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Cooperative quenching of intra-center luminescence in $Cd_{1\text{-}x}Mn_xTe$ under high density excitation

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ABSTRACT

Intra-center luminescence transients of 2 eV-band in $Cd_{0.25}Mn_{0.75}Te$ thin film and $Cd_{0.6}Mn_{0.4}Te$ /$Cd_{0.5}Mg_{0.5}Te$ multi quantum wells under strong excitation were investigated both experimentally and by Monte-Carlo simulation at temperature 77 K. Sharp fall at initial time span in the experimental transients is described by Monte Carlo model, in which Mn^{2+}-ion excitations interact with each other through dipole-dipole form. Good conformity of calculated and experimental data proved importance of far-field form of the interaction. Calculations showed that elemental act of the interaction includes a quenching of one excitation, the other one being instantaneously up-converted and returned to initial state with high probability. Initial quenching rate is more than two orders of magnitude higher than that of the luminescence emission. The quenching is assisted by energy transfer. Saturation of Mn^{2+}-ion system is calculated to be weak. A value of the quenching coefficient is $2.5 \times 10^{-13}\,\text{cm}^3\,\text{s}^{-1}$, which is as high as that of some regular crystals. Experimental transients of the hetero structures showed a reduction of the quenching at narrower quantum wells. Calculations proved the initial peak diminished and narrowed if the well width was decreased. The tendency may be helpful to estimate contribution of morphological changes in transient short constituent at decrease of a nanostructure dimension. The model can be extended for other semi magnetic semiconductors of II-VI group with isoelectronic substitution by ions of iron group.

1. Introduction

Mixed ternary crystals $Cd_{1\text{-}x}Mn_xTe$ are model objects to study a whole family of II-VI semi magnetic semiconductors (SMS). They are usually alloys, which lattice is made up partly with isoelectronic magnetic Mn^{2+}-ions. The presence of localized magnetic ions leads to unique magnetic properties important for fundamental science and applications [1,2]. At molar concentration $x > 0.4$ the ions are characterized by efficient intra-center luminescence (IL) at around 2 eV, which has been an object of extensive fundamental researches. High value of x results in enhanced quenching (concentration quenching), the latter being assisted by energy transfer (ET) between Mn^{2+}-ions [3–5]. On the other hand, increase of excitation density to enhance IL output causes non-linear effects of different kinds. Two-photon intra-center absorption and IL saturation at short wave length were observed in $Cd_{1\text{-}x}Mn_xTe$ ($x = 0.51$, 0.55) [6,7]. The saturation was explained in terms of bi-exciton formation. The bi-exciton is assumed to be a result of a short-ranged exchange interaction between excitations. They are unconditionally quenched for nearest-nearest excitations. Monte Carlo (MC) approach was proposed to describe further experimental data [8]. The MC model of the bi-exciton partially satisfied with the data obtained. Nevertheless, temperature behavior and IL relaxation dynamics under varying excitation intensity left unclear. Later, a non-linear behavior of the IL band and its temporal dynamics have been extensively researched in bulk samples of $Cd_{1\text{-}x}Mn_xTe$ ($x = 0.4$–075), $Cd_{1\text{-}x\text{-}y}Mn_xMg_yTe$ ($x = 0.05$–0.55, $y = 0.25$–0.55) and $Zn_{1\text{-}x}Mn_xSe$ ($x = 0.07$, 0.02) [9–13]. Under strong excitation the IL transients at initial time reveal strikingly sharp decay in comparison to the decay under weak excitation condition. Another manifestation of the non-linearity is phenomenological “saturation” of IL intensity. The effects enhance at higher temperature (from 4 K to 77 K) and molar concentration x. Experimentations with multi quantum well (MQW) structures of $Cd_{0.6}Mn_{0.4}Te/Cd_{0.5}Mg_{0.5}Te$ and $Zn_{1\text{-}x}Mn_xTe/$ $Zn_{0.6}Mg_{0.4}Te$ ($x = 0.03$, 0.2) have demonstrated similar features [14–17]. To explain the experimental results a model of cooperative effect due to interaction of excitations[1] was proposed, extending the bi-exciton model to up-conversion of one excitation at the expense of another one in approximation of balance equation system [11]. Thus, both excitations are quenched. The model being qualitatively agreed with experimental data did not take into account energy transfer (ET) between active ions

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[1] It is often called exciton-exciton interaction.

