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Mechanism of Radiative Mn^{2+} Intra-Shell Recombination in Bulk ZnMnS

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Origin of a fast component of the photoluminescence decay of Mn^{2+} intra-shell $^4T_1 \rightarrow {}^6A_1$ transition is discussed based on the results of photoluminescence, photoluminescence kinetics and optically detected magnetic resonance experiments performed for bulk ZnMnS samples with about 1% Mn fraction. It is demonstrated that a fast component of the photoluminescence decay, reported previously for quantum dot structure and related to quantum confinement effects, is also observed in bulk samples and is related by us to very efficient spin cross-relaxation effects.

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1. Introduction

It was proposed [1] that quantum confinement effects result in a dramatic reduction of a lifetime of Mn^{2+} intra-shell $^4T_1 \rightarrow {}^6A_1$ photoluminescence (PL). Mn^{2+} PL decay time is shortened from ms timescale, observed in lightly doped bulk crystals, to ns timescale, first reported by Bhargava and Gallagher [2] for Mn doped ZnS quantum dots. This observation was intuitively explained by Bhargava [1] by quantum-confinement-enhanced $s-p$ hybridization with the d states of Mn ions.

The validity of the model was recently argued by Bol and Meijerink [3]. These authors reported the observation of a normal ms-range PL decay of the Mn^{2+} PL in ZnMnS quantum dots and rejected the idea of pronounced influence of quantum confinement effects on the rate of radiative recombination. Bol and Meijerink related the observed fast component of the Mn^{2+} PL decay to a fast decay of an underlying low-energy wing of the blue band ZnS PL emission.

We reject the latter explanation, taking into account the results of the present PL kinetics and optically detected magnetic resonance (ODMR) experiments performed by us for above and for below band-gap excitation conditions. For both excitation processes we observed the appearance of a fast component of the PL decay, which is enhanced in the case of the above band-gap excitation. We will argue that the observed shortening of the PL decay time, observed upon above band-gap excitation, is of a different origin than that proposed by Bhargava [1, 2].

2. Experimental

ODMR and electron spin resonance (ESR) investigations were 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 argon laser and a second and fourth harmonics of YAG:Nd pulsed laser for PL excitation. In the ODMR experiment we measured PL changes (intensity or polarization rate) at magnetic resonance conditions, which were measured synchronously with on-off modulated microwave power. The experiments were performed on bulk ZnMnS crystals with about 1% Mn fraction grown by chemical transport method.

3. Experimental results and discussion

In Fig. 1 we show the PL kinetics observed at 2 K temperature at two different excitation conditions, for excitation within energy levels of Mn^{2+} ions and for the above band-gap excitation. These data clearly show that a fast component of the PL decay is observed also in bulk samples. Thus, we agree with the conclusion of Bol and Meijerink [3] that this component of the PL decay is not related to quantum confinement effects, as was proposed in Refs. [1, 2]. In addition to a "normal" ms-range component of the PL kinetics we observe a faster decay, with 100–150 μs PL decay time, and also the one in a sub-μs time range, better seen in the inset of Fig. 1.

We relate the former component, based on the results of our calculations, to a faster decay rate of adjacent Mn ions. In these calculations we modified the perturbation scheme introduced in Refs. [4, 5] and we estimated the expected shortening of the PL decay time in the case of adjacent Mn ions coupled by spin–spin exchange interaction. These calculations indicate that the pair mechanism leads to radiative relaxation times faster by maximum 100 times. 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-μs time range.

The fastest component of the PL decay is pronounced for the above band-gap excitation. Thus, it can be due to spin-dependent interaction between free carriers and Mn ions. To verify this point we performed the ODMR investigations of ZnMnS bulk crystals with about 1% Mn fraction.

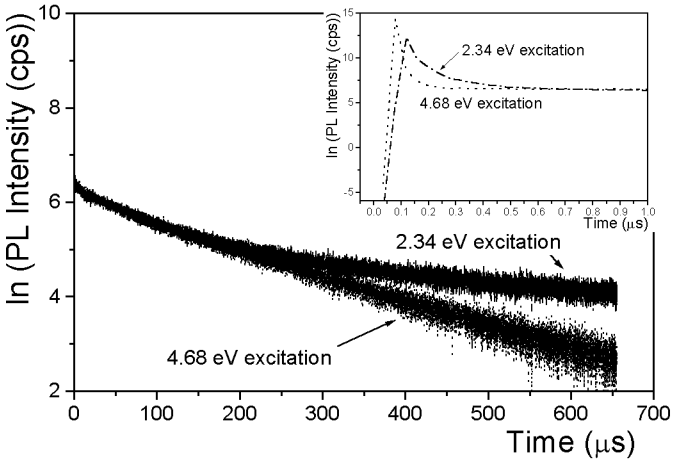

Fig. 1. PL kinetics of Mn^{2+} emission observed at two excitation conditions — for the excitation into the second excited state of Mn^{2+} ion and at the above band-gap excitation. In the inset we show the fastest component of the PL kinetics.

In Fig. 2 we show the ODMR signal detected by us via an increase in the PL intensity or by a change in the polarization rate of the $^4T_1 \rightarrow {}^6A_1$ intra-shell emission of Mn^{2+} ions. The same resonance signal is detected via green and blue color donor–acceptor pair (DAP) PL emissions observed by us together with the Mn^{2+} PL emission. By performing ODMR and ESR experiments in the same system and at the same conditions we could identify the ODMR signal (see Fig. 2).

