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Presentation

Exciton properties in quantum well structures of CdTe/CdMnTe

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In this review, properties of strongly localised excitons are discussed. Strongly localised excitons are observed at low temperatures in some of CdTe/CdMnTe heterostructures. The effect of strong localisation of excitons becomes more pronounced in structures with large Mn fraction in the CdMnTe barriers and also in some of modulation *n*-type doped structures. In consequence of a strong localisation, quite new properties of excitons are observed. Several such properties are discussed in this work.

1. Introduction

In this review, we describe properties of strongly localised excitons, which are observed in quantum well (QW) structures of CdTe/CdMnTe. We analyse the influence of magnetic interactions and strong potential fluctuations in a QW plane on exciton dynamics, on formation and recombination rate of free and bound excitons, on recombination energy of excitons, and also on strength of exciton–phonon coupling. We will show that properties of strongly localised excitons closely resemble those of zero-dimensional (0D) excitons in quantum dot (QD) systems. Their properties significantly deviate from those reported for, *e.g.*, GaAs/AlGaAs structures with atomically flat interfaces.

2. Dynamics of excitons

Several groups of researchers have studied exciton dynamics in QW structures of CdTe/CdMnTe. They reported a wide spread of the photoluminescence (PL) decay times, and explained their results assuming quite contradictory exciton properties. At temperature 2 K and for wide (typically 4–10 nm wide) CdTe QWs, the reported PL decay times varied between 100 ps [1]–[4] and 300–350 ps [4], [5]. O'Neill *et al.* [5] suggested that 350 ps, *i.e.*, the longest PL decay time measured, is the radiative decay time of free excitons (FEs). They also implied that the PL decay times in the range of 100 ps, as reported by other authors, are due to a competition of nonradiative recombination of FEs, which shortens the PL decay.

This explanation assumes that excitons at 2 K are free and are not trapped by either potential fluctuations or by trace impurities present in a QW plane. If effective, these two trapping processes can significantly reduce the PL decay time. Considering the latter process, a relatively large contribution of bound (neutral donor bound (DBE)) excitons was inferred from the PL and the optically detected cyclotron resonance (ODCR) experiments of the present author [3]. That is why we will first discuss the rate of DBE formation in CdTe/CdMnTe QW structures and try to evaluate the role played by donor-type trace impurities in the PL process.

3. Interlink between localised and DBE excitons

An example of the PL spectrum observed for one of the CdTe/CdMnTe QW structures is shown in Fig. 1. A two-line PL spectrum is observed, which the author relates to a simultaneous observation of FE and DBE excitons. Only in the

