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Mn^{2+} intra-shell recombination in bulk and quantum dots of II–VI compounds

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Abstract

Origin of a fast component of the photoluminescence (PL) decay of Mn^{2+} intra-shell $^4T_1 \rightarrow {}^6A_1$ transition in bulk and quantum dot structures is discussed based on the results of PL, PL kinetics and optically detected magnetic resonance experiments. It is demonstrated that a fast component of the PL decay, reported previously for quantum dot structure and related to quantum confinement effects, is also observed in bulk samples and is very much enhanced upon generation of free carriers. The appearance of this fast component of the PL decay is related to a very efficient spin cross-relaxation between localized spins of Mn ions and spins of free carriers.

Keywords: Luminescence; Optically detected magnetic resonance; ZnMnS; CdMnTe; Spin interactions

1. Introduction

It was proposed by Bhargava and co-worker [1,2] that quantum confinement effects in low dimensional semiconductor structures result in a dramatic reduction of the lifetime of Mn^{2+} intra-shell $^4T_1 \rightarrow {}^6A_1$ photoluminescence (PL). Very fast Mn^{2+} PL decay, shortened from ms to ns, was reported by Bhargava and Gallagher [2] for Mn-doped ZnS quantum dots and was tentatively explained by quantum-confinement-enhanced s–p hybridization with the d states of Mn ions.

The model was recently questioned by Bol and Meijerink [3], who observed a normal ms-range PL decay of the Mn^{2+} PL in quantum dots of ZnMnS and thus concluded that quantum confinement does not affect the rate of radiative Mn^{2+} recombination. Bol and Meijerink [3] related the fast component of the PL decay to a fast decay of an underlying low energy wing of the blue band ZnS PL emission.

In this work we report the observation of a fast component of the Mn^{2+} PL decay, which is found for both bulk ZnMnS crystals and for CdMnTe quantum dots. We argue that this fast component of the PL decay time is of a different origin than that proposed by Bhargava [1,2] and is due to very efficient spin cross-relaxation effects between localized spins of Mn ions and spins of free carriers.

2. Experimental

PL kinetics experiments were performed using either a second or fourth harmonics of YAG:Nd pulsed laser for the PL excitation and a photon counting system for detection or using a mode-locked Ti:sapphire solid-state laser with frequency doubling (λ=340 nm, 2 ps pulses) and a streak camera for signal detection.

The cathodoluminescence (CL) measurements were performed on a Leo 1550 computer-controlled field emission scanning electron microscope equipped with an Oxford Instruments MonoCL2 CL system and helium temperature gas flow stage.

PL, CL and PL kinetics investigations were supplemented with optically detected magnetic resonance (ODMR) and electron spin resonance (ESR) investigations, performed on a Q-band (36 GHz) system developed by the authors, with a microwave cavity mounted in a split-coil magnet of the Oxford Instruments, using a CW argon laser for the photo-excitation. In the ODMR experiment we measured PL changes (intensity or polarization rate) at

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magnetic resonance conditions monitored synchronously with on–off modulated microwave power.

The experiments were performed on bulk ZnMnS crystals with about 1% Mn fraction grown by the chemical transport method and on a self-organized CdMnTe quantum dot system grown by molecular beam epitaxy on ZnTe.

3. Results and discussion

In Fig. 1 we show PL kinetics of Mn^{2+} transition in bulk ZnMnS crystals studied at two different excitation conditions, i.e. for the excitation within energy levels of Mn^{2+} ions and for the above bandgap excitation. In addition to a 'normal' ms-range component of the PL kinetics we observed a faster decay, with 100–150 μs PL decay time. We applied the perturbation scheme introduced by Boulanger et al. [4,5] to estimate the role of different perturbation processes in reduction of Mn^{2+} PL decay time. Using the perturbation scheme introduced in Refs. [4,5] we could estimate the shortening of the PL decay time in the case of adjacent Mn ions coupled by strong spin–spin exchange interactions. These calculations indicate that the pair mechanism leads to a shortening of radiative relaxation times faster by, at most, a factor of 100. We can thus account for ~100 μs component of the PL decay, but we cannot explain the fast component of the PL decay reported by Bhargava and the one observed by us in a sub-microsecond time range, seen in the inset of the Fig. 1.