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(Mn^{2+}). However, ET is important factor in IL dynamics [6,8]. ET was successfully simulated for bulk and multi quantum wells of $Cd_{1\text{-}x}Mn_xTe$ at 4 and 77K with the help of MC model [18,19]. This paper aims to extend the MC method for many excitations. Cooperative effect is suggested to be the main mechanism responsible for the non-linear properties revealed in the IL under high intensity excitation.

2. The model

2.1. Physical background

$Cd_{1\text{-}x}Mn_xTe$ solid solution crystallizes in the zinc-blende structure. In the FCC sub-lattices of the system, a fraction x of Cd^{2+}-cations is randomly replaced by active ions, Mn^{2+}. Coordinates (x_i, y_i, z_i) of i-ion form stochastic variables. IL of transient group ions in II-VI-hosts has inherent wide homogeneous broadening even at low temperature. The broadening is accompanied by great Stokes shift $\Delta_s \approx 0.2$ eV [18]. The observed emission spectrum is therefore a multi-phonon sideband of the intra-center electronic transition ${}^4T_1 \rightarrow {}^6A$, which is additionally broadened by wide distribution of transition energies. The latter constitutes an inhomogeneous broadening of the IL. The discrepancy of ion energies is originated from a random occupation of lattice sites by Mn^{2+}-ions. Each Mn^{2+}-ion experiences a specific crystal field, which depends on the environment and varies from site to site. Ion energies E_i of the lowest ${}^4T_1$-state constitute another stochastic variable. The homogeneous and the inhomogeneous broadenings of the IL are approximated by Gaussian function, with variances being σ_h^2 and σ_{IL}^2 correspondingly. Since the ion energy varies randomly, there is in general no energy resonance when ET takes place. Besides, the great Stocks shift makes the mismatch still greater. An overlap integral responsible for an interaction between Mn^{2+}-ions decreases. At helium temperatures this results in a slow transfer rate. While temperature is risen, the homogeneous broadening enhances, increasing the overlap integral and ET rate. That compels excitations to hop quickly closer to each other, resulting in prominent growth of their interaction under strong excitation. Therefore, in this work the main interest is paid to experimental data and MC simulation at high temperature when IL still remains bright (77 K).

2.2. Monte Carlo model

In simulation energy parameters are calculated in units of experimental σ_{IL}, which is measured at the end of excitation pulse τ_{exc}. Rates and times are in units of photon emission rate $\gamma = 1/\tau_0$ and the emission life time τ_0 accordingly. The latter is measured at the tail of the low energy experimental transient of the IL band. The emission rate of Mn^{2+}-ions is a stochastic variable γ_k [19]. At each time step for each excitation, all possibilities of cooperative interaction, ET to unoccupied sites and the photon emission are tested in random way. Cooperative effect rate and an excitation rate are much greater by orders of magnitudes than those of ET and the photon emission. This requires very small time step, and the simulation becomes rather time consuming. To solve the problem the time step is made varying. That greatly economized simulation time.

To calculate the excitation rate G_{exc} one uses a super cell volume $V_0 = (7 \times R_0)^3$, R_0– a lattice constant of the crystal:

$$G_{exc} = \frac{\alpha(E_{exc})I_{exc}(t)}{h\nu_{exc}}V_0 \tag{1}$$

Here, $h\nu_{exc} = E_{exc} = 2.34$ eV – photon energy of optical excitation; $I_{exc}(t)$– excitation intensity; $\alpha(E_{exc})$– absorption index of the IL band. Here, matrix exciton does not influence excitation condition for $Cd_{0.25}Mn_{0.75}Te$ [1]. Generally, one has to consider non-instantaneous excitation. The condition becomes urgent if the rate of cooperative effect is comparable with the value of G_{exc}, and an excitation may quench during excitation pulse. MC calculations showed that it is the case (Section 4). To take that into account the intensity $I_{exc}(t)$ is considered a rectangular function with duration τ_{exc} (Section 3).

