

Free-exciton luminescence from $\text{ZnSe}_{1-x}\text{Te}_x$

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Temperature dependences of luminescence for the free exciton and the Te-induced self-trapped exciton in $\text{ZnSe}_{1-x}\text{Te}_x$ ($x \sim 0.005$) are studied. The intensity of the free-exciton line increases up to 50 K with the temperature and decreases above that temperature, while that of the self-trapped broadband monotonically decreases. This phenomenon is quantitatively analyzed in the framework of a kinetic model and discussed by using a configurational coordinate diagram.

II-VI compound semiconductor solid solutions with isoelectronic substitution have been studied since the 1960s by many authors. Recently $\text{ZnSe}_{1-x}\text{Te}_x$ has attracted much interest due to the unusual features in the luminescence emission spectra in the low-Te-concentration limit.¹⁻³ These spectra commonly show two emission bands, which are interpreted as radiative recombination of excitons localized at single Te atoms (Te_1) and Te clusters (Te_n , $n \geq 2$). The relative intensities of the two bands show strong Te concentration dependence. However, the nature of the localized excitons at Te impurities is interpreted on the basis of two different models, and remains quite controversial. One interpretation¹ is that the hole is primarily bound in a strongly localized state above the valence-band edge by a short-range potential resulting from the large difference between the electronegativities of Te and Se. An electron then can be bound by Coulomb attraction. The other interpretation² is that the excitons are localized by the combined action of the potential fluctuations and the lattice vibrations, which leads to an unstable situation such that excitons separate into either free or strongly localized states formed via extrinsic self-trapping.

In this paper, we present interesting experimental results of lightly Te-doped ZnSe [$\text{ZnSe}_{1-x}\text{Te}_x$ ($x \sim 0.005$)] crystals obtained by luminescence emission spectroscopy, particularly the temperature dependence of the intensities of peaks in luminescence spectra. These experimental results give evidence of self-trapping. We are able to confirm the existence of a potential barrier between free and localized states and to determine the barrier height by using the kinetic model.

The $\text{ZnSe}_{1-x}\text{Te}_x$ ($x \sim 0.005$) crystals were prepared by the Te-melt method⁴ in closed evacuated quartz ampoules at 700°C. The luminescence emission measurements were carried out in the temperature range 20–200 K. The excitation source for the luminescence emission spectra was the 365-nm line of a 250-W high-pressure Hg lamp.

Figure 1 shows luminescence emission spectra of $\text{ZnSe}_{1-x}\text{Te}_x$ with $x \sim 0.005$ at several temperatures under very weak excitation. The radiative efficiency of the emission at low temperature is very high compared with pure ZnSe by a few orders of magnitude. We point out important features in this spectrum. First, the emission

consists of a rather sharp peak which is explained as a free-exciton line peaking at 2.794 eV and a broad emission band at 2.65 eV (blue band), which is consistent with the result of Ref. 2. The broadband emission with full width at half maximum (FWHM) 170 meV and with a large Stokes shift (~ 150 meV) is assigned to the luminescence of excitons trapped by Te_1 atoms.¹⁻³ Comparing the free exciton line obtained here with data on $\text{ZnSe}_{1-x}\text{Te}_x$ solid solutions,⁵ we find that this corresponds to a Te concentration $x \sim 0.004$ in bulk, which is in fact within the uncertainty of the absolute calibration of concentration by x-ray microanalysis. As another feature, with increasing temperature, the intensity of blue-band emission decreases monotonically, while that of the free-exciton luminescence increases up to 50 K and decreases above this temperature. This phenomenon has not been observed in $\text{ZnSe}_{1-x}\text{Te}_x$ alloys ($x \geq 0.01$).¹⁻³ A summary of the temperature dependence of the integrated emission intensities for free and trapped excitons is shown in Figs. 2(a) and 2(b), respectively. The figures also include results of our calculations (solid curves) as detailed below, where both curves are normalized to unity at their maxima.

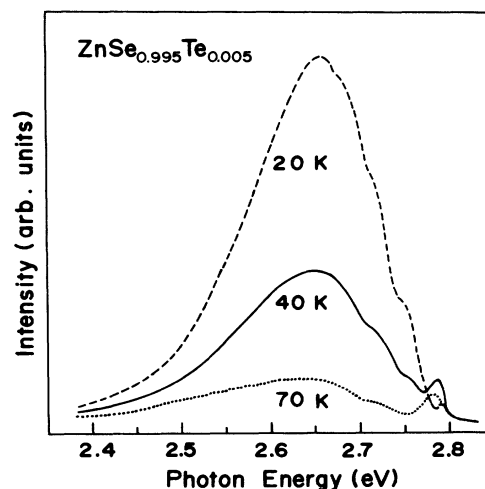


FIG. 1. Luminescence spectra for $\text{ZnSe}_{1-x}\text{Te}_x$ ($x \sim 0.005$) at different temperatures.

