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A picosecond photoluminescence study of exciton dynamics in $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$

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Abstract. Picosecond time-resolved photoluminescence studies have been made at temperatures down to 1.8 K and in magnetic fields up to 8 T of the dilute magnetic semiconductor $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ for $x = 0.09, 0.2$ and 0.3 . The dynamics of the lattice-disorder-induced and magnetically induced localisation of excitons are investigated, and it is concluded that magnetic localisation plays a major role. The luminescence for $x = 0.45$ is discussed in the Appendix.

1. Introduction

The spin of a carrier in a magnetic semiconductor such as EuO, when bound to a defect, couples to local magnetic moments of the host by exchange interaction which is strong and ferromagnetic in sign. The carrier combined with its magnetisation cloud is referred to as a bound magnetic polaron. It is well known that EuO undergoes a metal–insulator transition at $T_c = 50$ K associated with a transition from magnetic order to magnetic disorder (Torrance *et al* 1972). Below 50 K conduction in EuO is metallic due to the presence of donors (oxygen vacancies). Above 50 K collapse of the donor wavefunction occurs, giving an insulator. For carrier transport in non-magnetic solids there are delocalising tendencies (electron transfer) and localising tendencies (electron–phonon interaction), and for highly ionic systems self-trapping can occur at low temperatures (Hayes and Stoneham 1985). In the case of EuO there is additionally the strong carrier–magnon interaction to consider. Below T_c the uniform magnetisation does not contribute to localisation, but the localisation energy associated with the onset of magnetic disorder triggers collapse of the donor wavefunction in EuO at T_c , with loss of conductivity (Emin *et al* 1987). The application of a magnetic field B to the disordered state reduces the tendency of a carrier to form localised polarons and increases conductivity. However, if B becomes large enough to cause appreciable magnetically induced shrinking of the carrier wavefunction the magnetic binding energy of the polaron may be enhanced (see § 4).

In the dilute magnetic semiconductor (DMS) $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ the magnetic interaction between nearest-neighbour Mn^{2+} ions is antiferromagnetic in sign. For $x < 0.7$ this material has the zincblende structure with Mn^{2+} randomly replacing Cd^{2+} . The percolation limit for this structure is $x = 0.2$, and one would expect this system to remain paramagnetic for $x \leq 0.2$. However, Novak *et al* (1986) have shown that spin-glass

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behaviour occurs at low temperatures for values of x down to 0.01. This behaviour is due to magnetic dipole–dipole interaction between groups of Mn^{2+} ions, giving a dipolar spin glass. The transition temperature is $T_g \approx 0.5$ K for $x = 0.1$, 2 K for $x = 0.2$, and 5 K for $x = 0.3$. It should be added that the magnetic spins are distributed in clusters of various sizes; for $x = 0.05$, for example, the probabilities of singles, pairs (spinless), open triples and closed triples are 0.54, 0.24, 0.09 and 0.02 respectively, accounting for 89% of Mn^{2+} ; the rest is in larger clusters.

The ground state of Mn^{2+} is $3d^5$, ${}^6S_{5/2}$, and exchange interaction between the $3d^5$ electrons and spins in the s-like conduction band and p-like valence band of $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ gives rise to anomalously large Zeeman splitting of band-edge extrema; this results in unusual magneto-optical effects such as giant band-edge Faraday rotation (Gaj *et al* 1978a). Golnik *et al* (1983) have reported evidence for the formation of acceptor-bound magnetic polarons in $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$, i.e., a hole localised at an acceptor impurity and interacting with neighbouring Mn^{2+} spins; this interaction is generally ferromagnetic in sign and because of magnetic disorder in the mixed crystal gives rise to a spread of magnetic binding energies. Even in zero external magnetic field the bound electron polarises Mn^{2+} ions in its orbit, creating a resultant local field (Dietl and Spalek 1982). The effect of the exchange field on donor-bound electrons in $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$ was studied by Heiman *et al* (1983) using the technique of spin–flip Raman scattering. For $x = 0.1$ the spin–flip energy in zero applied field is ~ 1 meV.

Given the existence of large magnetic-field-induced band-edge splittings in DMS one expects correspondingly large shifts in the energy of excitons in DMS in a magnetic field, and a magnetic contribution to the binding energy even at $B = 0$. However, the behaviour of excitons is complicated in DMS by composition-dependent fluctuations of the crystal potential which give rise to localised states for excitons in the forbidden gap. It is assumed that there is a tailing of states into the gap with a mobility edge (ME) separating localised states from more extended states in which excitons are mobile. The existence of these disorder-induced states can be demonstrated by exciting with resonant monochromatic radiation, giving rise to a narrowing of exciton luminescence due to selective excitation of localised states (Cohen and Sturge 1982, Kash *et al* 1983, Permogorov *et al* 1985). If the exciting light is linearly polarised a high degree of polarisation of exciton luminescence is maintained for excitation below the ME but not above (polarisation is lost for propagation through band-like states). Above the ME the decay time of excitons is very short; localisation occurs rapidly ($\leq 10^{-9}$ s) by phonon emission and strongly influences processes of energy migration. This fast localisation has the consequence that in disordered systems luminescence from localised excitons is much stronger than that due to other forms of radiative decay.

Time-resolved spectroscopy is an important technique for studying the dynamics of exciton localisation in DMS (Harris and Nurmikko 1983a, b, Zhang and Nurmikko 1984, Zayhowski *et al* 1985). Here we describe time-resolved photoluminescence studies of $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ in which we observe a time-dependent spectral shift of the exciton recombination, showing the relaxation of excitons to lower-lying states. We also study effects of external magnetic fields on the dynamics of exciton localisation. We find that for low Mn concentrations ($x < 0.1$) excitons are localised by both acceptors and by alloy potential fluctuations, but for $x \geq 0.2$ the latter mechanism is relatively more important. In addition we find that magnetic localisation associated with magnetic polaron formation gives a major contribution to the binding energy of excitons in DMS. Short accounts of some aspects of this work have been reported previously (Wong *et al* 1986, 1987, Hayes *et al* 1988).