Excitation event is simulated in time cycle as follows. Outside the cycle a probability of i-ion to be excited is calculated by homogeneous broadening centered at the ion energy E_i:

$$\psi(E_i) \propto \exp[-(1/2\sigma_h^2)(E_i - E_\alpha)^2] \tag{2}$$

Here, E_α is excitation energy relative to ion energy distribution center 2.43 eV of the second ${}^4T_2$- absorption band [18]. Along with a rapid electron-phonon relaxation in picosecond time-scale an excitation of the i-ion into the ${}^4T_2$-state with probability given by the Eq. (2) takes place. Then rapid ${}^4T_2 \rightarrow {}^4T_1$ transition with time-scale less than set-up time resolution occurs within the same ion. The ${}^4T_1$-state energy of the ion is only partially correlated to that of the ${}^4T_2$-state because of local symmetry fluctuations [19]. Ion energies E_i^* in ${}^4T_2$- state is the forth stochastic variable.

The rate of ET from k- to i-ion unexcited is written in the form [18]:

$$W_m(k \rightarrow i) = W_{0m}\left(\frac{R_0}{R_{ki}}\right)^6 \times \exp\left\{-\frac{[\Delta_s - (E_k - E_i)]^2}{4\sigma_h^2}\right\} \tag{3}$$

Here, the spatial term describes the dipole-dipole interaction between the ions, W_{0m}– amplitude index of ET rate, R_{ki}–a distance between the interacting ions. The energy dependent term is formed by an overlap integral of side-bands corresponding to the ions (resonant interaction). As the Stokes shift Δ_s is great the exponential term is much greater for the case of $E_k > E_i$.

Exciton-exciton interaction manifested in IL quenching of Mn^{2+}-ions is described as follows. The interaction is also considered of dipole-dipole kind. If k-ion is close to i-ion, then excitation transfer from k-ion may take place, with the energy E_k being added to the energy of the i-ion (up-conversion) [11,20]. The quenching of the k-ions is the main feature of the interaction while the up-conversion of the i-ions has not been manifested in II-VI SMS with Mn^{2+}-ions (Section 4). Therefore the interaction is hereafter called cooperative quenching (CQ) to stress the main effect and the nature of the interaction as descried in [20]. The transfer of one excitation to another obeys to Dexter's rule, i.e. the rate is proportional to overlap integral of side-bands of the interacting ions [21]. Here, CQ rate is approximated in a simplified form:

$$W_{nq}(k, i) = \begin{cases} W_{nq0}\left(\frac{R_0}{R_{ki}}\right)^6, & \text{if} \quad E_k \geq E_i \\ W_{nq0}\left(\frac{R_0}{R_{ki}}\right)^6 \exp\left(\frac{-(E_i - E_k)}{k_B T}\right), & \text{if} \quad E_k < E_i \end{cases}, \tag{4}$$

where W_{nq0} – amplitude index of the CQ rate, k_B – Boltzmann constant.

If $E_k \geq E_i$, then the k-ion is quenched with great probability, with the up-conversion of the i-ion occurring. Its relaxation may occur in two different ways. The first one is to instantaneously relax into ${}^4T_1$-state with the same energy (E_i). As a matter of fact, the relaxation may not be instantaneous one in time scale of the experimental conditions as it was shown for $Zn_{0.8}Mn_{0.2}Te$ MQWs [22]. The second way is to give up the excitation energy to a trap or electron-hole pair of the matrix with probability p_{nq}. Then the i-ion quenches to be excluded from further simulation. Taking into account non-instantaneous relaxation of the ion up-converted may affect the p_{nq} value.

As stated above the model contains four stochastic variables. Correlations between them are considered elsewhere [18,19].

3. Experimental conditions

The experimental set up is mostly the same as described in [19]. MBE grown samples of $Cd_{0.25}Mn_{0.75}Te$ thin film (0.4 μm) and $Cd_{0.6}Mn_{0.4}Te/Cd_{0.5}Mg_{0.5}Te$ MQWs with 7 and 26 monolayers (*ml*) containing 100 ÷ 80 periods were used in the work. Mn^{2+}-ion concentration in the film was calculated using reflection and excitation spectra at temperature 5 K. Characterization of the MQWs was earlier done in [19]. Experiments were conducted with YAG:Nd^{3+}-laser,