Relaxation and dynamics of intra-center excitations in semi-magnetic $Zn_{0.8}Mn_{0.2}Te$ multiquantum wells

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A B S T R A C T

Intra-center luminescence dynamics was investigated under low excitation density in $Zn_{0.8}Mn_{0.2}Te/Zn_{0.59}Mg_{0.41}Te$ multiquantum wells both experimentally and by Monte Carlo simulation. A model developed earlier for bulk $Cd_{1-x}Mn_xTe$ is applied to the nanostructures with wells' width equal to 7 and 26 monolayers. Low temperature experimental transients showed build-up part. Besides time-resolved luminescence spectra of Mn^{2+}-ions' band indicate that energy of the band maximum shifts in two time scale. The Monte Carlo simulation showed that fast shift derives from transition between the lowest intra-center states $^4T_2 \rightarrow \,^4T_1$ within the same Mn^{2+}-ion. The explanation is supported by calculations applied to bulk $Cd_{0.4}Mn_{0.6}Te$ under similar excitation conditions. Mean relaxation rate of the $^4T_2 \rightarrow \,^4T_1$-transition is estimated to be $5\ \mu s^{-1}$. The slow relaxation is determined by energy transfer between Mn^{2+}-ions, its rate being four orders of magnitude less than that of the transition. Calculations showed weak correlation between energies of the $^4T_1$- and $^4T_2$-states which causes the transition energy fluctuations. This results in the transition rate dispersion, which is taken into account by exponential dependence on the transition energy. Loss of the correlation is shown to be mainly originated from symmetry breakdown. Noticeable non-exponential decay in Mn^{2+}-luminescence transients is described by stochasticity in decay rates.

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1. Introduction

Optical and magnetic properties of low-dimensional structures based on II–VI group compounds containing manganese have been extensively studied during two last decades. At low concentration manganese should be considered as isoelectronic dopant. When Mn^{2+}-ions substitute for host cations significantly solid solutions are formed known as dilute magnetic semiconductors (DMS) [1]. Outstanding magnetic properties of DMS [2] are very attractive for spintronics applications [3]. The compounds demonstrate bright intra-center luminescence (IL). The latter arises at around 2 eV under molar concentration x when band gap energy exceeds a threshold of IL excitation ($^6A_1 \rightarrow \,^4T_1$-transition within 3$d$-shell). The condition holds for all zinc chalcogenides under any substitution degree unlike for $Cd_{1-x}Mn_xTe$, in which the band gap begins to be quite wide only at $x \geq 0.4$ in bulk samples [1]. A dynamics of IL in DMS under low excitation density has been researched in bulk [4] and nanoparticles of $ZnS:Mn^{2+}$ [5,6,7] with small manganese concentration. Similar researches have been made in bulk

$Cd_{1x}Mn_xTe$ at $x \geq 0.4$ [8,9,10] and two-dimensional nanostructures with $Cd_{0.6}Mn_{0.4}Te$ in quantum wells (QWs) [11,12]. The properties in bulk $Zn_{1-x}Mn_xTe$ were concerned in Ref. [13], with calculation results being qualitatively in agreement with experimental data [14]. An analysis of experimental results of IL temporal properties has shown that there is Mn^{2+}–Mn^{2+} excitation energy transfer (ET) over ions' energy states, which form an inhomogeneous broadening in IL [8]. Unlike fluorescence line-narrowing in rare-earth ions' systems, IL of transient group ions in II–VI-hosts has inherent wide homogeneous broadening at low temperature. Its value for $Cd_{1x}Mn_xTe$ is almost equal to the former [8,10,15]. Theoretical description of the ET in solid solutions with several stochastic parameters (ion site-position, ion energy etc.) is a difficult problem and needs approximations [16]. It has been developed for rare-earth ions in dilute concentration limit. Monte-Carlo simulation (MC) seems to be an encouraging approach to describe systems similar to semi magnetic solid solutions and calculate Mn^{+2}-ion excitation dynamics. Recently, a MC model was proposed to describe ET in $Cd_{1-x}Mn_xTe$ bulk samples for $x = 0.4 - 0.7$ at 4.2 and 77 K under low excitation density and different excitation energies [10], the model being applicable to QWs either [12]. Experimentally affirmed dipole-dipole interaction between Mn^{2+}-ions was proposed to cause the