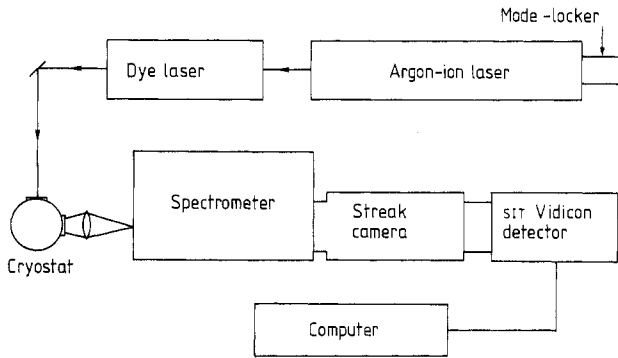


Figure 1. Apparatus for measuring picosecond time-resolved photoluminescence.

2. Experimental

The luminescence measurements were made using the experimental arrangement shown in figure 1. We used a synchronously pumped rhodamine 6 G dye laser as the excitation source: the pulse repetition rate was 76 MHz, pulse width ~ 5 ps, and the average output power was typically 200 mW. The photo-excited carrier densities were estimated from the measured photon fluence per pulse and the optical absorption length; the density was varied by inserting calibrated neutral-density filters into the laser beam.

The detection system used to measure time-resolved luminescence consisted of a 0.3 m Czerny–Turner monochromator and a synchronous streak camera which was triggered by the dye laser pulse train. The streak image on the camera phosphor was detected using a vidicon-based optical multi-channel analyser. The total time window available for detection was 1 ns, and the time resolution of the apparatus was 18 ps.

The samples we have studied were Bridgman-grown crystals with Mn concentrations of $x = 0.09$, 0.2 and 0.3. Luminescence measurements were obtained from samples maintained at low temperatures in a He gas flow cryostat; measurements at high magnetic fields were obtained from samples mounted in a split-coil superconducting magnet at 1.8 K. Luminescence was excited using above-band-gap laser light: for $x = 0.09$ we used $E_{\text{laser}} = 1.81$ eV, and for $x = 0.2$ and 0.3 we used $E_{\text{laser}} = 2.13$ eV. For $x = 0.45$ the excitation energy was $E_{\text{laser}} \approx 2.2$ eV, which lies in the band-tail region; the results obtained for this sample are presented in the Appendix.

3. Experimental results

3.1. Impurity-bound and disorder-localised exciton luminescence

3.1.1. Time-integrated luminescence. Figure 2(a) shows the luminescence spectrum of $Cd_{1-x}Mn_xTe$ ($x = 0.09$) at 4 K excited to give a relatively low carrier density ($\leq 10^{16} \text{ cm}^{-3}$). We assign the peak on the high-energy side, at 1.737 eV, to recombination of ‘free’ excitons. At lower energy there is a broad emission with a peak at 1.722 eV superimposed. As-grown $Cd_{1-x}Mn_xTe$ is normally p-type due to the presence of cadmium vacancies or acceptor impurities, and it is likely that the 1.722 eV peak is due to neutral acceptor-bound excitons (see Golnik *et al* 1983). The weaker band at ~ 1.536 eV may be due to donor–acceptor (DA) recombination.

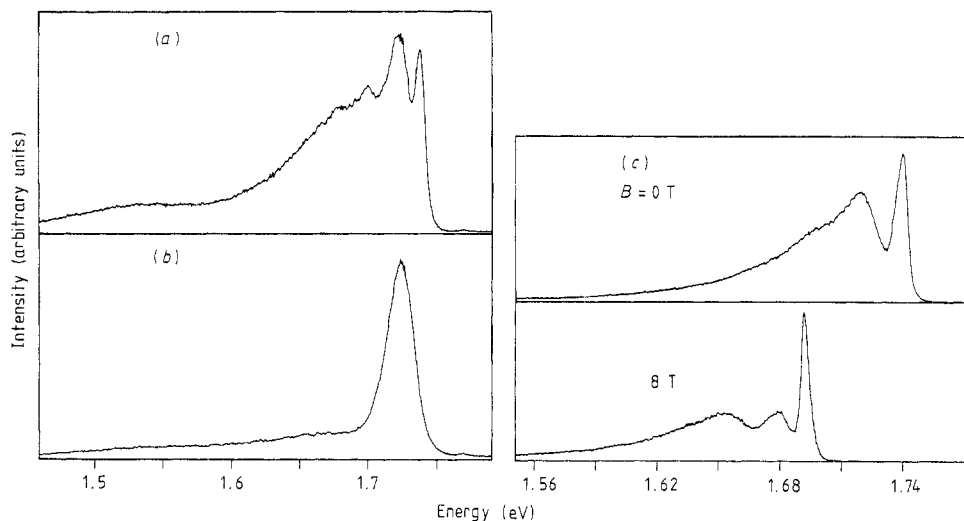


Figure 2. Time-integrated luminescence of $\text{Cd}_{0.91}\text{Mn}_{0.09}\text{Te}$ at 4 K with a maximum carrier density of (a) $\sim 10^{16} \text{ cm}^{-3}$ and (b) 10^{17} cm^{-3} . (c) shows the effect of an applied field of $B = 0 \text{ T}$ and 8 T at 1.8 K with light collected in the Voigt configuration.

The assignments suggested above are supported by the dependence of luminescence intensity on excitation intensity (figure 2(b)); ‘free’-exciton emission increases with increasing excitation intensity, whereas the emission from excitons bound to defects quickly saturates. Increasing pump power also causes a broadening and a shift to lower energy of the ‘free’-exciton peak. One characteristic of DA recombination is that more distant pairs saturate first with increasing excitation intensity, leading to a shift of the DA peak to higher energy (Thomas *et al* 1964). This effect has been observed for the DA peak of $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ ($x = 0.09$) (Wong 1987).

Figure 3 shows the luminescence spectra for $x = 0.2$ at 4 K. For this concentration the luminescence efficiency is almost an order of magnitude greater than for $x = 0.09$. Also, the low-energy emission associated with point defect trapping has almost disappeared, and the appearance of the spectrum is less sensitive to excitation intensity for densities $\leq 10^{17} \text{ cm}^{-3}$. The luminescence band (FWHM $\approx 15 \text{ meV}$) is centred at 1.891 eV; this is 20 meV below the free-exciton energy which we have determined from reflectivity measurements to be 1.911 eV at 4 K. We suggest that the weak, low-energy shoulder on this band is due to neutral-acceptor-bound excitons (see Nurmikko *et al* 1983). For $x = 0.3$ the luminescence band (FWHM $\approx 24 \text{ meV}$) occurs at 2.073 eV, approximately 31 meV below the free-exciton peak (as measured in reflection). Again the luminescence efficiency is much higher, and emission from point-defect-bound excitons is not resolved.