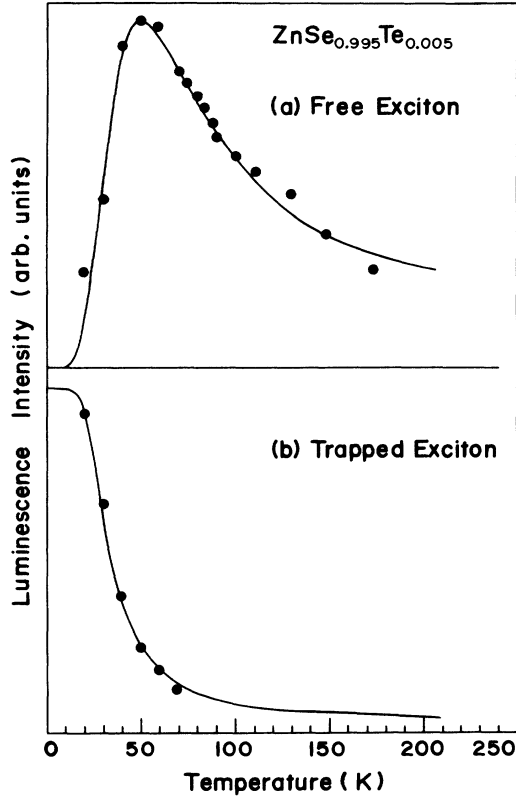


FIG. 2. Integrated luminescence intensities from (a) free excitons and (b) self-trapped excitons as a function of temperature. A comparison of experiment (dots) and model calculation (solid curves) used in the discussion is shown.

To understand this result, we use the extrinsic self-trapping model,^{6,7} which has been applied in alkali halides.⁸ In $\text{ZnSe}_{1-x}\text{Te}_x$ ($x \sim 0.005$), the crystal lattice is deformed in the vicinity of the Te isoelectronic impurities. Exciton-phonon interaction enhances trapping of an exciton at an impurity atom or a lattice defect, which forms a new state referred to as a self-trapped state. The luminescence emission spectrum, in this case, shows the coexistence of two types of exciton luminescence: a sharp free-exciton luminescence peak with no Stokes shift and a broad luminescence band from self-trapped excitons with a large Stokes shift. This indicates that the band states of excitons, similar to the exciton waves in a nondeformed lattice (free-exciton state), coexist with self-trapped states, and these two states are separated by a potential barrier ΔE forming the double-well potential⁹ in the adiabatic potential model.

For a quantitative analysis of the above arguments, a simple kinetic model will be discussed, taking into account an exciton-transfer process. That this model is applicable follows when it is noted that, at zero temperature, all the photogenerated excitons, in the very weak excitation limit, can relax into self-trapped states without occupying the lowest exciton band; this causes the blue-band emissions to dominate. As the temperature increases, excitons escape thermally from the self-trapped state and transfer inversely to the free-exciton state, ex-

plaining the increase in the recombination of free excitons. For the sake of the simplicity, we will assume in the discussion that excitons become trapped by the lattice distortion induced around single Te sites only, and neglect excitons trapped around double Te or larger Te clusters. This assumption is quite reasonable because the emission due to the excitons trapped at Te_1 is at least 20 times as large as that due to the excitons trapped at Te_2 or Te clusters at low temperature (20 K).

In the stationary case, the following rate equations must hold for low-intensity excitation with the exciton trapping rate A , after creation, if any saturation effects are neglected,

$$\frac{dN_{\text{Te}}}{dt} = 0 = A - \left[\alpha_{\text{Te}} + \frac{1}{\tau_{\text{Te}}} \right] N_{\text{Te}}, \quad (1a)$$

$$\frac{dn_{\text{exc}}}{dt} = 0 = \alpha_{\text{Te}} N_{\text{Te}} - \left[\alpha_{\text{exc}} + \frac{1}{\tau_{\text{exc}}} \right] n_{\text{exc}}, \quad (1b)$$

where N_{Te} is the concentration of excitons trapped at Te_1 centers and n_{exc} is the free-exciton concentrations. τ_{Te} is the radiative lifetime of trapped excitons and τ_{exc} is the radiative lifetime of free excitons. Here we neglect the temperature dependence of exciton trapping rates and radiative lifetimes. $\alpha_{\text{Te}}(T)$ is the corresponding thermal release rate at a temperature T , which could be assumed in the simple approximation as

