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Localisation of excitons at small Te clusters in diluted ZnSe_{1-x}Te_x solid solutions

S Permogorov†, A Reznitsky†, A Naumov†, H Stolz‡ and
W von der Osten‡

† A F Ioffe Physico-Technical Institute, 194021 Leningrad, USSR

‡ Fachbereich Physik, Universität-GH, 4790 Paderborn, Federal Republic of Germany

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Abstract. The low-temperature recombination luminescence of ZnSe_{1-x}Te_x solid solutions is studied in the Te concentration range $1\% \leq x \leq 2\%$. The dependence of the spectra on Te content and on excitation photon energy allows us to discriminate three different emission components. They are ascribed to recombination of excitons localised at clusters very probably consisting of two and more than two Te atoms. Selective excitation reveals substantial inhomogeneous broadening of states due to fluctuations in the local environment of the clusters. The phonon side-band structure concomitantly observed gives strong support to our model in which the large-radius exciton is tightly bound through the hole. The excitation spectra of the 1LO phonon replica intensity and of its polarisation degree provide information on the energy distribution of the localised states and their dynamic properties. The strong modification of the localised state emission spectrum found at higher Te concentration can be qualitatively understood by the increasing cluster interaction.

1. Introduction

Pseudo-binary solid solutions of II–VI semiconductors of the type AB_{1-x}C_x are formed by substitution of either cations or anions by isoelectronic atoms of other chemical nature. In the diluted case the substituting atoms can be considered as isoelectronic impurities. Since the electronic radius and the electron affinity of the substituting impurity atom differ from that of the replaced host atom, the random distribution of the impurities over the lattice sites produces both structural and potential disorder in the solid solution. As a result of this disorder, localised states may appear in the energy spectrum of the solid solution near the fundamental edge.

The concentration behaviour of the energy spectrum in the solid solution depends critically on the position of the electronic level produced by the isolated impurity atom relative to the energy bands of the parent compound. If the impurity level is situated in the forbidden energy gap, the well known situation of the isoelectronic trap arises (Hopfield *et al* 1966). In this case an isolated impurity atom can localise an electron or a hole by the short-range potential, with typical binding energies in II–VI compounds of several hundreds of millielectronvolts (Cuthbert and Thomas 1968). Coulomb attraction of the carrier with opposite charge then leads to formation of a localised exciton, the radiative recombination of which sensitively indicates the presence of the isoelectronic trap. With increasing impurity concentration a new fundamental edge is formed within

the forbidden gap corresponding to persistence-type behaviour of the energy spectrum, considered by Onodera and Toyozawa (1968).

If the isoelectronic impurity produces a level within the allowed electronic band of the parent compound, amalgamation-type behaviour (Onodera and Toyozawa 1968) is expected to occur, well described in the framework of the virtual-crystal approximation. Owing to the repulsive interaction between the resonant impurity states and the band states of the parent crystal, a smooth shift of the fundamental edge with increasing impurity concentration takes place. The spatial fluctuations of the impurity concentration produce exponentially decreasing tails in the density of states at the band edges in which localisation of excitons (or carriers) is possible (Halperin and Lax 1966, Baranovskii and Efros 1978).

A rather peculiar situation may occur if the position of the impurity level is situated within the allowed electronic band but close to its edge (Ivanov and Pogorelov 1979). In this case an isolated impurity atom does not produce any localised state, and a smooth shift of the fundamental band gap with concentration is expected. A localised state, however, may appear for small clusters consisting of two or three impurity atoms in nearest-neighbour positions. The localised state (with localisation energy ϵ) can be fairly shallow and can have an electronic radius $r = \hbar/(2m\epsilon)^{1/2}$ large in comparison with the lattice constant. As a result, even at very small substitutional concentrations, the interaction of these clusters with other impurities can cause substantial inhomogeneous broadening of the energy levels. Moreover, formation of localised states by clusters involving impurity atoms in non-nearest positions will be possible.

In this paper we communicate results obtained from studying the emission spectra of $\text{ZnSe}_{1-x}\text{Te}_x$ solid solutions with small Te content ($1\% \leq x \leq 2\%$) at liquid-helium temperature. Whereas in a preceding publication the luminescence in these materials was shown to be due to a complex superposition of various components (Stolz *et al* 1988), our present measurements prove that the radiative recombination originates from excitons localised at clusters composed of a few Te atoms. Our investigations under resonant monochromatic excitation and the observed dependence of the emission spectra on Te concentration and on excitation intensity enable us to discriminate bands corresponding to exciton localisation at clusters of different types. In a narrow range of Te concentration between 1 and 2%, a strong redistribution of relative intensities of these bands is observed, suggesting the modification of the density-of-states spectrum near the fundamental edge with increasing Te concentration. Also the details observed in the phonon wings of the emission spectra are in qualitative agreement with the model of cluster localisation.