We suggest that the broad emission bands for the $x = 0.2$ and $x = 0.3$ samples arise from excitons localised by potential fluctuations in these disordered magnetic alloys. The ‘free’-exciton emission at 1.773 eV for the $x = 0.09$ sample is also associated with similar but weaker localisation processes. Disorder-induced localisation of excitons has been investigated in a number of nonmagnetic alloys such as $\text{GaAs}_x\text{P}_{1-x}$ (Gershoni *et al* 1986) and $\text{CdS}_{1-x}\text{Se}_x$ (Cohen and Sturge 1982).

Figure 3(a) shows that the luminescence peak for $x = 0.2$ shifts by $\sim 5 \text{ meV}$ to higher energy and decreases in width by $\sim 6 \text{ meV}$ when the temperature increases from 4 K to 30 K. Although no shift to higher energy was observed for $x = 0.3$ a slight narrowing of

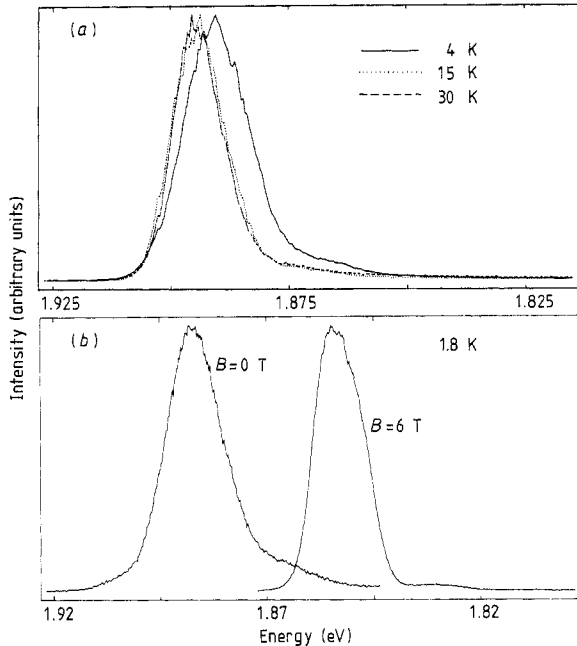


Figure 3. Effects of (a) temperature and (b) magnetic field on the time-integrated luminescence of $Cd_{0.8}Mn_{0.2}Te$.

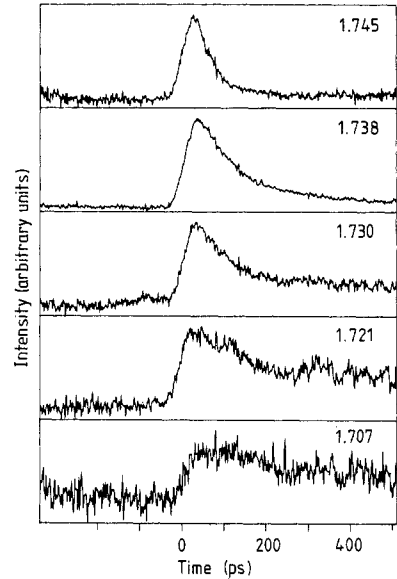


Figure 4. Time-resolved luminescence of $Cd_{0.91}Mn_{0.09}Te$ at 4 K at different luminescence energies (given in each panel in eV) throughout the 'free'-exciton peak (see figure 2(a)).

the band occurs. These effects have also been observed by Zhang and Nurmikko (1984) who suggested that at higher temperatures there is increased occupation of higher-energy localised states. However, the reduction of magnetic interaction at higher temperatures will also give rise to a shift to higher energy and, in addition, a decrease in linewidth (see § 3.2).

The observed FWHM at 4 K for all x is much greater than the expected thermal broadening (<1 meV). The distribution of band edge electronic states associated with a mixed crystal will make a substantial contribution to the broadening. An approximate estimate of this type of broadening can be made using a statistical model developed by Schubert *et al* (1984) for $Al_xGa_{1-x}As$. For $x = 0.09$ the calculated FWHM for $Cd_{1-x}Mn_xTe$ using this theory is ≈ 7 meV, which agrees with the observed value. However, the calculated FWHMs for $x = 0.2$ (10 meV) and $x = 0.3$ (12 meV) are substantially less than the measured values, suggesting that another mechanism is contributing at higher x (see § 3.2). This theory also predicts a shift of the exciton energy from the free value of a few meV for $x = 0.2$: again, this is substantially smaller than the observed shift of 20 meV.

3.1.2. Time-resolved luminescence. It is clear from the time-integrated measurements described in the previous section that luminescence for $x \geq 0.2$ is mostly from excitons localised by random potentials associated with compositional fluctuations. Using time-resolved photoluminescence techniques we can determine the time-dependent relative population of excitons over the energy spectrum of localised states. In particular, by taking time-resolved measurements at closely spaced energies in the region of the broad-