To verify the important role of spin cross-relaxation effects in shortening of the Mn^{2+} PL decay time we applied the ODMR technique. In Fig. 2 we show the ODMR signal detected via an increase in the PL intensity of the $^4T_1 \rightarrow {}^6A_1$ intra-shell emission of Mn^{2+} ions. To identify the origin of the ODMR signal we compared the

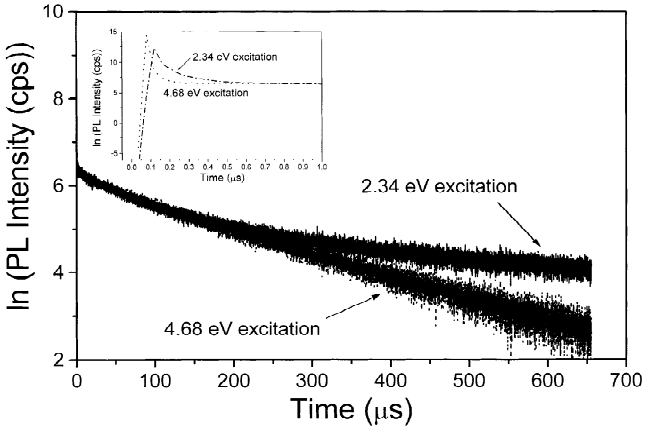

Fig. 1. PL kinetics of Mn^{2+} emission observed at two excitation conditions—for the excitation into the second excited state of Mn^{2+} ion and at the above bandgap excitation. In the inset we show the fast component of the PL decay measured under the same conditions.

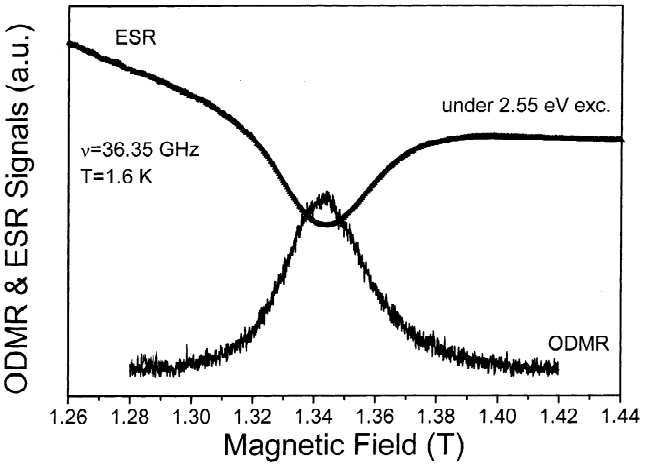

Fig. 2. The ESR and ODMR signals of Mn^{2+} ions in ZnMnS bulk crystal detected in a Q-band ODMR–ESR magnetic resonance set-up.

ODMR and ESR resonance signals measured in the same system and at identical conditions. Identical signals are observed in both cases, as can be seen in Fig. 2. Thus, we detect magnetic resonance of Mn^{2+} ions in the $^6A_1$ ground state in the ODMR study.

The signal detected in the ODMR shows however very different properties. ESR signal saturates for microwave power attenuation less than 15 dB and is not observed at high microwave power. This is due to a very slow spin-lattice relaxation (T_1) in the system studied. In contrast, the ODMR signal increases with the microwave power, which indicates a very fast T_1 time for the Mn ions studied in the ODMR. This proves very efficient spin–flip processes for Mn ions studied with the ODMR. The relevant cross-relaxation mechanisms were proposed by Zink and co-workers [6] and by Kluge and Donecker [7].

Our ODMR investigations confirm relaxation of spin selection rules of Mn^{2+} intra-shell PL and allow us to relate them to efficient spin cross-relaxation effects for adjacent Mn ions. For close associates of Mn ions spin cross-relaxation processes are efficient and the PL decay time is shorter than that observed for isolated Mn ions. Associations of Mn ions contribute to a faster component of the PL observed at a higher energy wing of the PL, as detected from the ODMR–PL experiment shown in Fig. 3. In the ODMR–PL we studied the range of the PL from which the ODMR signal comes. Fig. 3 shows that Mn^{2+} resonance in the ground state affects mostly the radiative recombination rate at the high energy wing of the PL band.