2. Experimental details

For our investigations we used bulk monocrystalline $\text{ZnSe}_{1-x}\text{Te}_x$ samples in the composition range $1\% \leq x \leq 2\%$. The exact Te content was determined with up to $\pm 0.1\%$ accuracy by employing an electron microprobe x-ray technique. Vapour- and melt-grown samples were found to show essentially similar spectra. However, crystal quality and general brightness of the luminescence were significantly higher for the vapour-grown samples. The experiments were performed at $T = 2$ K, using a standard set-up that consisted of a tunable dye laser, a double monochromator and a computer-controlled photon counting system (see Stolz *et al* 1988). The dye laser was tunable between 2.60

and 2.90 eV. The maximum power used for excitation was 30 mW focused to a $30\ \mu\text{m}$ spot at the sample.

3. Experimental results

Incorporation even of a relatively small amount of Te into ZnSe crystals leads to a drastic change of the emission spectrum compared to that of pure ZnSe. While pure ZnSe exhibits luminescence simultaneously containing free exciton, donor-acceptor and deep-level emission bands as typical for II-VI semiconductors, in $\text{ZnSe}_{1-x}\text{Te}_x$ ($x = 1\%$) this spectrum is replaced by a broad and intense band that has its high-energy edge at the position of the free-exciton reflection line (Reznitsky *et al* 1984). This new luminescence was assigned to radiative recombination of excitons localised at Te clusters, whereby the microscopic nature of these clusters remained unspecified. Based on results from cathodoluminescence studies, a similar interpretation was later given by Akimova *et al* (1985), while more recently impurity-induced self-trapping of excitons was believed to be responsible (Lee *et al* 1987).

The localised exciton in $\text{ZnSe}_{1-x}\text{Te}_x$ for small x is regarded to consist of a hole, localised by the short-range cluster potential, and an electron bound to this hole by Coulomb attraction. The main contribution to the exciton localisation energy originates from the tight localisation of the hole, whereas the binding energy of the electron to the hole and its localisation radius are close to the free-exciton binding energy and radius, respectively. Correspondingly, important properties of the localised exciton states like inter-cluster interaction and migration probability will depend predominantly on the hole localisation radius, which for sufficiently deep states may be of the order of the lattice constant.

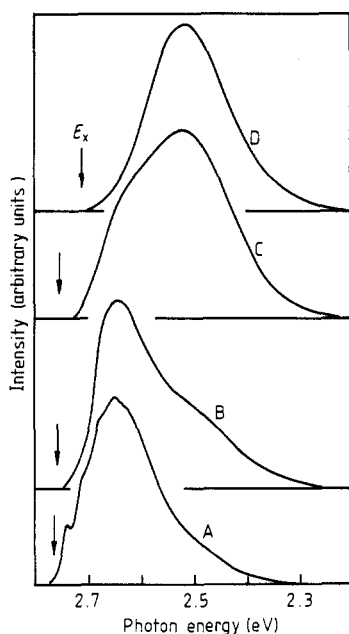


Figure 1. Luminescence spectra of $\text{ZnSe}_{1-x}\text{Te}_x$ as a function of Te concentration x : A, $x = 1.0\%$; B, $x = 1.2\%$; C, $x = 1.6\%$; D, $x = 2.0\%$. The energy positions E_x of the free-exciton reflection line are marked by arrows. $T = 2\ \text{K}$.

3.1. Concentration dependence of the emission spectra

Figure 1 displays the concentration dependence of the luminescence spectra of $\text{ZnSe}_{1-x}\text{Te}_x$ solid solutions in the Te concentration range 1–2%. As is obvious, a relatively small increase in concentration x produces strong changes in the recombination spectrum. At the lowest Te concentration, the band exhibits fine structure. Increasing x , the high-energy edge of the band shifts slightly to lower energies. This shift parallels that of the exciton reflection line, the position of which is marked by the arrows in the figure and corresponds to the concentration dependence of the band gap for $\text{ZnSe}_{1-x}\text{Te}_x$ (Naumov *et al* 1987a). At the same time, the fine structure of the band is smeared out, and a new band with maximum around 2.5 eV appears. At highest concentrations, this new band dominates in the spectrum, whereas all other bands at higher energies disappear. The observed concentration dependence of the spectrum implies that the emission in $\text{ZnSe}_{1-x}\text{Te}_x$ has a composite character. It is natural to assign the different components to radiative recombination of excitons localised by different types of Te clusters.