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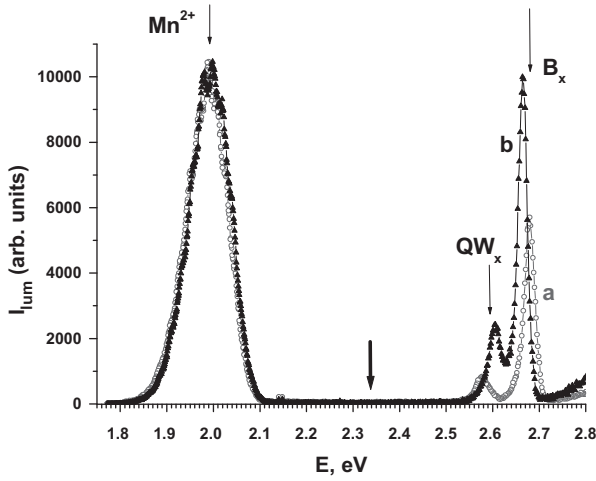
Fig. 1. Time-integrated luminescence spectra in $Zn_{0.8}Mn_{0.2}Te/Zn_{0.59}Mg_{0.41}Te$ multi-quantum wells at $T=5$ K: (a) quantum wells' width in monolayers $ml=26$ (hollow circles), and (b) $ml=7$ (dark triangles). Thin arrows signify intra-center luminescence band (Mn^{2+}), quantum wells' exciton of $Zn_{0.8}Mn_{0.2}Te$ (QW_x), barriers' exciton of $Zn_{0.59}Mg_{0.41}Te$ (B_x). Thick arrow indicates excitation energy $E_{exc}=2.34$ eV used to obtain time-resolved intra-center luminescence of Mn^{2+}-ions.

ET [17]. For bulk samples a hopping-assisted quenching was stated to be noticeable part of energy transfer dynamics. Self-consistent MC calculations showed that energy correlation between the lowest ${}^4T_1$- and ${}^4T_2$- excited states of the 3d-shell was very weak. Symmetry breakdown was stated to be an origin of the non-correlation [12]. Temperature rise compels fast ion energy fluctuation, which leads to a diminution of luminescence inhomogeneous broadening [10,15]. For MBE-grown bulk and multiquantum wells' (MQWs) samples noticeable non-exponential decay of Mn^{2+}-luminescence transients is revealed [12]. It was described by a stochasticity in decay rates. The non-exponential feature does not seem to be linked with expected dimensional reduction described in Ref. [18] or an interface influence proposed in Ref. [19] as MBE-grown film of $Cd_{0.5}Mn_{0.5}Te$ revealed the same strength of the non-exponential feature. In samples with narrower quantum wells a homogeneous broadening is calculated to be significantly enhanced [12]. However, the result and its explanation need more experimental data.

There have been only a few papers on dynamics of IL in $Zn_{1-x}Mn_xTe$ MQWs [20,21]. In the papers luminescence spectra of the structures with different manganese concentrations and quantum well widths are studied at excitation densities ranging from 10^5 to 10^7 W/cm^{-2}. It is shown that relative intensities of the quantum well and barrier excitons and dependences of the intensities on optical excitation density are controlled mainly by manganese content in the QWs, which affect an efficiency of energy transfer from the excitons to 3d-shell of Mn^{2+}-ions. At higher intensity of optical excitation saturation of Mn^{2+}-excited states, cooperative quenching and inelastic interaction with excitons of high density are responsible for IL intensity saturation and degradation. It is stated that value of IL decay constant depends mainly on the manganese content. Comparison of IL properties for the structures with different quantum well widths showed that manganese interface ions affect the IL decay and the band shape. This paper aims to supply with more data on IL dynamics of $Zn_{0.8}Mn_{0.2}Te$ MQWs under low excitation density and give quantitative results.