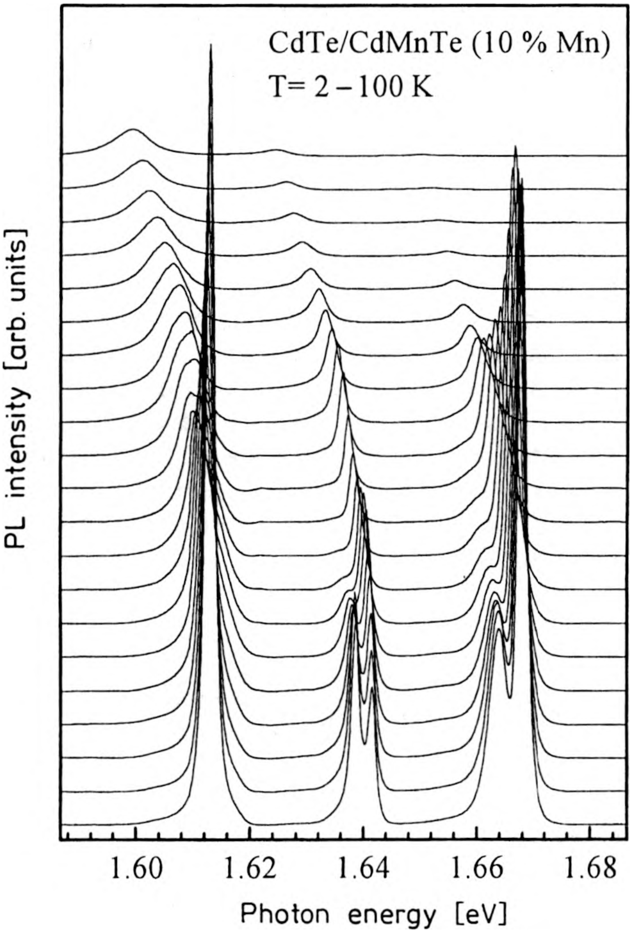

Fig. 1. Temperature dependence of the PL spectrum of CdTe/CdMnTe QW structure with 10% of Mn in the CdMnTe barriers, consisting of three CdTe QWs, 10 nm, 6 nm and 4 nm wide. The PL was measured under cw excitation conditions and for constant excitation intensity (the 514.25 nm line of an argon laser). The temperature varied between 2 K and 100 K.

intentionally *n*-type doped structures such a two-line PL spectrum can be attributed to simultaneous observation of free and negatively charged excitons [6], [7]. The latter PL emission, due to so-called trions, shows characteristic polarisation dependences of absorption (PL excitation) and PL spectra [6], [7], which is not observed for the low-energy PL shown in Fig. 1.

In most of the cases the FE and DBE PLs are spectrally separated, as can be seen in Fig. 1. Then, the contribution of the FE and DBE recombination transitions to the PL can be easily resolved. This enables us to follow intensity and temperature dependences of the FE and DBE transitions. The DBE emission saturates fast with an increasing excitation density and also decreases fast with an increasing temperature. The DBE PL is not observed above 40 – 50 K, as can be seen in Fig. 1. The FE PL rises with increasing excitation density and is observed up to much higher temperatures. These properties of the two PL transitions allow us to identify their contribution to the low-temperature PL of the QW structures studied.

The DBE contribution to the PL can also be decreased by an applied microwave power at cyclotron resonance (CR) conditions in the ODCR experiments. The results of the relevant experiment are shown in Fig. 2. Microwave-heated free carriers under the CR conditions can impact ionise DBE excitons. DBE excitons dissociate from the donor sites and are then free to move as FE excitons in a QW plane. Thus, interaction with microwave-heated hot carriers can increase the concentration of the FE excitons [8], which is observed in the ODCR study as a decrease of the DBE PL and an increase of the FE PL, see Fig. 2.

Despite a common observation of the DBE PL, our investigations [9], [10] do not support the model which relates the spread of the PL decay times to FE trapping at donor sites. We explain the spread by pronounced effects of localisation of excitons in a QW plane, mainly induced by fluctuations of a QW width [9], [10].

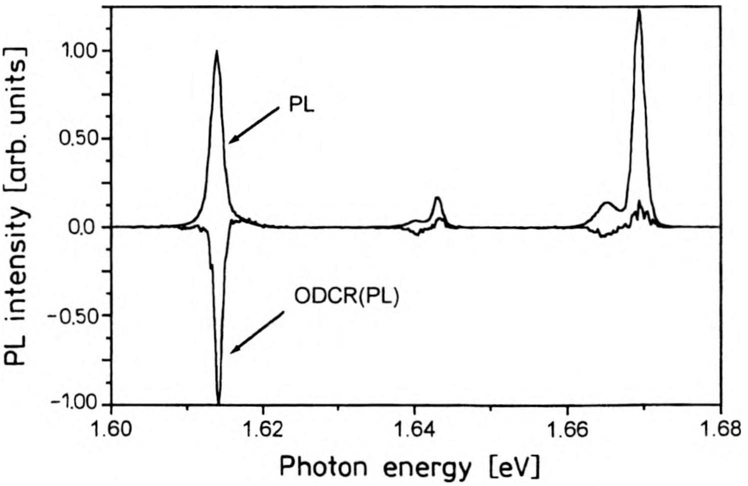

Fig. 2. Influence of microwave radiation on 2 K excitonic emission from CdTe/CdMnTe QW structure with 10% of Mn in the barriers, consisting of three CdTe QWs 10 nm, 6 nm and 4 nm wide.