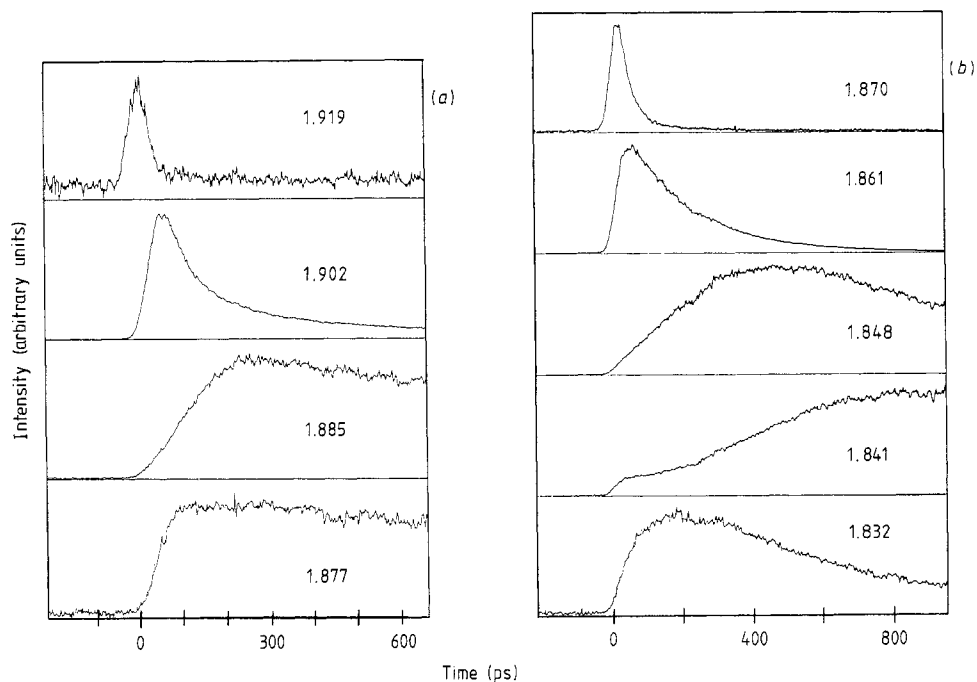


Figure 5. Time-resolved luminescence of $\text{Cd}_{0.8}\text{Mn}_{0.2}\text{Te}$ for (a) 4 K, $B = 0$ and (b) 1.8 K, $B = 6$ T, at different luminescence energies (given in each panel in eV) throughout the emission peak (see figures 2(a), (b)).

band emission we can study the dynamics of energy migration through the spectrum of localised states.

Figure 4 shows the temporal rise and decay of luminescence for $x = 0.09$. At 1.745 eV, on the high-energy wing (see figure 2), both the rise and decay times are ≈ 75 ps; the fast decay is due to rapid trapping of 'free' excitons by acceptors. In the region where emission from 'free' and acceptor-bound excitons overlap (1.721 eV) the decay time increases to 2–3 ns, characteristic of allowed radiative decay.

The luminescence decay for $x = 0.2$ (figure 5(a)) is different from that for $x = 0.09$. At 1.919 eV, on the high-energy wing of the emission band (see figure 3(a)), the rise time is resolution-limited (≤ 20 ps) and the decay time is also short (≤ 30 ps). Towards the centre of the band both the rise time and the decay time increase; at 1.885 eV, on the low-energy side of the time-integrated luminescence, the rise time is ≈ 250 ps and the decay time is ≈ 3 ns. However, at 1.877 eV the rise time has decreased again although the decay remains slow. It seems that this reduction of the rise time is due to efficient trapping by acceptors (see also Harris and Nurmikko 1983a, b); this effect is not so pronounced for $x = 0.3$ since acceptor-bound-exciton emission is not resolved.

An exciton localised by potential fluctuations at low temperature can either recombine or migrate to lower-energy states by emission of acoustic phonons. For $x \geq 0.2$ initial excitation above the band gap is followed by rapid capture (≤ 20 ps) into localised states, with subsequent relaxation within these states. At low temperature we therefore expect time-resolved spectra to shift to lower energy with increasing time, in agreement with observation (figure 6). It is apparent from figure 6 that the loss of intensity at the high-energy end of the emission is rapid but slows at lower energy as the density of

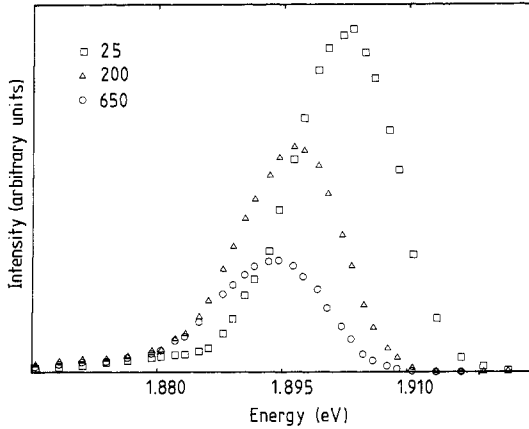


Figure 6. Spectral emission of $Cd_{0.8}Mn_{0.2}Te$ at 4 K at various times after excitation (given as key in ps).

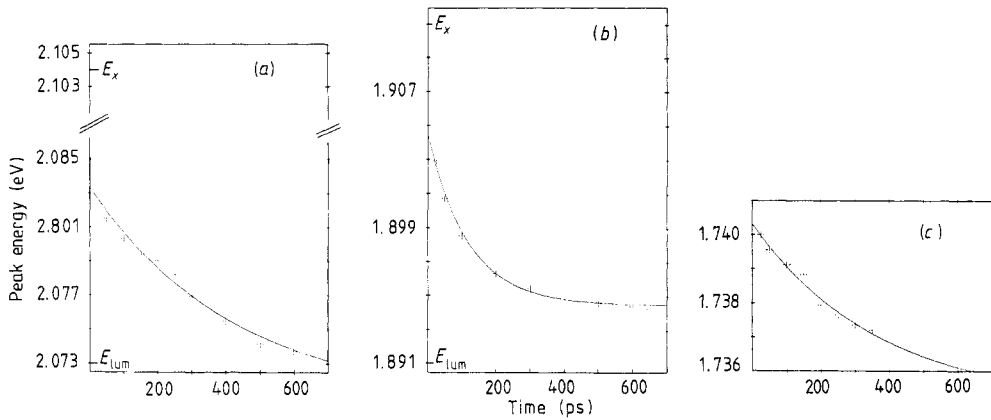


Figure 7. Time dependence of the spectral red shift of the luminescence peak of $Cd_{1-x}Mn_xTe$ at 4 K for (a) $x = 0.3$, $\tau = 420$ ps, (b) $x = 0.2$, $\tau = 120$ ps, and (c) $x = 0.09$, $\tau = 365$ ps. E_x corresponds to the exciton energy measured in reflection, and E_{lum} is the energy of the peak in the time-integrated luminescence.

localised states decreases. This decrease contributes to a lengthening of both rise and decay times as energy decreases (figure 5(a)).