3.2. Dependence of emission spectra on excitation intensity

To decompose the emission bands of the localised excitons, we took advantage of the dependence of the luminescence band shape on excitation light intensity expected if the superimposed bands have different radiative lifetimes and different saturation behaviours. Figure 2(a) shows the emission spectra of the $x = 1\%$ sample for two excitation intensities chosen to be different by two orders of magnitude. Although we did not attempt to study the dependence on excitation power in detail, the total emission intensity was found to increase almost linearly with excitation power in this range. The increase, however, is slightly greater for the high-energy components of the band than for those at lower energies.

To extract the spectral shape of the individual components, we employed the method discussed by Fock (1972). It is applicable if the relative intensities of the individual components of the band can be altered independently by some external parameter, like e.g. excitation intensity, without affecting the individual band shapes or energy positions. In that case the emission spectra taken under different experimental conditions may be considered as linear combinations of their components. The spectral shapes of these components are then simply obtained by algebraic operations involving a sufficient number of experimental records provided the individual bands do not overlap indistinguishably.

To illustrate the idea of the method, one may regard the emission spectrum S composed of two bands $A(\omega)$ and $B(\omega)$. From two spectra S_1 and S_2 , different in their experimental conditions,

$$S_1 = a_1A(\omega) + b_1B(\omega) \quad S_2 = a_2A(\omega) + b_2B(\omega) \quad (1)$$

we can calculate the spectrum

$$S_3 = S_1 - (a_1/a_2)S_2 = (b_1 - b_2a_1/a_2)B(\omega) \quad (2)$$

containing only one component $B(\omega)$ and permitting us to determine the second one, $A(\omega)$, from equation (1). The normalisation factor a_1/a_2 can be derived from S_1 and S_2 for the spectral region where the contribution of $A(\omega)$ is dominant. It is quite obvious that the method can be applied to real physical systems only with a certain degree of

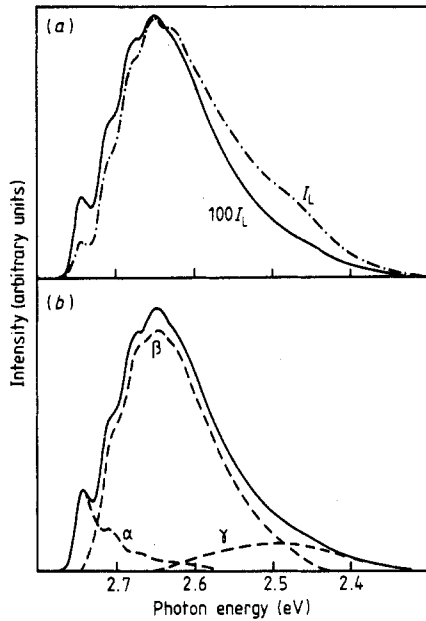


Figure 2. (a) Luminescence spectra of $\text{ZnSe}_{1-x}\text{Te}_x$ ($x = 1\%$) at $T = 2$ K excited above the exciton gap with light intensities I_L and $100I_L$. The spectra are normalised to their peak intensities. (b) Decomposition of one of the spectra ($100I_L$) into different components α , β , γ (see text).

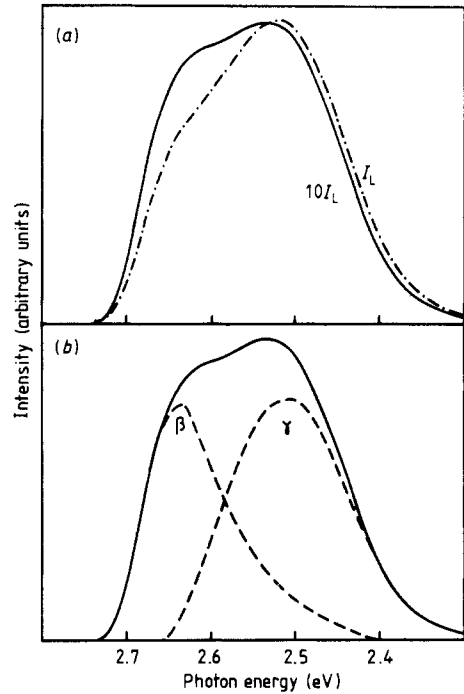


Figure 3. Same as in figure 2, but for $\text{ZnSe}_{1-x}\text{Te}_x$ ($x = 1.6\%$). The excitation intensities in this case differ by a factor 10 only.

approximation. It may still be useful if the number of components can be conjectured prior to decomposition.