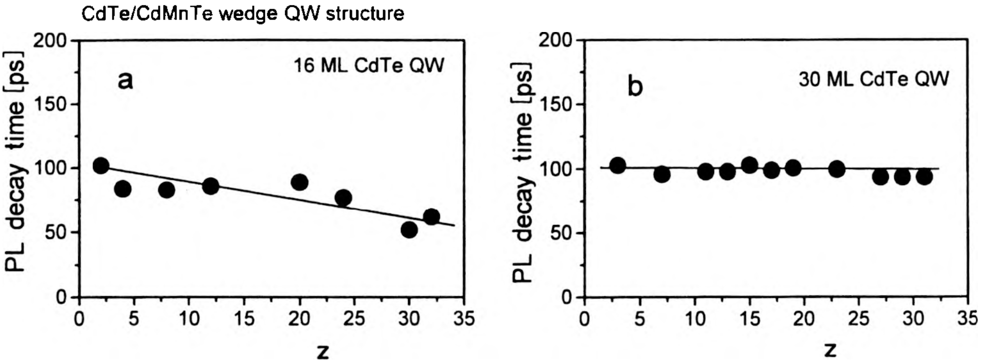

Fig. 3. Dependence of the decay time of the FE emission in 16 ML (a) and 30 ML (b) QWs in the δ-doped with In (in the middle of CdTe QW) wedge CdTe/CdMnTe structure. Doping level varies within the length of the sample in the z-direction.

To verify this model we studied properties of excitons in CdTe/CdMnTe QW structures, which were δ-doped with In either in the middle of CdMnTe barriers, or in the middle of CdTe QWs. We will show the experimental data for two CdTe QWs, which were doped in the middle, with the doping level varying in four steps within the length of the sample. The so-called wedge QW structure contains an undoped region, where donor impurities are due to some inadvertent contamination of the structure, lightly and moderately doped regions, and heavily doped regions, with the doping level exceeding 10^{12} cm^{-2}. In Figure 3**a**,**b**, a remarkable property of the PL kinetics of the FE and DBE transitions in the 16 ML and 30 ML wide CdTe QWs is shown. For the narrower QW, the decay time of the FE PL only slightly shortens with an increasing doping level (see Fig. 3**a**). Moreover, for the 30 ML wide QW, the one with the strong localisation effects, the decay time of the FE PL, which is about 100 ps, does not change when moving the excitation spot within the length of the sample, *i.e.*, with a varying doping level (see Fig. 3**b**).

The results shown in Fig. 3 were obtained under nonresonant excitation conditions. We found that the relative intensity of the FE and DBE transitions critically depends on the excitation energy. For the resonant excitation conditions (at light hole FE energy) a strong FE PL is observed, with only a weak DBE contribution (even for doped regions of the QW). In turn, once the excitation energy is shifted into the continuum of the electron-hole states, only the DBE emission is observed [10].

All these results are strikingly different from those observed for the bulk samples, or for QW structures with weak localisation effects. DBE excitons in bulk samples, or in QW structures with weak localisation effects, are formed by either a subsequent trapping of a free electron and then of a free hole, or by trapping of a FE. Apparently, the second mechanism is less efficient in CdTe/CdMnTe QW structures with strong localisation effects. Its efficiency can be increased at elevated temperature [10] or by delocalising excitons by interaction with microwave-heated hot carriers.