Our measurements of the time-dependent shift of the luminescence peak for the three samples at 4 K are summarised in figure 7. Over the time scale covered the peak shifts for $x = 0.2$ and 0.3 are ≈ 10 meV. The results for $x = 0.09$ are less extensive than for the others since the intensity is weaker; we observe a shift of ≈ 3 meV over the first 350 ps, but at this time the relaxation is incomplete. The magnitude of the shift decreases with increasing temperature, falling by a factor of four between 4 K and 30 K for $x = 0.2$; this happens largely because the average magnetic binding energy decreases at higher temperatures (Wong 1987). By fitting a single exponential to the data we obtain a characteristic time for the transition to lower-energy states of 365 ps for $x = 0.09$, 120 ps for $x = 0.2$ and 420 ps for $x = 0.3$ (see also Zhang and Nurmikko 1984). The variation of relaxation time with x is unusual and we shall return to it in § 3.2. We find that the theory developed by Schubert and Tsang (1986) to describe the time evolution

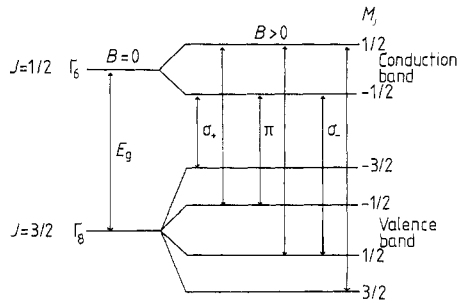


Figure 8. Schematic representation of the Zeeman splitting of the band edge of $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ (see text). Allowed transitions and their polarisations are indicated.

of the spectral shape of exciton luminescence in a non-magnetic alloy semiconductor is inadequate to describe this behaviour (Wong 1987).

In concluding this section we mention, for comparison, results of time-resolved measurements on excitons in $\text{CdS}_x\text{Se}_{1-x}$. This material also has a direct band gap, of energy ≈ 2.1 eV. Kash *et al* (1983) found that for $x = 0.53$ the luminescence peak shifted less than 4 meV to lower energy in 10 ns, whereas we find for $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ a shift of ≈ 10 meV after 800 ps for $x = 0.2$. This comparison suggests that alloy disorder alone is inadequate to account for the behaviour of the DMS. Indeed, our measurements are qualitatively similar to the time-dependent luminescence spectra of $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ reported by Zayhowski *et al* (1985) and attributed by them to magnetic polaron formation. Also Warnock *et al* (1985), using optical pumping experiments, concluded that BMP formation is an important process in DMS, accompanying nonmagnetic disorder-induced localisation. It is possible to estimate the total magnitude of the shift of the luminescence peak due to lattice disorder alone using a theory developed by Cohen and Sturge (1982), and for $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ ($x = 0.2$) this predicts a shift of only a few meV. Since our measured shift is 20 meV it would appear that magnetic binding is important. We shall explore magnetic effects directly in the next section.

3.2. Magnetically induced localisation

In considering the effects of magnetic ions on the band states of $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ we neglect in the first instance the random distribution of Mn^{2+} ions and consider only the mean magnetisation (i.e., the molecular-field approximation, which is reasonable for extended wavefunctions). We assume also that it is a reasonable approximation to neglect both Landau splitting and intrinsic spin splitting of the band states in our magnetic fields (1–2 meV) in comparison with the exchange splitting (40–50 meV) (see Gaj *et al* 1978a, b, Aggarwal *et al* 1985). Free excitons at the band edge are formed by excitation of electrons from the p-like Γ_8 valence band to the s-like Γ_6 conduction band. Application of a magnetic field to the 1S ground state of the exciton produces a splitting of both the Γ_6 and the Γ_8 states (figure 8). The exchange energy of the exciton may be written in the form:

$$E_{\text{ex}} = -x\langle S_z \rangle (N_0 \alpha M_e + \frac{1}{3} N_0 \beta M_h) \quad (1)$$

where x is the molar fraction of Mn^{2+} ions, $\langle S_z \rangle$ is the average value of the z component of the Mn^{2+} spin, N_0 is the number of unit cells per unit volume, α and β are exchange integrals for electrons and holes, and M_e (M_h) is the z component of the electron (hole) angular momentum. The value of $\langle S_z \rangle$ will depend on x and on B :

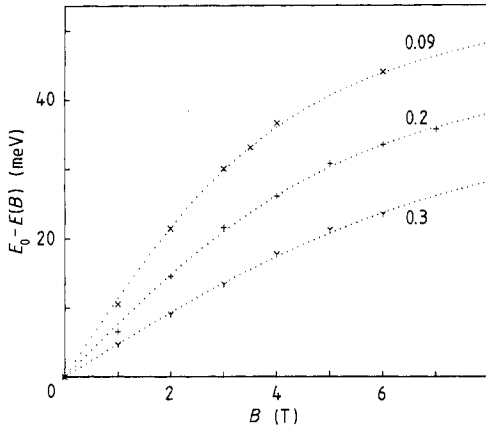


Figure 9. Comparison of the magnetic-field-induced measured and calculated (dotted lines; see text) shifts of the luminescence peak of $Cd_{1-x}Mn_xTe$ at 1.8 K for $x = 0.09, 0.2$ and 0.3 (as indicated on the curves). The Voigt configuration was used.

$$\langle S_z \rangle = -\frac{5}{2}(\bar{x}/x)B_{5/2}\{5\mu_\beta B/k[T + T_0(x)]\} = S_0 B_{5/2}\{5\mu_\beta B/k[T + T_0(x)]\} \quad (2)$$

where x is an effective molar concentration of isolated Mn^{2+} ions, $B_{5/2}$ is the Brillouin function for $S = \frac{5}{2}$ and $T_0(x)$ is determined by the concentration-dependent magnetic interaction.