Therefore, we relate the 100 μs decay component to radiative recombination of adjacent Mn ions coupled by an exchange interaction. The latter process cannot account for the sub-microsecond component of the PL decay. Our experimental results suggest that the fastest component of the PL decay, the one in a sub-microsecond time range, can be related to spin–flip processes between Mn ions and free carriers. The inset in Fig. 1 indicates that the shortest

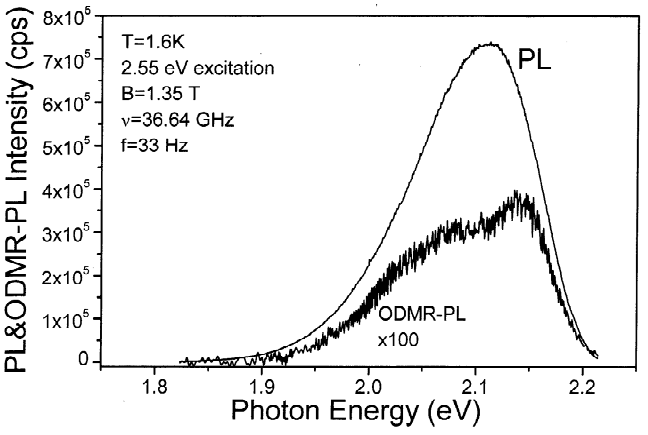

Fig. 3. PL emission and ODMR–PL spectra measured under the excitation into the second excited state of Mn^{2+}. The ODMR–PL spectrum was measured with detection set at the Mn^{2+} resonance conditions with signal intensity detected at different energies within the PL band.

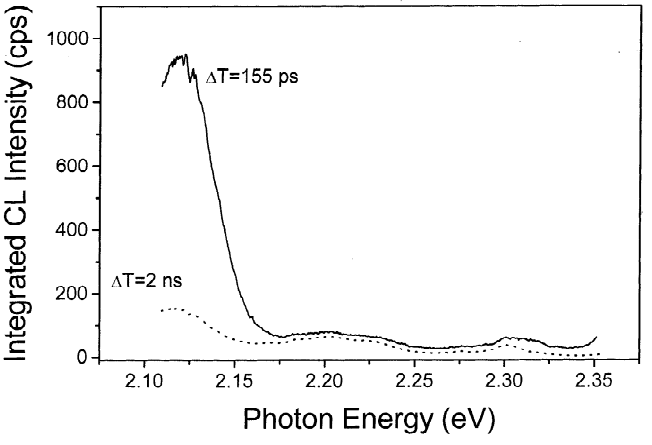

Fig. 5. Time-resolved PL spectra from CdMnTe quantum dots measured under pulsed (2 ps long pulses, 75 MHz repetition rate) excitation, integrated over 155 ps after the exciting pulse (upper curve) and over 2 ns of the PL decay, excluding the first 155 ps after the photo-excitation.

PL decay rate is observed at the above bandgap excitation conditions.

To confirm this conclusion we performed additional PL, CL and PL kinetics investigations of the system of self-organized CdMnTe quantum dots. In this system we could spectrally and in-time separate the contribution of the Mn^{2+} PL from all other PL emission bands and thus reject the possibility that the fast component of the PL decay is due to some spectral overlap of the Mn^{2+} PL emission with some other PL bands, as suggested by Bol and Meijerink [3].

In Figs. 4 and 5 we show the results of the micro-CL and time-resolved PL investigations, which allow us to identify PL bands due to quantum dots of different sizes and Mn^{2+} intra-shell PL. Relatively sharp lines are observed in the micro-CL spectrum excited from a small area of the sample (Fig. 4). This allows the separation of the PL/CL originating from quantum dot emission. Quantum dot emission also shows quite different PL kinetics. This PL decays in picoseconds time range, as shown in Fig. 5, whereas the Mn^{2+} PL emission shows much slower decay time.

We performed detailed PL kinetics investigations to verify if the fast component of the PL decay is observed in this quantum dot system and, if so, to reveal its origin. The results of the relevant experiments are shown in Figs. 6 and 7. A very pronounced fast component of the Mn^{2+} PL decay is observed. The most crucial results are obtained from the comparison of the PL kinetics of quantum dots and of Mn PL emissions, shown in Fig. 7. This comparison indicates that the rise and decrease (fast component) of the Mn^{2+} PL correlate with the time of trapping of light-generated free carriers into excitons. This we can conclude, comparing rise and decay kinetics of quantum dot PL, is of an excitonic origin, and of Mn^{2+} PL. This observation confirms our initial observation for the bulk ZnMnS system and indicates that interaction with free carriers may be responsible for the observed fast component of the Mn PL decay.