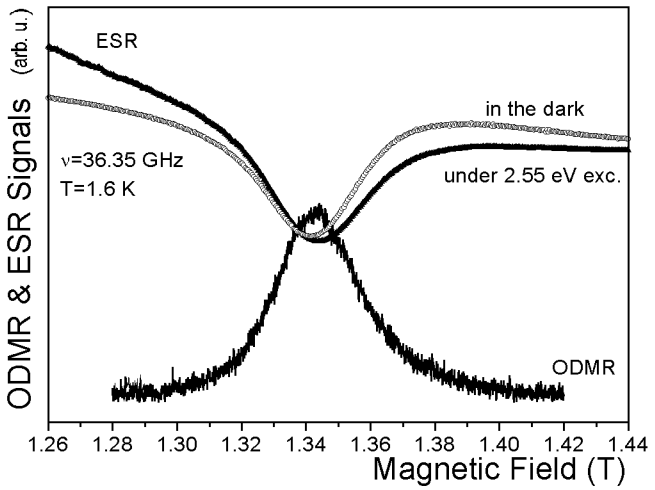

Fig. 2. The ESR and ODMR signals of Mn^{2+} ions in ZnMnS bulk crystal detected in a Q-band magnetic resonance setup at the same experimental conditions.

Identical signals are observed in both cases. Thus, we detect magnetic resonance of Mn^{2+} ions in the $^6A_1$ ground state in the ODMR study.

We observed the ESR signal at 15 dB dumping of the microwave power. The ESR signal saturates and is not observed at an increased microwave power. In contrast, the ODMR signal increases in the intensity with an increasing microwave power, which indicates a very fast T_1 time for the Mn ions studied in the ODMR. This must be due to very efficient spin-flip processes for Mn ions studied with the ODMR and suggests the possible explanation of the ODMR detection mechanism.

To identify the relevant mechanism of the ODMR detection we should first answer the question why the magnetic resonance of Mn^{2+} in the ground state affects the rate of radiative recombination of either Mn^{2+} or DAP PL emissions. The relevant mechanisms were proposed by Zink and co-workers [6] and by Kluge and Donecker [7]. Zink et al. [6] proposed a cross-relaxation process of a spin flip between excited DAP and Mn ions or between a pair of two adjacent Mn ions, of which one is in the ground state and one is in the excited state. In turn, Kluge and Donecker [7] proposed spin-dependent transfer. In the latter process DAPs and Mn ions transfer their excitation energy and the process depends on their spin orientation.

Our ODMR experiments indicate that efficient relaxation of spin selection rules of Mn^{2+} intra-shell PL can be related to efficient spin cross-relaxation effects for adjacent Mn ions. We propose that this effect is entirely responsible for highly efficient Mn^{2+} PL observed by us for ZnMnS bulk crystals and also for ZnMnS quantum dots studied by Bhargava [1, 2]. For close associates of Mn ions spin cross-relaxation process is efficient and the PL decay time is short. Such Mn ions contribute to a faster component of the PL observed at a higher energy wing of the PL, as detected by us from the ODMR-PL experiment shown in Fig. 3. In the latter experiment we studied the range of the PL from which the ODMR signal comes, i.e., Fig. 3 shows the dependence of the intensity of the ODMR signal on the detection energy. We conclude that a slow decay component of the PL decay is related to the PL decay of isolated Mn ions, when spin selection rules are affecting the rate of the Mn^{2+} PL recombination and its contribution can be optimized in the ODMR experiment by applying slow modulation rates of microwaves and detecting signal at low-energy wing of the PL.

The PL investigations performed by us under polarized light excitation and at detection set at different polarization components of the PL emission indicate relatively long spin memory effects for these isolated Mn ions. In that case the spin selection rules for radiative transitions are not relaxed and the Mn^{2+} PL emission is fairly inefficient and occurs in ms time range. In turn, we relate the 100 μs time range to radiative recombination of adjacent Mn ions coupled by an exchange interaction.

As already mentioned, the latter process cannot account for the sub-μs component of the PL decay. Our experimental results suggest that the fastest compo-

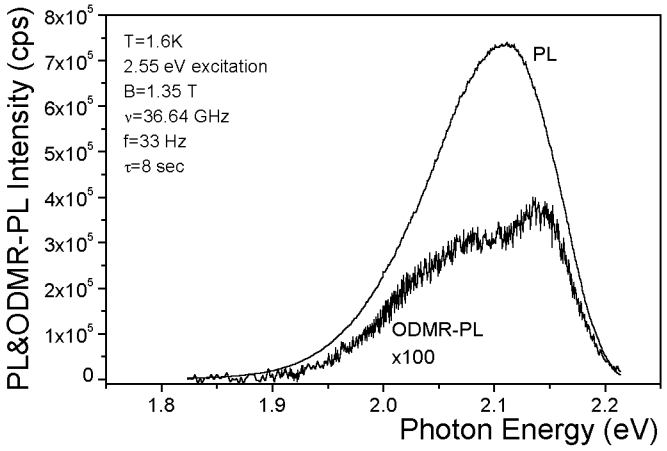

Fig. 3. Comparison of the PL emission and ODMR-PL spectrum. The latter spectrum was measured at detection set at the Mn^{2+} resonance conditions with signal intensity detected at different energies within the PL band.

nent of the PL decay, the one in a sub-μs time range, can be related to spin-flip processes between Mn ions and free carriers. This is why we observe the shortest PL decay rates at the above band-gap excitation. Our new experimental results, performed for CdMnTe quantum dots, which are not discussed here, confirm this explanation of the PL kinetics data.

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