Mechanisms of manganese-assisted non-radiative recombination in Cd(Mn)Se/Zn(Mn)Se quantum dots

A V Chernenko¹, A S Brichkin¹, N A Sobolev² and M C Carmo²

¹ Institute of Solid State Physics, RAS, 142432 Chernogolovka, Russia
² Departamento de Física and I3N, Universidade de Aveiro, 3810-193 Aveiro, Portugal

E-mail: chernen@issp.ac.ru

Received 25 May 2010, in final form 5 July 2010
Published 18 August 2010
Online at stacks.iop.org/JPhysCM/22/355306

Abstract

Mechanisms of non-radiative recombination of electron–hole complexes in Cd(Mn)Se/Zn(Mn)Se quantum dots accompanied by interconfigurational excitations of Mn²⁺ ions are analyzed within the framework of the single-electron model of deep 3d levels in semiconductors. In addition to the mechanisms caused by Coulomb and exchange interactions, which are related because of the Pauli principle, another mechanism due to sp–d mixing is considered. It is shown that the Coulomb mechanism reduces to long-range dipole–dipole energy transfer from photoexcited quantum dots to Mn²⁺ ions. The recombination due to the Coulomb mechanism is allowed for any states of Mn²⁺ ions and e–h complexes. In contrast, short-range exchange and sp–d recombinations are subject to spin selection rules, which are the result of strong lh–hh splitting of hole states in quantum dots. Estimates show that efficiency of the sp–d mechanism can considerably exceed that of the Coulomb mechanism. The phonon-assisted recombination and processes involving the upper excited states of Mn²⁺ ions are studied. The increase in PL intensity of an ensemble of quantum dots in a magnetic field perpendicular to the sample growth plane observed earlier is analyzed as a possible manifestation of the spin-dependent recombination.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

A great deal of attention attracted to quantum dot (QD) structures is due to the possible use of their quantum states in various fields of spintronics and for the generation and detection of light [1]. Semimagnetic (diluted magnetic semiconductor (DMS)) II–VI quantum dots are promising objects for these purposes because a high degree of spin polarization of electrons and holes can be achieved in relatively weak magnetic fields.

However, incorporation of Mn ions into CdSe/ZnSe QDs substantially reduces the quantum yield of radiation as soon as the optical transition energy exceeds the energy of the internal Mn transition ∼ 2.15 eV. It is found that Cd(Mn)Se/Zn(Mn)Se QD photoluminescence (PL) is completely quenched due to non-radiative recombination at relatively small Mn content x ≃ 3–5% [2–6].

The PL quenching is due to non-radiative recombination of QD e–h complexes accompanied by excitation of Mn²⁺ ions. The Coulomb interaction between 3d and band electrons is usually considered as a reason for processes of energy transfer from e–h complexes to Mn²⁺ ions [7, 8].

The interest in possible mechanisms of energy transfer arose after observation of a strong increase in PL intensity of an ensemble of Cd(Mn)Se/Zn(Mn)Se QDs in magnetic field B || Oz reported by many authors [2–6]. Simultaneous increase in the QD PL lifetime was also reported [5, 9, 10].

The explanation of the increase is based on suppression of the spin-dependent non-radiative recombination of e–h pairs by magnetic field. According to the model proposed in [11] non-radiative exciton recombination is possible because of the direct exchange interaction between band carriers and 3d electrons. This model provides selection rules for the process: 

\[ S_B' = S_B, \]  

where \( S_B \) and \( S_B' \) are Mn²⁺ spin projections.
in the direction of magnetic field $B$ in the initial and final $\text{Mn}^{2+}$ states, respectively. Selection rules predict that the non-radiative recombination of bright excitons is forbidden for the states of $\text{Mn}^{2+}$ ions with $S_B = \pm 5/2$ whereas it is allowed for $\text{Mn}^{2+}$ ions with other $S_B$. Since the number of $\text{Mn}^{2+}$ ions with $S_B = -5/2$ increases with magnetic field, non-radiative recombination is suppressed. The rules correctly explained the strong increase in PL intensity in Cd(Mn)Se/Zn(Mn)Se QDs but failed to explain its dependence on the direction of the magnetic field [2]. To explain the observed dependence a modification of selection rules was suggested in [2] $S_z + S_{\text{ex},z} = S_z^e$, where $S_z$ is the projection of $\text{Mn}^{2+}$ spin on the Oz axis, which is perpendicular to the sample growth plane, $S_{\text{ex},z} = s_x^e + s_y^e$ is the projection of exciton spin (instead of the total angular momentum $J_z = J_z^b + J_z^c$) on Oz. This suggestion is based on PL studies of Cd(Mn)Se/Zn(Mn)Se and CdSe/ZnSe/ZnMnSe QDs, which revealed that hh and lh hole states are strongly split due to strain and dimensional quantization [12, 13]. The carriers in the upper hh band are characterized by both the moment projection $J_z^b = \pm 3/2$ and the spin projection $s_z^b = \pm 1/2$. The Coulomb and exchange mechanisms are assumed to obey the same selection rules [2].

