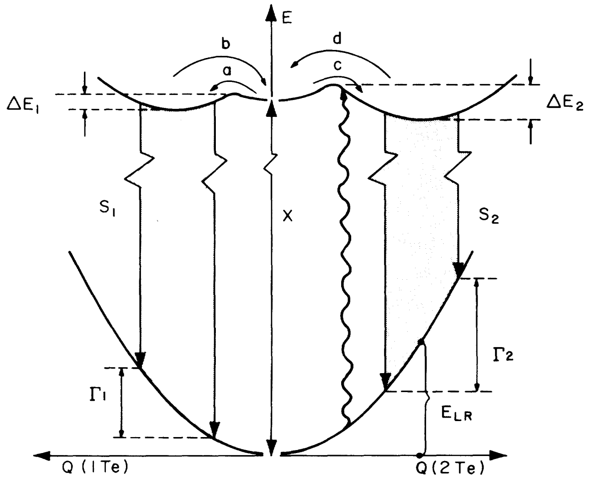

FIG. 3. Schematic diagram of the model used in the discussion, showing the total energy of the system in the presence of an exciton (upper curves) and in the electronic ground state (lower curve). Q represents a configuration coordinate for a single Te site (left-hand side) or two nearest-neighbor Te atoms (right-hand side). X is for a free exciton at rest. Descending arrows depict the recombination from localized excitons, the ascending arrow the direct creation of an exciton self-trapped around two Te.

We interpret the appearance of S_2 instead of S_1 under resonant excitation at low temperature $T < 70$ K as a *direct creation* of self-trapped excitons from the fluctuating ground state of the crystal (ascending arrow in Fig. 3). This process persists down to $T \sim 10$ K because of the large zero-point energy of the Einstein oscillator or the phonon gap mode of the crystal.[14] The same transition can also be observed directly in transmission experiments as a weak absorption tail below the free-exciton edge (see Fig. 2). We emphasize at this point the different behavior resulting from localization via self-trapping such as here, where resonant excitation on the low-energy side of the free exciton leads to an emission which is broader than that obtained under band-to-band excitation, as compared to the alternative mechanism of localization, usually observed in other II-VI or III-V alloys, where similar excitation conditions give rise to a sharp resonance fluorescence due to the decay of a selected subset of localized states.

The very large spatial diffusion of the luminescence S_2 appears at first sight to run in contradiction with an interpretation based on strongly localized excitons. However, it can be explained quite naturally in terms of radiative transfer from S_1 to S_2. The relatively weak absorption tail corresponding to the direct creation of excitons trapped around two Te nearest-neighbor sites overlaps spectrally the emission from S_1, insuring thereby a spatially nearly uniform excitation of all such sites throughout the sample. An explanation involving carrier propagation, on the other hand, would require an unrealistic diffusion coefficient, given the recombination time of the carriers, of the order of 10^{-8} sec.[12]

Finally, we remark on the microscopic aspect of the localization phenomena considered here. The tetrahedral bonding in $\mathrm{ZnSe}_{1-x}\mathrm{Te}_x$ can provide a favorable condition for trapping of the heavy-hole quasiparticle through coupling by the p orbitals of the valence-band maximum. As we have shown in this Letter, the results presented can be consistently explained if one also assumes associated local lattice distortions around tellurium sites, which in turn enhance exciton capture. The system of ZnSe:Te appears to represent a limiting case for this type of localization in II-VI compound semiconductors, with the short-range potential of Te barely sufficient to trigger self-trapping. The critical role of Te seems to be substantiated by the contrasting examples of CdS:Se and CdS:Te. The former case provides a classical example of weak localization through random potential fluctuations,[1,2] whereas published results[15] on the luminescence of CdS:Te show similarities to the present case, suggesting that strong localization via extrinsic self-trapping takes place.

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[13] In the discussion, we do not distinguish between direct exciton capture (or release) or the sequential process by which a hole is first trapped, followed by electron capture (or an electron is first released followed by hole activation). We believe that the distinction between single- and two-step events is largely meaningless here since relevant energies such as exciton binding $E_x \sim 20$ meV, ΔE_1, ΔE_2, and kT are comparable in magnitude (see below).

[14] At lower sample temperatures $T \leq 100$ K we have observed an almost constant width for Gaussian S_2. Such a behavior is expected if the Einstein approximation for the lattice vibrations is valid or it could correspond to a phonon gap mode associated with Te. In that case, the temperature in Eq. (1) is replaced by an effective temperature

$$kT^* = (\hbar\omega_0/2)\coth(\hbar\omega_0/2kT),$$

where $\hbar\omega_0$ is the energy of the Einstein oscillator or the phonon gap mode. From a fit to the data, we estimate a value $\hbar\omega_0 \sim 15-20$ meV.

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