Allowed optical transitions for both Faraday (σ_+ , σ_-) and Voigt (σ , π) configurations are shown in figure 8. Our observations are made on the Voigt configuration and polarisation studies on the $x = 0.2$ sample showed the luminescence to be unpolarised in magnetic fields of up to 5 T. We have also carried out polarisation studies on the luminescence of $Zn_{1-x}Mn_xTe$ for $x = 0.17$ in magnetic fields of up to 5 T, and we find the exciton luminescence in that material to be mainly σ -polarised, consistent with predominant emission in the $M_J = -\frac{1}{2} \rightarrow -\frac{3}{2}$ transition (see figure 8) (Hayes *et al* 1988). We have no clear-cut explanation for the absence of polarisation in the $Cd_{1-x}Mn_xTe$ emission for $x = 0.20$, but local strain may be a contributing factor. The energy of the σ -polarised $M_J = -\frac{1}{2} \rightarrow \frac{3}{2}$ transition is

$$E = E_0 - \frac{1}{2}N_0x\langle S_z \rangle(\alpha - \beta) \quad (3)$$

where E_0 is the luminescence energy for $B = 0$. Gaj *et al* (1978a, b) find $\beta/\alpha \approx -4$ and E decreases with increasing B (and $\langle S_z \rangle$).

3.2.1. Effects of applied magnetic fields on time-integrated luminescence. Figure 2(c) shows effects of applied fields on emission of $Cd_{1-x}Mn_xTe$ for $x = 0.09$. It is apparent that with increasing B (i) the spectrum shifts to lower energy ($g_{\text{eff}} \approx 95$); (ii) the peaks become narrower; and (iii) the intensity ratio of the 'free'-exciton peak to that of the acceptor-bound exciton peak increases. We suggest that (ii) and (iii) are due largely to increased localisation of excitons in the disordered crystal because of increased magnetic binding energy (but see Heiman *et al* 1986). Similar effects are seen for $x = 0.2$ (figure 3) and $x = 0.3$. However, initial broadening occurs for $x = 0.2$ for application of relatively small fields (≈ 3 T); this is due to the spread of magnetic levels before localisation becomes significant (see § 3.2.2).

We show in figure 9 the dependence of luminescence peak position on B for $x = 0.09, 0.2$ and 0.3 . The calculated curves were obtained from equation (3) using values for the parameters given in table 1. If we take $\alpha N_0 = 220$ meV and $\beta N_0 = -880$ meV (Gaj *et al*

Table 1. Parameters used in equations (2) and (3) to calculate the curves in figure 9.

x	$(\alpha - \beta)N_0S_0$ (meV)	$T_0(x)$ (K)
0.09	1219	5.6
0.2	466	7.6
0.3	268	11.6

1978a, b) we obtain, using the second column of table 1 and the assumption that the emission is due to the $M_J = -\frac{1}{2} \rightarrow -\frac{3}{2}$ transition, $S_0 = 1.11, 0.42$ and 0.24 for $x = 0.09, 0.2$ and 0.3 respectively; the fall in S_0 from $\frac{3}{2}$ is due to increased antiferromagnetic pairing with increasing x . Magneto-reflectivity studies by Gaj *et al* (1978b) indicate values of S_0 of about 1, 0.71 and 0.52 for closely similar manganese concentrations. Comparison of our values of S_0 with those of Gaj *et al* (1978b) suggests that the simple approach outlined above for magneto-optical effects in $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ works reasonably well for $x = 0.09$ but is less applicable for higher values of x (see also Wolff 1988). We should add that Heiman *et al* (1987) have recently found that at high fields the magnetisation of $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ can be decomposed into a Brillouin component and a linear component. However, in the range of fields covered by us addition of a linear component does not significantly improve the fit to our data.

3.2.2. Time-resolved luminescence in a magnetic field. Figure 5(b) shows the effect of an applied magnetic field of 6 T on the time evolution of luminescence at different energies through the exciton emission band for $x = 0.2$ (cf figure 3(b)). At 1.870 eV, on the high-energy side of the band, the rise-time is not appreciably affected by B . However, at lower energies (1.848 and 1.841 eV) there is a substantial increase in rise time, from about 200 ps at $B = 0$ to ≈ 600 ps at $B = 6$ T. This may be due in part to localisation of excitons which prevents ready access to lower-energy localised states. At 1.832 eV the rise time is less strongly affected by the field because this emission is dominated by the acceptor-bound excitons. The rapid rise near $t = 0$ for 1.841 eV shows that there is a contribution to the decay profile by acceptor-bound excitons. For $x = 0.3$ the emissions from disorder-localised and acceptor-bound excitons are not resolved and the effects of B on the exciton dynamics are less pronounced (Wong 1987).

Figure 10 shows the time-dependent shift to lower energies of the peak emission at 1.8 K for $x = 0.09, 0.2$ and 0.3 with different values of B . Information about $x = 0.09$ is less detailed than for the other samples because of lower intensity. However, it is apparent from figure 10 that application of $B = 6$ T reduces the magnitude of the time-dependent shift partly because of spin alignment, which contributes to the shift at $t = 0$, and partly because of field-induced localisation. For $x = 0.2$ the magnitude of the time-dependent peak shift to lower energy increases from a maximum of ≈ 11 meV at $B = 0$ to ~ 16 meV at $B = 4$ T (see also Oka *et al* (1986) who find a similar behaviour for $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$). For higher field strengths the shift falls, and for $B = 8$ T it is less than for $B = 0$. These effects are explainable if we assume that there is a spatial distribution of magnetic energies, ΔE , associated with the luminescence, arising from variation in magnetic environment of excitons. The initial increase in the shift with increasing B is associated with increasing ΔE . However, for $B \geq 4$ T movement to disorder-associated lower-energy states becomes restricted and the shift becomes smaller. It seems that the latter effect is more important for $x = 0.09$.

For $x = 0.3$ we observe similar effects of B on the time-dependent shift. However, the decrease in magnitude of the shift occurs for higher B (≥ 6 T) since increased localisation is required at higher x . At this concentration a slowing of the intensity decay is observed in the 200–400 ps range for low values of B but the detailed nature of the relaxation in this time range is not understood.

4. Discussion

The relative contributions to the localisation energy of excitons in $Cd_{1-x}Mn_xTe$ by ionic disorder and magnetic disorder are not readily separable experimentally. It is possible to estimate the energy reduction of the relaxed exciton emission from that of the free exciton (measured in reflection) using the theory of Cohen and Sturge (1982) and this gives a value of ≥ 1 meV for $x = 0.2$. This is much smaller than the observed shift of 20 meV (§ 3.1.1). However, Dietl and Spalek (1982, 1983) have shown that the exciton energy is shifted to lower values for zero applied field by the effective internal magnetic field, and Harris and Nurmikko (1983b) have estimated that this shift for $Cd_{0.9}Mn_{0.1}Se$ is ~ 15 meV. These comparisons suggest that our observed shift for $Cd_{1-x}Mn_xTe$ for $x = 0.2$ is largely magnetic in origin.