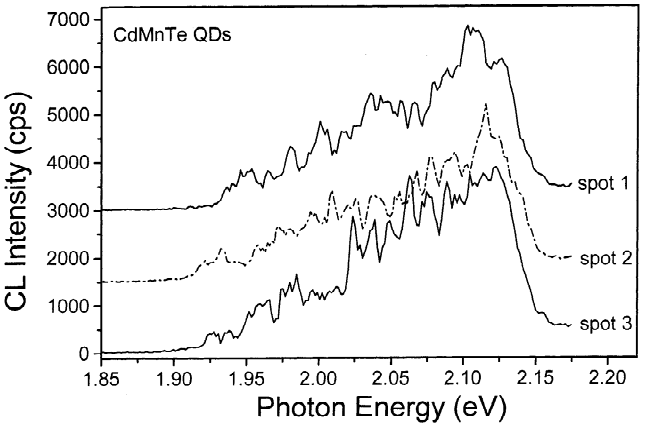

Fig. 4. Micro-PL spectra taken at three different spots of 100×100 nm size and at the conditions optimized for the excitation of emission from CdMnTe quantum dots.

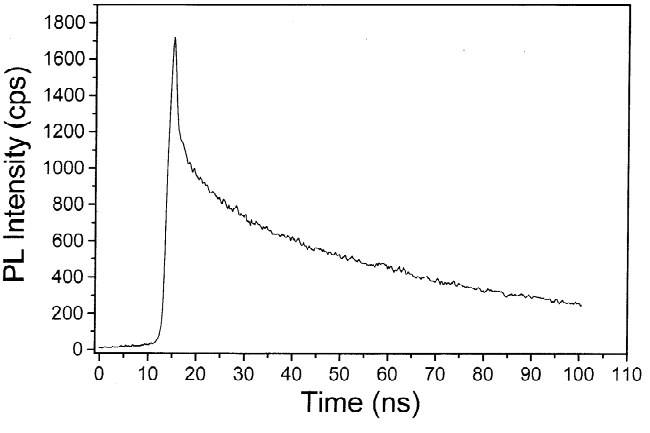

Fig. 6. PL kinetics spectrum from CdMnTe quantum dots measured at 2 K, excited by 2 ps long pulses. The first 100 ns of the PL decay is shown.

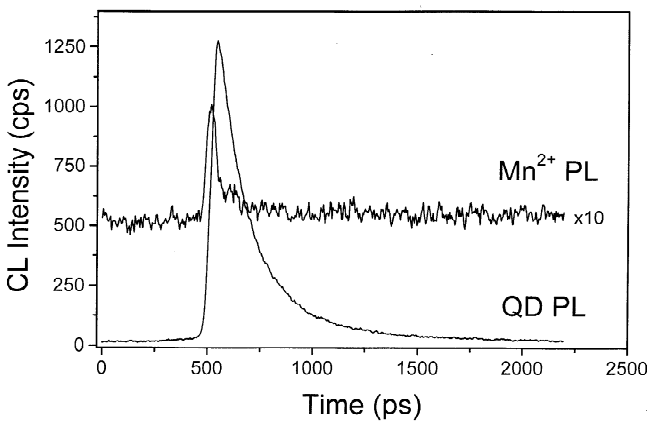

Fig. 7. PL kinetics spectrum measured at 2 K, excited by 2 ps long pulses at 75 MHz repetition rate showing the first 2.5 ns of the PL decay spectra for the excitonic CdMnTe quantum dot (QD) emission and the response of the intra-shell Mn^{2+} PL to the photo-excitation.

We propose that very efficient spin–flip scattering of free carriers (mainly of free holes [8]) results in relaxation of spin selection rules for the intra-shell PL of Mn^{2+} ions. Such a strong interaction between two spin systems may also result in variation of spin temperature of the Mn subsystem [9].

Concluding, our experimental results confirm the presence of the fast component in the Mn^{2+} PL decay kinetics, but reject the idea that this fast component is related to quantum confinement effects and is only present in low dimensional structures. We relate this process to efficient spin–flip interaction between two spin subsystems of localized spins of Mn ions and spins of free carriers.

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