The analysis presented below shows, however, that spins of atomic configurations were not properly regarded in [2] and some correction of previous results is required. Besides, the sp–d mixing specific to DMS was omitted while its contribution to the non-radiative recombination can be essential. The consideration based on the single-electron model of the 3d level in a semiconductor reveals that the spin projection $s_z^b = \pm 1/2$. The Coulomb and exchange mechanisms are assumed to obey the same selection rules [2].

This paper is organized as follows. In section 2 a model Hamiltonian of a DMS QD structure is considered. Mechanisms of the non-radiative recombination to the Coulomb interaction and sp–d mixing are analyzed in section 3. The link between the model and the impact excitation of $\text{Mn}^{2+}$ ions is also discussed in section 4. Spin–dependent selection rules for non-radiative recombination and their manifestations in experiments are considered in section 5.

2. Model Hamiltonian

The Hamiltonian of the structure containing one QD and one $\text{Mn}^{2+}$ ion has the form of an Anderson Hamiltonian [14–16]:

$$
\hat{H}_0 = \hat{H}_{\text{QD}} + \hat{H}_{\text{Mn}} + \hat{H}_{\text{hyb}} + \hat{H}_{e},
$$

where $\hat{H}_{\text{QD}}$ is the Hamiltonian of the QD electron system, $\hat{H}_{\text{hyb}}$ is the hybridization Hamiltonian, $\hat{H}_{\text{Mn}}$ is the Hamiltonian of the $\text{Mn}^{2+}$ 3d shell and the Hamiltonian of the potential exchange interaction is $\hat{H}_e$.

The QD Hamiltonian:

$$
\hat{H}_{\text{QD}} = \hat{H}_c + \hat{H}_v + \hat{H}_e
$$

contains Hamiltonians of the conduction $\hat{H}_c = \sum_{\mu c} \epsilon_{\mu c} \hat{c}_{\mu c}^+ \hat{c}_{\mu c}$, $c_{\mu c}$, and valence $\hat{H}_v = \sum_{\nu} \epsilon_{\nu} \hat{b}_{\nu}^+ \hat{b}_{\nu}$ electrons. Here $\mu$ and $\nu$ enumerate electron and hole states in the QD. Conduction and valence electron states are $|\psi_{\mu c}^e\rangle = c_{\mu c}^+ |0\rangle$ and $|\psi_{\nu}^v\rangle = |b_{\nu}\rangle$. Electron, hole, exciton and trion states are eigenstates of $\hat{H}_{\text{QD}}$. Hole states are related to valence electron states via a time-reversal operation $|\psi_{\nu}^v\rangle = |\psi_{\nu}^e\rangle$.

The term $\hat{H}_e$ contains e–h Coulomb and exchange interactions. The Coulomb term mixes single-electron states and leads to the reduction of the e–h energy whereas the e–h exchange term splits e–h states with $J = 1, 2$. Without loss of generality we retain only the exchange term and neglect the Coulomb interaction because the confinement of e–h states in QDs is determined by the dimensional quantization and because its contribution to energy transfer is negligible, as will be clear in section 3.

The dots under study have a very anisotropic lens-like form, i.e. the diameter $D$ is several times larger than the height $L$. Photoluminescence studies of Cd(Mn)Se/Zn(Mn)Se and CdSe/ZnSe/ZnMnSe QDs reveal that most QDs have symmetry $C_{2v}$. These studies show that hh and lh hole states are strongly split due to strain and dimensional quantization [12, 13]. The e–h exchange interaction splits e–h states with $J = \pm 1$ (‘bright excitons’) and $J = \pm 2$ (‘dark excitons’). The gap between bright and dark states is around 2–3 meV [12]. The wavefunctions of the bright exciton in those structures are $|\psi_{\nu}^e\rangle = 1/\sqrt{2}(|\Psi^+\rangle \pm |\Psi^-\rangle)$, where $|\pm 1\rangle$ are exciton states with $J_z = \pm 1$ and $|\psi_{\nu}^v\rangle = |\pm 2\rangle$ are dark exciton states.