The existence of a non-zero local field for $B = 0$ caused by polarisation of Mn^{2+} ions in $Cd_{0.9}Mn_{0.1}Se$ by localised carriers has been demonstrated by Heiman *et al* (1983) using spin-flip Raman scattering and similar measurements have been reported for $Cd_{1-x}Mn_xTe$ (for a recent review see Ramdas and Rodriguez 1988). The variation in the local magnetic field from site to site will cause inhomogeneous broadening of exciton luminescence which will be reduced at higher temperatures (§ 3.1.1). Reduction of the local magnetic field at higher temperatures will also cause a shift in the luminescence to higher energy (§ 3.1.1) and will give rise to a reduction in magnitude of the time-dependent spectral shift (Itoh and Komatsu 1987).

Awschalom *et al* (1987) used band-edge excitation with 4 ps pulses of circularly polarised light in a pulse/probe study of the dynamics of magnetic polaron formation in $Cd_{1-x}Mn_xTe$ for $x = 0.2$. Using a SQUID magnetometer they concluded that the polaron formation time was ≈ 250 ps, a time associated with the polarisation of local Mn^{2+} spins. This time is very much shorter than the 10–100 ms spin-lattice relaxation, T_1 , measured in very dilute Mn^{2+} systems at low temperatures. However, the work of Harris and Yngvesson (1968) on paramagnetic $(IrCl_6)^{2-}$ complexes in $(NH_4)_2PtCl_6$ showed that T_1 for single iridium ions rapidly decreases with increasing iridium concentration and they suggested that this effect is due to cross-relaxation to clusters of three or more exchange-coupled ions; for such clusters modulation of the isotropic exchange by lattice vibrations can induce rapid relaxation. Although they measured a decrease in T_1 of more than three orders of magnitude on increasing the iridium concentration from 0.67% to 8.5%, it seems that this effect is not adequate to explain our results.

Recently Zayhowski *et al* (1987) have studied the dynamics of polaron formation in $Cd_{1-x}Mn_xSe$ and $Cd_{1-x}Mn_xTe$ and have concluded that a spin diffusion mechanism makes a major contribution to the rapid formation time. In the exciton the hole is more localised than the electron and is more important in determining the energetics of magnetic polaron formation. However, for the magnetic polaron to form spin must diffuse to magnetic ions external to the polaron, and Zayhowski *et al* (1987) conclude that the delocalised electron is an effective intermediary. During the diffusion process magnetic energy is given to carriers in the form of kinetic energy or to lattice phonons.

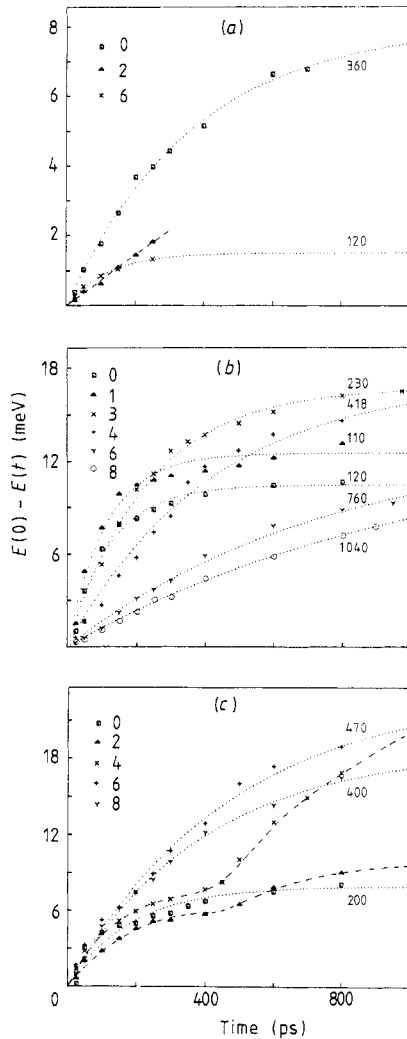


Figure 10. Effect of applied magnetic fields (given in keys in T) on the time dependence of the spectral red shift of the luminescence of $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ at 1.8 K for $x =$ (a) 0.09, (b) 0.2 and (c) 0.3. The values on the curves are of τ in ps.

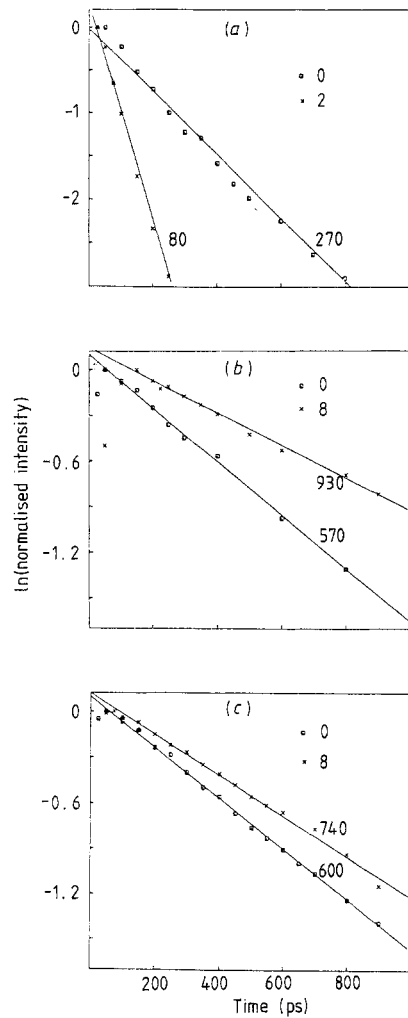


Figure 11. Time dependence of the peak intensity of the luminescence of $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ at 1.8 K in the absence and presence of a magnetic field. $x =$ (a) 0.09, (b) 0.2, (c) 0.3. The key gives the values of β in T. The values on the lines are of τ in ps.