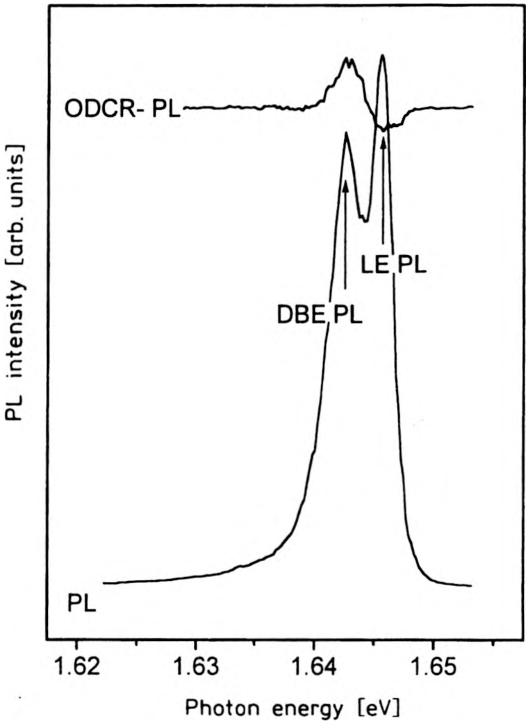

Fig. 4. Influence of microwave radiation on 2 K excitonic emission from 10 nm wide QW in CdTe/CdMnTe structure with strong localisation effects. PL of localised excitons (LE) is reduced in the intensity by interaction with hot carriers heated by microwave radiation.

The latter possibility is presented in Fig. 4, where the response of the PL to the microwave power applied is shown. The response to the microwave power is different from that shown in Fig. 2, when measured for the structure with a weak localisationof excitons. Free carriers heated by microwave radiation can scatter at localised excitons, resulting in their delocalisation and thus in the enhanced rate of the DBE formation. Thus, to get efficient DBE formation rate we must delocalise excitons, which must freely move in a QW plane to be trapped at donor sites. This result indicates that a weak link between free and bound excitons relates to pronounced localisation effects of FE excitons, and is only observed in QWs with strong localisation.

4. Effects related to formation of magnetic polarons

The CdMnTe is a diluted magnetic semiconductor (DMS). In the narrow CdTe QWs, with the width of 3 mm and less, the exciton wave function can penetrate to the magnetic CdMnTe barriers. Then the low-temperature PL properties are affected by formation of magnetic polarons and by magnetic fluctuations in the CdMnTe barrier [11]. The effect can still be increased by a small Mn inter-diffusion to QW regions. These effects, together with an initial localisation of excitons caused by QW width fluctuations, result in a large width of the PL lines, in a red-shift of the PL energy (by the magnetic polaron energy), and in changes in the PL kinetics.

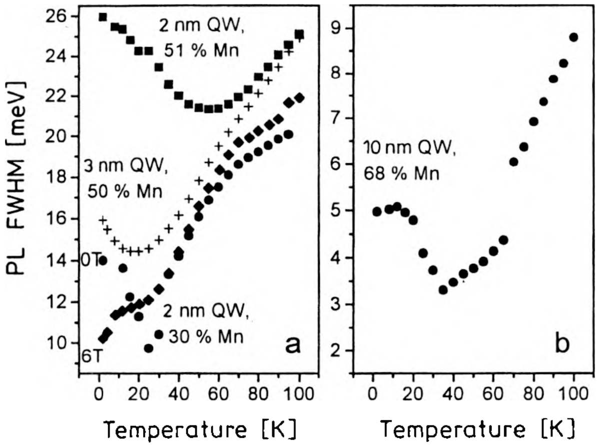

Fig. 5. Temperature dependence of the width of PL (full width at half maximum (FWHM)) for excitons in the 2 nm and 3 nm wide CdTe QWs in CdTe/CdMnTe structures. Effect of an external magnetic field on width of the PL line and on its temperature dependence is shown for excitons in the 2 nm QW in the sample with 30% Mn fraction in the CdMnTe barriers (a). Figure b shows FWHM(T) for excitons in 10 nm QW in the structure with 68% Mn fraction in the CdMnTe barriers.

In Figure 5a, an example of such effects is shown. The temperature dependence of the width of PL lines was measured for excitons in narrow CdTe QWs. The width of the PL line first narrows with an increasing temperature, but then starts to increase at higher temperatures. The narrowing of the PL lines is accompanied by changes of the PL kinetics. A fast component of the PL kinetics, which appears only at the lowest temperatures, and is related to the formation of magnetic polarons [9], disappears at elevated temperatures (above 10–20 K). This change of the PL kinetics is due to the temperature-induced destruction of a magnetic ordering.