For the spectra of the $x = 1\%$ sample in figure 2, one expects independent emission components to occur in the central part and on both wings. Accordingly, by using the method described, a decomposition was made into bands α , β and γ as shown by the broken curves in figure 2(b). The two high-energy bands (α , β) exhibit clear phonon structure with an energy period close to the LO phonon energy in ZnSe (31.5 meV), whereas the γ band is structureless. This reflects different strengths of electron-phonon coupling of these states, which, from the intensity distribution of the various phonon components, is found to increase with localisation energy. Although only LO structure is apparent in the spectra, earlier results proved also that acoustic phonons from all over the Brillouin zone participated in the transitions (Stolz *et al* 1988). Comparing the results obtained from analysing 10 original recordings, we estimate the error in determining the maximum positions to be less than 5% of the corresponding band half-width, whereas the positions of the band edges are accurate only to about 20% of that value.

Figure 3 shows the corresponding results and the decomposition for the sample with $x = 1.6\%$. In this case, the emission spectrum contains two bands, which are close in position and shape to the β and γ bands for the sample with $x = 1\%$. In this case, however, no phonon structure is found for the β band.

The results of spectral decomposition strongly support the interpretation of the concentration dependence presented in § 3.1. At least three different kinds of localised states can be distinguished in $\text{ZnSe}_{1-x}\text{Te}_x$ solutions with small Te content. While the nature of these states basically remains the same, the contribution of states with larger localisation energy to the total luminescence increases with increasing Te content.

3.3. Selective excitation of localised excitons

The decomposition of the recombination luminescence spectra agrees nicely with previously reported results of selective excitation measurements (Stolz *et al* 1988). In these experiments, excitation at different photon energies in resonance with the localised exciton states resulted in a redistribution of intensities in the spectrum, revealing its composite origin and the existence of different kinds of localised states (cf. figure 1 of Stolz *et al* 1988).

From these measurements, we also found the energy spectrum of the localised states to be inhomogeneously broadened, selective resonant excitation within these states giving rise to additional detailed structure in the emission. As already discussed (Stolz *et al* 1988, Permogorov *et al* 1988), this structure images the exciton localisation at small isoelectronic clusters and consists of two contributions different in physical origin. One is a series of narrow lines shifted with regard to the exciting laser line by integer numbers of LO phonon energies. Owing to their polarisation properties, these lines are unambiguously assigned to phonon replicas of the zero-phonon luminescence transitions of the localised exciton states selectively excited within the inhomogeneously broadened bands. The other contribution consists of a series of broader maxima also recurring periodically with the LO phonon energy. These maxima represent the phonon wings in the luminescence, indicating exciton interaction with phonons from the whole Brillouin zone. While these latter features reflect the strong local lattice deformations due to the localisation of the hole by the cluster, the sharp LO replicas originate from Fröhlich interaction expected for large-radii excitons. It is the dependence of these various structures on excitation photon energy that will be discussed in the following, thereby providing details of exciton localisation and the spectral distribution of localised states near the fundamental exciton edge.

3.3.1. Phonon wings at different excitation photon energies. As displayed for the $x = 1\%$ sample in figure 4, the shape of the phonon wing depends considerably on excitation photon energy (E_L) within the bands of resonant states. Its structure is most pronounced for excitation near the high-energy edge of the β band (curve D, $E_L = 2.710$ eV). In this case the peaks of fine structure are in good correspondence with the maxima of the phonon density of states for ZnSe (curve A in figure 4; Hennion *et al* 1971), which indicates the tight localisation by Te clusters. For excitation close to the high-energy edge of the α band (curve B, $E_L = 2.760$ eV), the phonon structure in the wing is much smoother and in addition exhibits a maximum at around 4.5 meV, which is not present in the spectrum of the β band. It can be supposed that for these more shallow states the localisation radius is fairly large. This favours the interaction with long-wavelength phonons over that with phonons from the Brillouin zone boundary to which the maxima in the density of states correspond. Besides, energy transfer can strongly influence the shape of the α band.