We have found that application of a sufficiently large B gives rise to magnetically induced localisation of excitons, preventing migration to lower-energy states (§ 3.2.2). The effect of B on the wavefunction of the exciton is characterised by the dimensionless parameter $\gamma = \hbar\omega_c/R$ (Yafet *et al* 1956), where $\omega_c = eB/m^*$ is the cyclotron frequency with m^* an effective mass, and R is the exciton Rydberg. Using an estimated value of $R \approx 9$ meV for $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ we find $\gamma \approx 0.7$ for $B = 8$ T. This relatively small value of γ reduces the radius of the exciton by only a few per cent and has little effect on the localisation energy and luminescence intensity.

Zucker *et al* (1987) have reported results of measurements of resonant Raman scattering on $\text{GaAs}/\text{Ga}_{0.73}\text{Al}_{0.27}\text{As}$ quantum wells which may have relevance to our

results. They find that application of a magnetic field perpendicular to the plane of the wells causes a ‘giant’ increase in the intensity of the Raman scattering of the 36.6 meV LO phonon of GaAs at 15 K when the incident laser light is resonant with the heavy-hole exciton transition. This increase is partly due to a reduction in the homogeneous exciton linewidth and partly to an increase of the exciton oscillator strength. The latter is due to a contraction of the exciton wavefunction by B (compare above). The exciton linewidth Γ shows an activated behaviour, $\Gamma \approx \exp - (\Delta\varepsilon/k_B T)$, and $\Delta\varepsilon$ is determined by phonon-assisted transitions between localised and delocalised states. The localised states are due to impurities or structural defects. Zucker *et al* (1987) find that $\Delta\varepsilon$ increases with increasing B , analogous to our magnetic-field-induced localisation, but there is as yet no detailed understanding of the localisation mechanism in either case.

Application of B also has consequences for the lifetime of the energy-dependent (see figure 6) peak intensity. For $x = 0.2$ the effect of B is similar to a reduction in temperature, preventing migration to non-radiative decay centres and increasing the lifetime (figure 11(b)); at $B = 8$ T the decay time is ~ 930 ps, comparable to the value expected for allowed electric-dipole decay. However for $x = 0.09$ the application of $B = 2$ T reduces the lifetime to ≈ 80 ps (figure 11(a)), presumably due to enhanced non-radiative decay. There is no clear-cut explanation of the enhancement of the non-radiative recombination by B for this concentration, although ionisation of the exciton is a possibility (see Heiman *et al* 1986).

Finally, we point out that Itoh and Komatsu (1987) have also carried out picosecond time-resolved measurements on luminescence of $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ for $x = 0.2$. In contrast with our results and also to those of Oka *et al* (1987), they find that the application of B decreases the magnitude of the time-dependent spectral red shift without any initial increase. Itoh and Komatsu suggest that the time dependence of the red shift can be decomposed into a fast initial change ($t \leq 40$ ps) characteristic of magnetic polaron formation, and accounting for most of the spectral shift, followed by a later diffusive component an order of magnitude slower. Our data (figure 10) suggest that there is more justification for this interpretation for $x = 0.2$ than for $x = 0.09$ or 0.3.

In conclusion, it will be apparent from our discussion of $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ that although there are broad areas of understanding of the energetics and dynamics of excitons in this complex system, there are points of detail that remain elusive. Recent studies of the energetics of excitons in $\text{Zn}_{1-x}\text{Mn}_x\text{Te}$ (Hayes *et al* 1988) suggest that this system is intrinsically less complex than $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ and it is our intention to extend our picosecond studies to the zinc compound.

Appendix

The photoluminescence peak of $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ for $x = 0.45$ is shown in figure A1. At the higher manganese concentration there are two intense peaks rather than one (cf figures 2 and 3); the higher-energy peak is associated with disorder-localised excitons and it is possible that the lower-energy peak is an internal transition, ${}^4\text{G} \rightarrow {}^6\text{S}$, of Mn^{2+} (Lee and Ramdas 1984, Moriwaki *et al* 1982, Vecchi *et al* 1981). With an excitation energy of 2.206 eV (close to the high-energy limit of our dye laser) we are below the free exciton energy, estimated from $E_{\text{ex}} = 1.595 + 1.592x$ to be 2.311 eV for $x = 0.45$ (Lee and Ramdas 1984). Increasing the excitation energy from 2.195 to 2.206 eV increases the intensity of the exciton relative to the internal Mn^{2+} luminescence, and the exciton peak increases in energy by ~ 10 meV, from 2.167 to 2.176 eV (figure A1). Also the linewidth

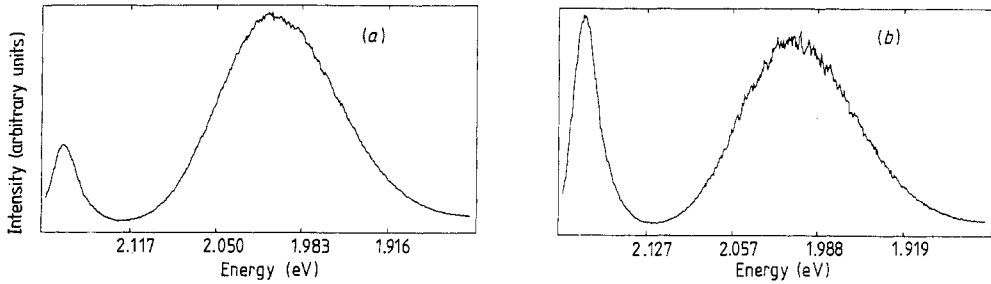


Figure A1. Time-integrated luminescence of $\text{Cd}_{0.55}\text{Mn}_{0.45}\text{Te}$ at 4 K using laser excitation of energy (a) 2.195 eV and (b) 2.206 eV.

of the exciton luminescence for $x = 0.45$ (FWHM = 23 meV) is smaller than for $x = 0.3$ (FWHM = 25 meV; see § 3.1.1) because of access to a smaller part of the spectrum of localised states in the higher band gap system.

Neff *et al* (1987) have recently proposed that the 2.17 eV band is due to a transition from the ^4G state of Mn^{2+} to the maximum of the valence band. It is difficult experimentally to pin down the degree of localisation of this broad transition. The lifetime of the 2.17 eV band was found by Gebhardt *et al* (1981) to be of the order of microseconds, consistent with a fairly localised spin-forbidden transition. The ^4G state has a considerable effect on the dynamics of carriers, providing an important centre for capture and recombination.

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