In Figure 5a, temperature dependences of the PL line width measured at 0 T and 6 T external magnetic field for a narrow QW in one of the structures under study are compared. A strong external magnetic field saturates magnetic moments on Mn^{2+} ions in the CdMnTe barriers and thus reduces effects due to magnetic interactions between excitons and magnetic barriers. The saturation of magnetisation eliminates the main contribution to the PL line width. Results shown in Fig. 5a thus indicate that the PL broadening in narrow CdTe QWs is related to magnetic fluctuations in the CdMnTe barriers. We conclude that nearly 50% of the initial width of the PL lines from the narrow QWs is of the "magnetic origin", *i.e.*, relates to effects of magnetic fluctuations.

5. In the limit of a strong localisation

For wider QWs wave function of excitons does not penetrate to magnetic barriers. The anomalous FWHM(T) dependence of excitons in the 10 nm wide CdTe QW, as shown in Fig. 5b, cannot thus be explained by a decrease of magnetic fluctuations at elevated temperatures, resulting in the observed reaction of the energy distribution of magnetic polarons, and, therefore, must be of different origin. We relate this anomalous PL temperature dependence to the effects of strong localisation of excitons in CdTe QWs with large Mn fraction in the CdMnTe barriers.

Even a weak localisation of excitons can result in a change of exciton-phonon interaction and thus in a modification of PL dynamics, and of temperature dependences of PL line width and of PL kinetics [9], [12], [13]. First, localisation reduces coherence length/area of excitons and thus increases the PL decay time [12]. The PL line is then inhomogeneously broadened and PL migration among localised sites can be observed [13]. Second, temperature dependences of PL line width and of PL decay time can deviate from linear ones, expected for free excitons in ideal QW structures [9], [10], [12], [14]. A linear dependence results from an increase of the density of acoustic phonons with increasing temperature, which can be approximated by a term proportional to the temperature [15]. For strongly localised excitons, interaction with acoustic phonons is too weak at low temperatures to delocalise these excitons. In consequence, excitons remain site-localised and their PL kinetics and PL line width are temperature independent [14].

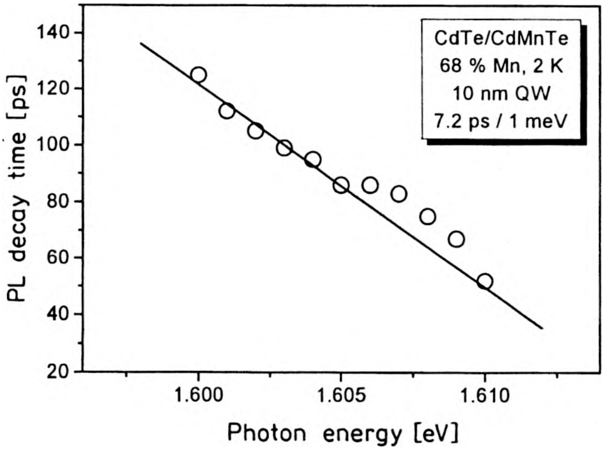

Fig. 6. Energy dependence of the PL decay time measured at 2 K for excitons in the 10 nm wide QW in the CdTe/CdMnTe sample with 68% Mn fraction in the CdMnTe barriers.

We measured time-resolved properties of PL emissions in order to explain anomalous temperature dependence of the type shown in Fig. 5b. This anomalous dependence was observed only for excitons in wide QWs, showing strong localisation effects. Figure 6 shows the energy dependence of the PL kinetics observed at 2 K for excitons in the 10 nm wide QW in the sample with 68% Mn fraction in the CdMnTe barriers. The PL decay time is the shortest at the high-energy wing of the PL (about 50 ps) and varies across the whole PL line. Due to a large density of localised states in this QW, and due to a relative weak exciton-phonon coupling, excitons at 2 K do not thermalise to sites of the lowest energy within their decay time, and, in consequence, energy dependent PL decay is observed across the whole PL emission. The observed energy dependence of the PL decay time is nearly linear (with a slope of 7.2 ps/meV at 2 K), which has no obvious explanation at present [14].