$$\alpha_{\text{Te}}(T) = \alpha_{\text{Te}}^0 \exp \left[-\frac{\Delta E}{kT} \right] \quad (2a)$$

and $\alpha_{\text{exc}}(T)$ is thermal dissociation rate of free excitons,

$$\alpha_{\text{exc}}(T) = \alpha_{\text{exc}}^0 \exp \left[-\frac{E_x}{kT} \right], \quad (2b)$$

where ΔE is the height of the energy barrier separating free and trapped exciton states and E_x is the exciton binding energy. From Eq. (1), the normalized emission intensities $I_{\text{Te}} \sim N_{\text{Te}}/\tau_{\text{Te}}$, $I_{\text{exc}} \sim n_{\text{exc}}/\tau_{\text{exc}}$ are obtained:

$$I_{\text{Te}} \sim \frac{1}{C_{\text{Te}} e^{-\Delta E/kT} + 1}, \quad (3a)$$

$$I_{\text{exc}} \sim \frac{e^{-\Delta E/kT}}{(C_{\text{Te}} e^{-\Delta E/kT} + 1)(C_{\text{exc}} e^{-E_x/kT} + 1)}, \quad (3b)$$

with the abbreviations

$$C_{\text{exc}} = \tau_{\text{exc}} \alpha_{\text{exc}}^0, \quad C_{\text{Te}} = \tau_{\text{Te}} \alpha_{\text{Te}}^0. \quad (4)$$

Figure 2 shows results of calculations for the intensities $I_{\text{Te}}(T)$ and $I_{\text{exc}}(T)$ used to determine the barrier height ΔE . The normalized intensities are plotted as a function of the temperature and compared with the experimental results. By taking ΔE about 10 meV, the calculated intensity curves match quite well with the experimentally measured intensities. Here, the exciton binding energy $E_x = 18$ meV for ZnSe was used. The good agreement serves as an important demonstration of the consistency of our model.

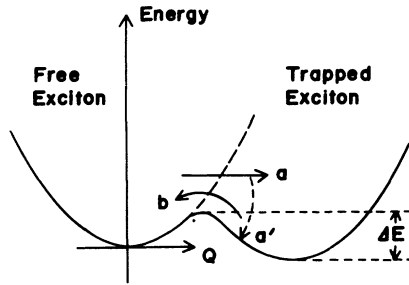


FIG. 3. Schematic diagram of the adiabatic potential curve for $\text{ZnSe}_{1-x}\text{Te}_x$ ($x \sim 0.005$).

A corresponding configurational coordinate diagram is shown schematically in Fig. 3 to illustrate the self-trapping process. When the $\text{ZnSe}_{1-x}\text{Te}_x$ ($x \sim 0.005$) crystal is excited with the above energy-gap excitation at low temperature, free electron-hole pairs or free excitons are formed, captured, and subsequently recombine mostly around the single Te atoms, giving rise to a broad luminescence dominated by the blue band (process $a \rightarrow a'$ in Fig. 3). At higher temperatures, the thermal activation process becomes dominant, by which the excitons jump back over the barrier ΔE to the free-exciton state (process b in Fig. 3). This explains the increase of free-exciton recombination as shown in Figs. 1 and 2.

In conclusion, we point out that the observation of the

coexistence of free excitons and the self-trapped excitons in the luminescence from $\text{ZnSe}_{1-x}\text{Te}_x$ ($x \sim 0.005$) is interpreted in terms of the double-well potential structure with the potential barrier based on the extrinsic self-trapped exciton due to the local lattice distortions around Te_1 atoms. The temperature dependence of integrated luminescence intensities of both free and trapped excitons confirms the existence of the potential barrier and leads to a determination of the barrier height of $\Delta E = 10$ meV, assuming the inverse transfer of excitons. This phenomenon indicates that the potential barrier height is small enough compared with the excitonic binding energy, for trapped excitons thermally activated back over that barrier, which is an unusual observation in semiconductors.

As compared with other published experimental results,¹⁻³ the temperature behavior of free excitons is mainly governed by the potential barrier height. The potential barrier height increases so rapidly with the Te concentrations that free excitons emerge only in the very narrow range of Te concentrations in $\text{ZnSe}_{1-x}\text{Te}_x$. Additionally, it is considered to be very difficult to observe the free-exciton peak from $\text{ZnSe}_{1-x}\text{Te}_x$, even with the Te concentrations only a slightly exceeding 0.01, due to the presence of Te clustering.

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