For excitation near the onset of the γ band (curve E, $E_L = 2.660$ eV) the phonon wing is also rather smooth. Experimentally, its detection in this region was difficult since

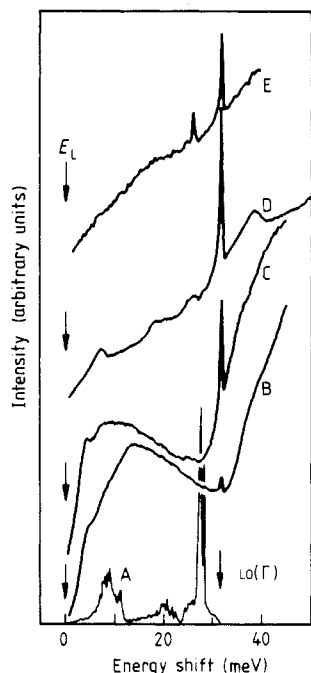


Figure 4. $\text{ZnSe}_{1-x}\text{Te}_x$ ($x = 1\%$): luminescence spectra showing phonon wing fine structure and LO phonon replica of resonantly excited zero-phonon transitions at $T = 2$ K. Laser excitation at $E_L = 2.760$ eV (B), 2.755 eV (C), 2.710 eV (D) and 2.660 eV (E). For easy comparison of structures all spectra are plotted with E_L coinciding, the energy scale representing the Stokes shift with respect to the exciting laser line (arrows). Curve A reproduces the phonon density of states $D(\hbar\omega)$ of ZnSe (Hennion *et al* 1971).

E_L was close to the end of the available tuning range of our dye laser. In addition, relatively strong anti-Stokes emission was observed, very probably arising from two-step transitions. The most interesting feature under these excitation conditions is the peak at about 26 meV, which is almost as narrow and intense as the LO line (at 31.5 meV). The energy of this additional phonon peak does not coincide with a maximum in density of states in the phonon spectrum of ZnSe (compare with curve A). Since it is not observed for excitation in the α and β bands but rather shows up only at the lowest E_L , it is likely to originate from a local vibration close in energy to the breathing (LO) mode of ZnTe (see e.g. Bilz and Kress 1979). The appearance of such a mode may be expected for clusters of two or more Te atoms embedded in the ZnSe lattice.

3.3.2. Excitation spectra of 1LO lines. To obtain the distribution of localised exciton states, we studied the 1LO line intensity as a function of the exciting laser photon energy E_L , which in principle should reflect the inhomogeneously broadened spectrum of zero-phonon transitions. As an example, figure 5 illustrates experimental tracings for the sample with $x = 1\%$ where a series of 1LO luminescence lines were recorded for various E_L differing by about 5 meV each. After normalisation to the incident laser intensity and background subtraction, the integrated intensities were obtained from these data. They are displayed (I_{1LO} , filled symbols) as a function of excitation photon energy in figure 6 for the samples with $x = 1.0\%$, 1.1% and 1.6% along with parts of the luminescence spectra (L) obtained under above-band-gap excitation.

In all crystals investigated, the excitation spectra exhibit structure that is in very good agreement with the composite nature of the recombination luminescence. For the sample with the smallest Te concentration ($x = 1\%$), two pronounced maxima occur. They coincide well with the two high-energy maxima of the emission band, their energetic difference being slightly larger than the 1LO phonon energy. In agreement with the

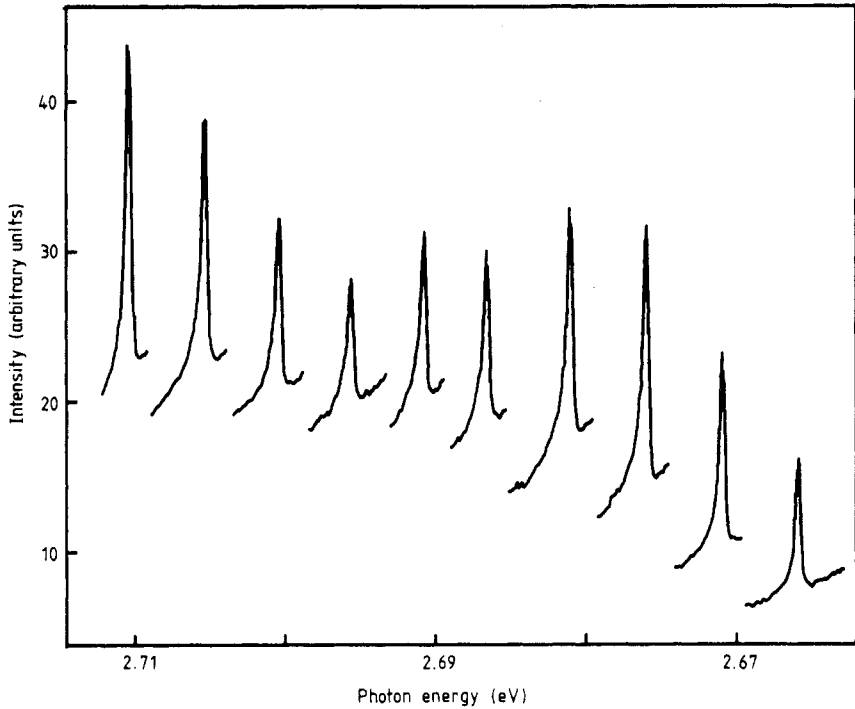


Figure 5. $\text{ZnSe}_{1-x}\text{Te}_x$ ($x = 1\%$): experimental record of 1LO luminescence lines excited at different laser photon energies E_L . Zero-point intensity suppressed. The scale of the abscissa corresponds to the energy of the emitted light. $T = 2$ K.