As a consequence of strong localisation effects and slow energy thermalisation, a relatively wide inhomogeneously broadened PL line is observed. At elevated temperatures, phonon-assisted exciton migration/tunnelling becomes more efficient, and excitons can faster empty localised states of higher energy. Phonon-assisted exciton migration to states of lower energy results in the observed narrowing of the PL line. At temperatures being further elevated excitons are still localised, but migration/tunnelling of excitons can now proceed also to states of higher energy. The width of the PL lines increases now. It further increases at higher temperatures, when the delocalised excitons scatter with acoustic phonons.

We point out here that the similar anomalous temperature dependence of PL line width and also of PL kinetics was observed for 0D excitons in quantum dot structures [16], [17]. These properties of 0D excitons were explained by the tunnelling of excitons between quantum dots which differed in size. Thus, by analogy, we relate the properties shown in Figs. 5a and 6 to processes of phonon-assisted migration/tunnelling of excitons between variaus localised sites, *i.e.*, sites in a QW plane of diffreent potential energy.

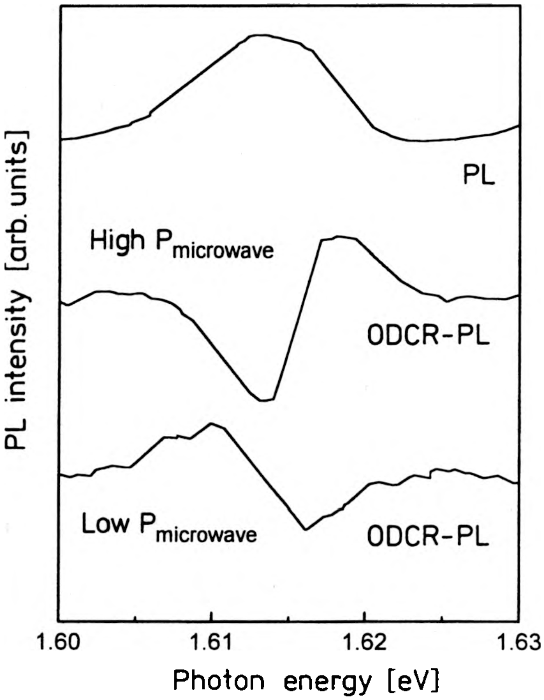

Fig. 7. 2 K PL and ODCR-PL spectra of localised excitons in 10 nm wide QW in CdTe/CdMnTe QW structure with strong localisation effects.

Exciton tunnelling can be enhanced by interaction with microwave-heated hot carriers. In consequence, we could induced changes of the PL line width by applying microwave radiation. At low microwave power, interaction of microwave-heated hot carriers with localised excitons increases their tunnelling rate to sites of lower potential energy. Thus, the PL line narrows and shifts down-in-the-energy. This results in a derivative like response shown in Fig. 7. For an increased microwave power, tunnelling can also occur to sites of higher energy, which also results in a derivative like response of the PL to microwave power applied, but of the opposite sign than that shown for data taken at low microwave power. This time, the PL line broadens and shifts up-in-the-energy. Response of the PL to microwave power was measured for detection set in phase with modulated microwaves.