2. Materials and experiment

MBE grown samples of $Zn_{0.8}Mn_{0.2}Te/Zn_{0.59}Mg_{0.41}Te$ MQWs contain 100 periods, QWs having 7 and 26 monolayers (ml)

(2.1 and 7.9 nm correspondingly), barriers being 40 ml (≈ 12 nm). The structures were grown on GaAs substrate with $<100>$ orientation. Bulk sample of $Zn_{0.93}Mn_{0.07}Se$ grown by diffusion method was taken for comparison.

Luminescence was excited by YAG:Nd^{3+}-laser, with photon energy $E_{exc}=2.34$ eV, pulse width $\tau_{exc}=0.14$ µs. The E_{exc} falls into intra-center absorption band of the ${}^4T_2$-state and short wave wing of the ${}^4T_1$-state, the bands being noticeably lower of fundamental absorption edge [22,23] (see also Fig. 1 in part 4 and [20,21]). The τ_{exc} determined total time resolution of an experimental set-up. To obtain time-resolved data the samples were kept in Leybold–Heraeus cryostat at 13 K and irradiated by light beam of the lowest possible intensity in unfocused spot. The spectra were recorded with 0.3 m grating spectrometer. Time-integrated spectra were obtained with help of double 0.25 m spectrometer MDR-204 and 4 K Cold Head RDK-101D of Sumitomo Heavy Industry. Weak power laser with light quantum of 3.06 eV was used to excite samples above energy gap of $Zn_{0.59}Mg_{0.41}Te$ barrier.

3. Method and model

To analyze experimental data MC random walk method for single excitation as described in Refs. [10,12] was applied in this work. The method gives possibility to follow up an excitation motion in time and space. Stochastic variables are Mn^{2+}-ions' coordinates x_k, y_k, z_k for k-ion, their energies E_k of transition ${}^4T_1 \rightarrow {}^6A_1$, and decay rates g_k. Mn^{2+}-ions with molar concentration x are randomly scattered to substitute for Zn^{2+}-ions in face-centered cubic lattice of QWs. Cyclic boundary conditions are abolished along x-axis that is normal to QWs. In distinct of a model applied previously the E_k are supposed to be completely correlated with local ions' concentration $x(k)$ because intra-center absorption strongly depends on the x [22,23]. Variance of energy distribution σ_{en} describes an inhomogeneous broadening of ions' energy distribution. The energy is taken as follows:

$$E_k = \beta(x(k) - x) \tag{1}$$

here, x is the mean concentration (0.2), β is the constant factor. The linear approximation fits quite well to data obtained in Refs. [22,23]. A homogeneous broadening of Gaussian shape describes side-bands of an ion under its emission or absorption. The broadening is specified by a variance σ_h. ET rate $W_m(k \rightarrow i)$ from k- to i-ion is written as follows [10]:

$$W_m(k \rightarrow i) = \varphi(R)f(E_k \rightarrow E_i) \tag{2}$$

The spatial term is given by dipole–dipole ions' interaction [17]

$$\varphi(R) = W_{0m}(R_0/R)^6 \tag{3}$$

here, W_{0m} is an amplitude index of the ET rate; R_0 is the lattice constant (6.16 Å for zinc blend structure with $x=0.2$ [1]); R is the distance between interacting ions. Energy dependent term in (2) is formed by an overlap integral of interacting ions' side-bands (resonance interaction) [24]. $Zn_{0.8}Mn_{0.2}Te$ Stokes shift value Δ_s required for the calculation of the $f(E_k \rightarrow E_i)$ is assumed to be $\Delta_s \approx 0.28$ eV for $T=2-10$ K according calculations based on data from Refs. [13,22,23]. Then [24]:

$$f(E_k \rightarrow E_i) \equiv f(\Delta E) = \exp\left\langle -\left(\frac{1}{4\sigma_h^2}\right)[\Delta_s - (E_k - E_i)]^2 \right\rangle \tag{4}$$

For the MQWs under consideration hopping-assisted quenching rate is small under low temperature T. At higher T the quenching can be perceptible [12].

An ion excitation is realized as follows. Under excitation energy $E_{exc}=2.34$ eV ${}^6A_1 \rightarrow {}^4T_2$-transition into the second excited state of Mn^{2+}-ions takes place with high probability. According to the