spectral decomposition in figure 2, this result proves that the second maximum in the emission spectrum of this sample is not a phonon replica of the first one but rather corresponds to the distribution of zero-phonon lines of an independent electronic transition. The intensity of the 1LO line can be expressed as

$$I_{1\text{LO}} \sim [\rho(E_L)W_R^{1\text{LO}}/(W_R + W_N)]I_L. \quad (3)$$

Here I_L is the intensity of the exciting laser, $\rho(E_L)$ is the spectral density of zero-phonon transitions into the exciton states at laser photon energy E_L , $W_R^{1\text{LO}}$ is the probability for radiative transitions with emission of 1LO phonon, and W_R and W_N are the total radiative and non-radiative transition probabilities, respectively. Since we employed a nearly 180° scattering geometry and since the absorption coefficient for the emitted light was always much smaller than at the exciting light photon energy, there is no need for any absorption correction.

Assuming that, for shallow localised exciton states in semiconductor solid solutions, the main contribution to the non-radiative probability originates from exciton tunnelling to states with larger localisation energies, W_N may be quite generally written as

$$W_N \sim \rho(E') \exp(-R_m/R_0). \quad (4)$$

This tunnelling probability depends critically on the density of available states $\rho(E')$ with lower energies E' , the mean spatial separation of these states (R_m) and the electronic radius (R_0) of the more tightly localised carrier in the initial state, which in the present case is the hole. Since we expect W_N to decrease sensitively with increasing exciton

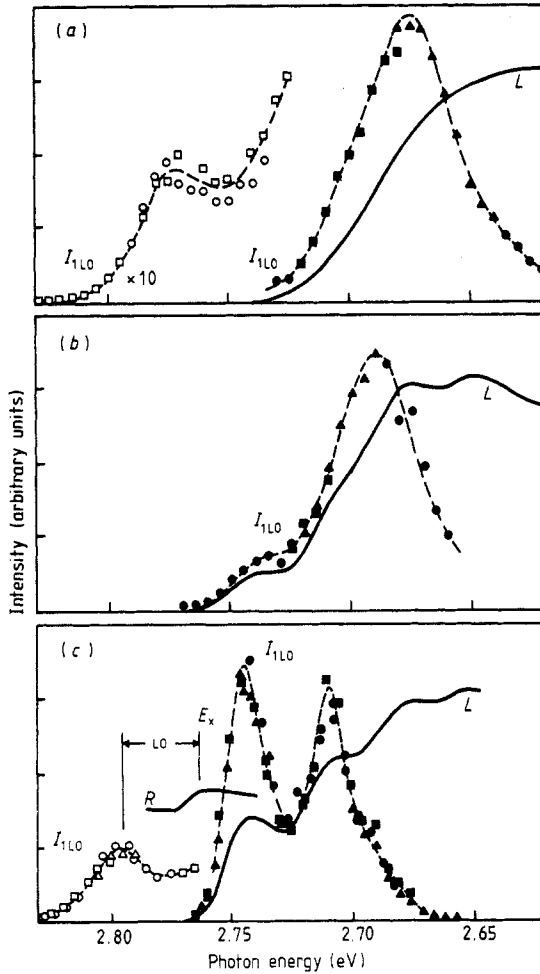


Figure 6. Excitation spectra of the 1LO scattering intensity I_{1LO} along with parts of the luminescence spectra (L) of $\text{ZnSe}_{1-x}\text{Te}_x$ for different Te concentrations x : (a) $x = 1.6\%$; (b) $x = 1.1\%$; (c) $x = 1.0\%$. R denotes the free-exciton reflection spectrum and E_x the energy of the exciton gap.

localisation energy (because of both smaller localisation radius R_0 and exhaustion of the density of states $\rho(E')$ at lower energies), the excitation spectrum I_{1LO} will not reproduce the density of localised states over the entire spectral range. Rather, this will be the case only where the probability for non-radiative energy transfer is small, i.e. at lower photon energies. We therefore believe that the low-energy peak in I_{1LO} (at around 2.709 eV) reproduces the maximum in density of localised states whereas at least the high-energy part of the first peak (at 2.744 eV) may be strongly affected by the tunnelling processes.