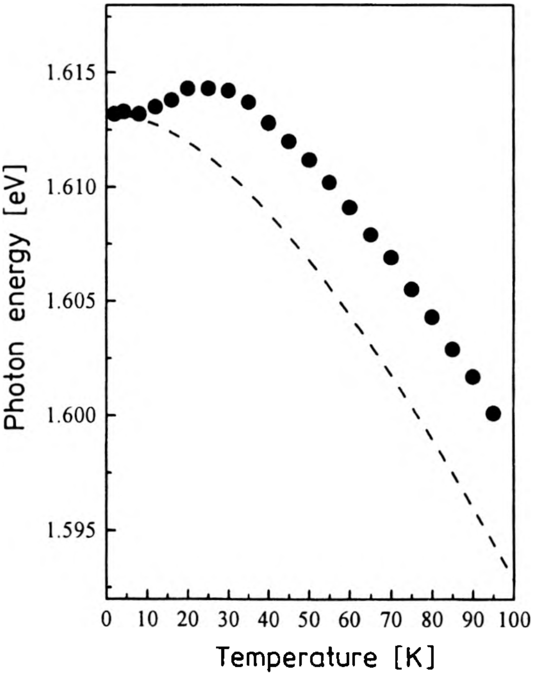

Fig. 8. Temperature dependence of the PL emission energy from the 10 nm wide QW in the sample with 68% Mn fraction in the CdMnTe barriers. The temperature dependence of the CdTe band gap is also shown (broken line). Emission energies are normalised to the same value at 0 K.

The temperature-induced migration/tunnelling of excitons to sites of higher energy is also reflected in a "strange" temperature dependence of the energy of the PL emission ($E(T)$), as shown in Fig. 8. The PL energy first increases, before decreasing, when it follows the expected temperature dependence of the band gap. Once more such anomalous temperature dependence was reported for 0D excitons in QD structures [16], [17]. Thus strongly localised excitons closely resemble the 0D excitons in quantum dot structures.

6. Hot PL of unthermalised excitons in quantum wells with strong potential fluctuations

Due to a strong exciton-phonon coupling, FE excitons thermalise fast their excess kinetic energy, following a nonresonant photo-excitation [10], [12], [15]. Hot carriers/excitons dissipate excess energy by a multi-phonon emission of optical phonons, which is a fast thermalisation process, occurring in a subpicoseconds time scale. The remaining energy is dissipated by an emission of acoustic phonons. The latter process is less efficient and proceeds in one-to-few picosecond time scale, *i.e.*, the time scale comparable to radiative decay time of FEs (10–50 ps). Not surprisingly, some evidence of nonequilibrium distribution of excitons was reported [18].

As already indicated, in a real QW structure (with rough interfaces) excitons can be localised. Such localised excitons can have an excess of potential energy, and not only of kinetic energy. This is because the energy of localised excitons at $\mathbf{k} = 0$ site-fluctuates, depending on their position in a QW plane. For further discussion it is also important that localisation of excitons/carriers results in a reduced strength of exciton-phonon coupling [15]. These two facts led us to the observation of a new type of the hot PL in structures with a very strong localisation of excitons, as shown in Fig. 9. We observed a series of PL steps at the high-energy wing of the PL, with

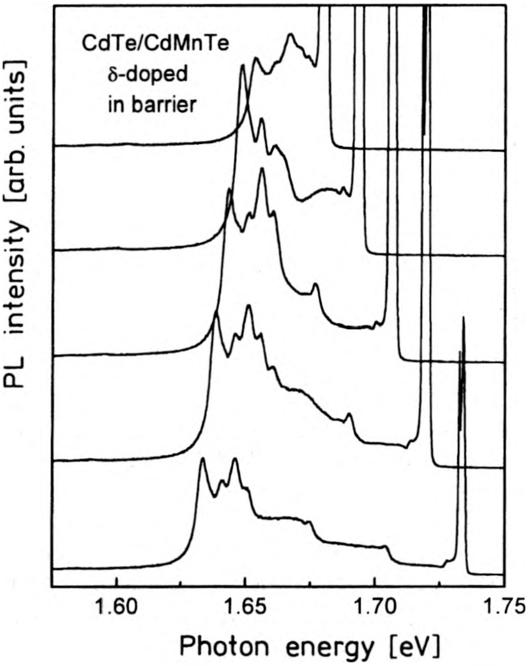

Fig. 9. Hot PL spectrum in modulation doped with In (in CdMnTe barriers) CdTe/CdMnTe structure. PL was measured at 2 K under pulsed excitation. The sharp line at high-energy wing of the PL is due to laser. Excitation energy was changed to follow changes of the PL emission.

steps separated by the LO-phonon energy. These steps are observed below the laser line, separated from the excitation energy exactly by the LO-phonon energy, when excitation energy overlaps the high-energy wing of the PL.