The excitation spectrum I_{1LO} for the sample with $x = 1.1\%$ in principle is similar to that for $x = 1\%$. The main differences are the shift of the spectrum to lower energies (due to the concentration dependence of the band gap mentioned above) and the relative decrease in intensity of the high-energy maximum. We believe that this decrease is caused by the energy transfer probability W_N , which is larger for these states as compared with the 1% sample. Besides, a substantial broadening of the low-energy maximum occurs, which can be attributed to the spreading of the density of states within the forbidden gap.

For the sample with $x = 1.6\%$ we find a further shift and broadening of the excitation spectrum. Although a 1LO line could be detected for excitation in resonance with the γ

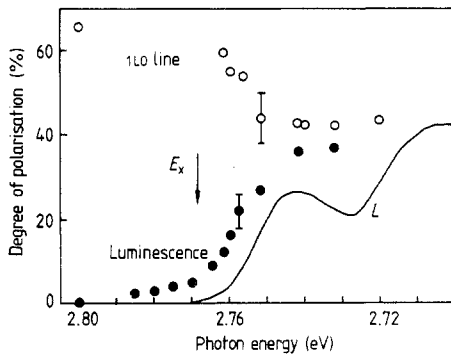


Figure 7. $\text{ZnSe}_{1-x}\text{Te}_x$ ($x = 1\%$): degree of induced linear polarisation P_L versus excitation photon energy. The full circles show P_L of the luminescence intensity measured 35 meV below the excitation photon energy (see text); the open circles represent P_L for the 1LO line. Also shown is part of the luminescence spectrum (L) in this energy range obtained for above-band-gap excitation. The exciton gap energy E_x is marked by an arrow. $T = 2$ K.

band, we were not able to resolve any structure corresponding to the onset of this band in its excitation spectrum. Obviously at higher concentration this structure becomes broad and weak and overlaps with the tail of resonant states for the β band.

In addition to structure coinciding with the localised exciton luminescence bands, the excitation spectra in figure 6 exhibit weaker maxima, which are situated 1LO phonon energy above the free-exciton resonance (I_{1LO} , open symbols for samples with $x = 1.0\%$ and 1.6%). On the basis of energy position and polarisation properties (cf. § 3.4 and also Stolz *et al* 1988) they can be assigned to the maxima in cross section of 1LO resonant Raman scattering. Since resonant Raman scattering involving real intermediate states, like in the present case, corresponds to luminescence (Klein 1973), it can be described by a relation similar to equation (3). The small intensity of the Raman process as compared to the 1LO luminescence (3–5%) comes from the high probability of non-radiative transfer (W_N), which is determined by energy relaxation of free excitons. The maximum in Raman cross section is due to the maximum in W_R and corresponds to the strong resonance of the outgoing photon with the exciton transition as usually observed for ordered (Permogorov and Travnikov 1976) as well as for disordered (Klochikhin *et al* 1976) direct-gap semiconductors. Again in accordance with the exciton resonance, the maximum in Raman cross section is found to shift to lower energies with increasing Te concentration.

3.4. Polarisation measurements and exciton mobility edge

Since $\text{ZnSe}_{1-x}\text{Te}_x$ solid solutions crystallise in the cubic (zincblende) structure, the luminescence spectrum of localised excitons should be essentially unpolarised. Under resonant excitation with linearly polarised light, however, an induced linear polarisation of emission can appear owing to the ‘hidden anisotropy’ of the exciton system (Verbin *et al* 1983). The polarisation stems from the local anisotropy of the localised states and is observed only if the absorption and emission of light take place in the same localised centre without energy transfer to others. As a consequence, the excitation spectrum of induced polarisation can be used to detect the exciton mobility edge separating free and localised states (Permogorov *et al* 1983).

Corresponding experimental results for the sample with $x = 1\%$ are shown in figure 7. The full circles represent the degree of linear polarisation of luminescence $P_L = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp})$ as a function of excitation photon energy. I_{\parallel} and I_{\perp} are the emission intensities for polarisation parallel and perpendicular to that of the exciting light. The degree of polarisation was determined from the emission spectrum at energies 35 meV

below the laser excitation line in order to avoid any complications due to superimposed first-order Raman scattering processes. The luminescence is found to be unpolarised only for excitation far above the exciton resonance (i.e. for energies above 2.80 eV). At lower excitation photon energies, the luminescence exhibits a small but finite positive degree of polarisation, implying that even in this spectral region part of the localised states is excited through the phonon wings in the absorption spectrum. P_L increases substantially at the high-energy edge of the luminescence band, reaching its saturation value only around the first maximum of the luminescence. The saturation value amounts to about 40%, which is close to its theoretical limit (50%; Verbin *et al* 1983). Although the analysis of the polarisation data is complicated by the strong interaction of the electronic transitions with phonons, we can still conclude that the states with localisation energies up to roughly 30 meV are affected by the energy transfer processes. As a result, no abrupt mobility edge can be detected in $\text{ZnSe}_{1-x}\text{Te}_x$ solid solutions. One can still define an effective mobility edge as the energy position of the turning point in the degree of polarisation.

The open circles in figure 7 show the degree of polarisation for the 1LO emission line as a function of excitation energy. At high energies, in this case P_L amounts to more than 60%, characteristic of forbidden Fröhlich Raman scattering and clearly confirming our interpretation of the maximum in the 1LO excitation spectrum in this energy range (see figure 6). For excitation in resonance with the luminescence band, P_L for the 1LO line attains a value compatible with the process of resonantly excited luminescence.

4. Discussion and summary of results

All our experimental results for $\text{ZnSe}_{1-x}\text{Te}_x$ solid solutions with small Te content are in good agreement with the model of exciton localisation by isoelectronic clusters briefly outlined above. The selective excitation experiments and the dependence of the emission spectra on Te concentration and on excitation intensity reveal the existence of at least three different kinds of localised states, which can be assigned to clusters of different nature. For all clusters a substantial inhomogeneous broadening of the zero-phonon energies is established. An additional broadening of the luminescence spectra comes from exciton-phonon interaction, which is relatively strong and depends on localisation energy. The tight localisation of holes by Te clusters is evident from phonon density-of-states maxima appearing as phonon wing fine structure of the emission spectra under monochromatic resonant excitation. On the other hand, concomitantly observed intense LO replicas are due to Fröhlich interaction of LO phonons with electrons, the localisation of which is close to the free-exciton Bohr radius.

The general evolution of the energy spectrum of $\text{ZnSe}_{1-x}\text{Te}_x$ with Te concentration is characterised by the shift of the band gap to lower energies. Besides, pronounced changes in the density of states and in the dynamic properties of localised excitons are observed. The strong concentration dependence of the emission and excitation spectra (figures 1 and 6) can be understood by considering the dependence of the hole localisation radius on localisation energy. At the lowest Te concentrations most clusters may be regarded as isolated. Nevertheless, a strong inter-cluster interaction exists, giving rise to the inhomogeneous broadening of the energy spectra. From the excitation spectra of figure 6 one may conclude that at Te concentrations even as small as 1% no energy gap exists between localised and free-exciton states, implying the presence of very shallow localised states. For these states the localisation radius $r = \hbar/(2m\epsilon)^{1/2}$ is large, favouring

the energy migration experimentally detected in the excitation spectra of the degree of polarisation for the emission (figure 7). For higher Te concentrations not only the number of clusters increases. Also the localisation radius r for states of a given energy becomes larger caused by the low energy shift of the band gap and, hence, reduction of localisation energy ε . As a consequence, the density of states is strongly modified and a fast shift of the mobility edge to lower energies is observed (Reznitsky *et al* 1988). At sufficiently high Te concentrations, the model of cluster localisation cannot be applied any more, exciton localisation then being due to long-range compositional fluctuations (Naumov *et al* 1987b).

The concentration shift of the band gap in $\text{ZnSe}_{1-x}\text{Te}_x$ indicates that the energy level of an isolated Te atom falls inside the valence band of ZnSe. This conclusion is in agreement with previous results (Iseler and Strauss 1970), which showed that the exciton localisation in ZnSe:Te takes place not at isolated Te atoms but at Te pair clusters.

We assign the emission band β in figures 2 and 3 to cluster states formed by Te pairs in nearest-neighbour positions whereas the more shallow states forming band α are very probably due to clusters with the atoms in not-nearest positions. The low energy band γ may be associated with clusters containing more than two Te atoms, an assignment strongly supported by the local vibration appearing close in energy to the ZnTe LO phonon for excitation in the γ band (compare figure 4). Our interpretation concerning the microscopic nature of Te clusters is in good agreement with the conclusions based on earlier cathodoluminescence studies in diluted $\text{ZnSe}_{1-x}\text{Te}_x$ (Akimova *et al* 1985).

At present, we are unable to decide whether the formation of Te clusters is purely statistical or not. Direct studies by EXAFS have not revealed any deviation from random Te distribution (Mikkelsen and Boys 1985). On the other hand, the simultaneous occurrence of emission bands correlated with certain types of clusters in ZnSe/ZnTe superlattices (Kolodziejewski *et al* 1988) in this case suggest preferential formation for reasons of internal strain compensation.

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