The authors of [19]–[21] reported on PL peaks separated by the LO-phonon energy. Such PL peaks were detected for both II–VI [19], [20] and III–V heterostructures [21], and, recently, we have detected them for the ZnCdSe/ZnSe heterostructures. However, in all these cases, the sharp PL peaks were observed at each multiple of the LO-phonon energy, and not the PL steps, as shown in Fig. 9. It was concluded from the PL kinetics measurements that LO-phonon-separated PL peaks are not due to the Raman process. These peaks were tentatively explained by a phonon-assisted emission of separately localised electrons and holes.

We have already indicated that the hot PL spectrum shown in Fig. 9 has a different character from the hot PL emissions reported in [19]–[21]. We observe a step-like PL at the high-energy wing of the PL emission. This hot PL was observed in addition to a complicated excitonic part of the PL, explained elsewhere [22].

Steps can only be observed if coupling with acoustic and optical phonons is of the same strength, which strikingly differs from the situation found for FE excitons in QW structures with flat interfaces [10], [12], [15]. Energy dissipation is still slightly faster during the LO-phonon emission and is slightly slower during the acoustic phonon emission, which explains the step-like shape of the PL at high-energy wing, with a slight enhancement of the PL intensity at each of the LO-phonon multiple (Fig. 9).

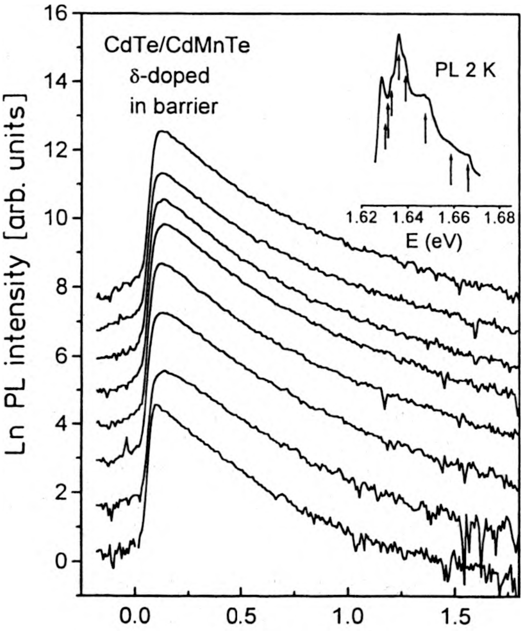

Fig. 10. 2 K PL kinetics in modulation doped CdTe/CdMnTe structure measured at 8 different spectral positions within the PL, as shown in the inset.

Figure 10 shows the PL kinetics measured for the detection set at 8 different energies within the anomalous step-like PL spectrum. Identical PL kinetics are observed at different photon energies within the whole PL emission, which means that the PL decay time is now faster than the thermalisation time. Otherwise, fast thermalisation at high-energy wing of the PL should result in a known energy dependent PL kinetics, as discussed, *e.g.*, in [13]. The step-like PL disappears fast with an increasing temperature, when excitons become delocalised. Thus, all our data indicate that the observed anomalous step-like hot PL directly or indirectly relates to a strong exciton/carrier localisation.

7. Conclusions

The present studies show that excitons in some of QW structures of CdTe/CdMnTe, especially in those with large Mn fraction in the CdMnTe barriers, have remarkably different properties from those observed, *e.g.*, in GaAs/AlGaAs structures. We report here on several effects to support this statement. These effects are related to a strong localisation of excitons occurring at low temperatures. In particular, we show that a new type of exciton dynamics is observed. We also show that a dramatic reduction of an exciton-phonon coupling results from a strong localisation. In consequence, we observed, *e.g.*, a new step-like hot PL, not detected in other systems. Finally, we also show that the FE-to-DBE link is broken by in-plane exciton localisation.

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