The effect of the periodic lattice potential on band electrons is taken into account within the effective mass approximation, which may be used since we are interested in the properties of states near the bottom of the conduction and the top of the valence bands. In the effective mass approximation conduction electron states are $\psi_{\nu}^e(\mathbf{r}) = F_{\nu} \phi_{\nu}(\mathbf{r}) + \chi_{\nu} \phi_{\nu}(\mathbf{r})$, where $\phi_{\nu}(\mathbf{r})$ and $\chi_{\nu}(\mathbf{r})$ are solutions of the effective mass equations. Here, S, X, Y and Z are zone center Bloch functions of appropriate symmetries. The electron states on the bottom of the first band of dimensional quantization within a symmetric quantum well of width $L_w$ can be found elsewhere [17]. Bloch amplitudes of free electrons with $k \parallel \mathbf{Q}$ that account for $k^2$ terms within Kane’s model are $\psi_{\nu}^e(\mathbf{r}) = (1 - (\hbar k)^2/(2m^*_0)\rho_{\nu}^2 \pm \rho_{\nu}^2/\sqrt{4(1/E_{\text{g}} + \Delta)})/(\sqrt{4(1/E_{\text{g}} + \Delta)})/(\sqrt{4(1/E_{\text{g}} + \Delta)})Z_{\nu}^\pm(\mathbf{r})$ [18]. Here $p = (S|p_S^+|X) = i(p_m^0/h) P$ is the Kane parameter and $m_0$ is the free-electron mass [19]. These results show that the admixture of Z functions to $\psi_{\nu}^e(\mathbf{r})$ is much larger than those of X and Y functions.

The admixture of lh to hh states takes place in QDs of $C_{2v}$ symmetry and lower [13], it is small and unimportant for our aims. Therefore, we assume that
The single-electron states are expressed via eigenstates \( \phi_\lambda(\mathbf{r}) \) of \( H_{\text{imp}}(\mathbf{r}) = \sum F_\lambda \phi_\lambda(\mathbf{r}) \), where \( F_\lambda \) are appropriate coefficients and summation is made over quantum numbers characterizing crystal states.

The single-electron potential of a perfect crystal structure may be written as \( V^0 = \sum_\lambda v_\lambda^0 (\mathbf{r} - \mathbf{R}_\lambda^0) + V^0_c(\mathbf{r}) \) [26], where \( V^0_c(\mathbf{r}) \) is the potential due to band electrons and \( V^0_\lambda (\mathbf{r} - \mathbf{R}_\lambda^0) \) is the potential of core electrons and nucleus at \( \mathbf{R}_\lambda^0 \). In the presence of an impurity the potential may be written as \( V = \sum_\lambda v_\lambda (\mathbf{r} - \mathbf{R}_\lambda) + V_c(\mathbf{r}) \), where \( \mathbf{R}_\lambda \) are new atomic sites. Therefore the perturbation is

\[
H_{\text{imp}} = V - V^0 = \sum_\lambda (v_\lambda (\mathbf{r} - \mathbf{R}_\lambda) - v_\lambda^0 (\mathbf{r} - \mathbf{R}_\lambda^0)) + U_c(\mathbf{r})
\]

\[
\simeq \sum_\lambda (v_\lambda (\mathbf{r} - \mathbf{R}_\lambda^0) - v_\lambda^0 (\mathbf{r} - \mathbf{R}_\lambda^0)) - \sum_\lambda \left( \frac{\partial v_\lambda (\mathbf{r} - \mathbf{R}_\lambda^0)}{\partial \mathbf{R}_k^0} \right)_0 \times (\mathbf{R} - \mathbf{R}_\lambda^0) + U_c(\mathbf{r}),
\]

where \( U_c(\mathbf{r}) = V_c(\mathbf{r}) - V^0_c(\mathbf{r}) \).

By neglecting lattice relaxation (\( \mathbf{R}_\lambda = \mathbf{R}_\lambda^0 \) the potential of a substitutional impurity at \( \mathbf{a}_0 \) may be written as \( H_{\text{imp}}(\mathbf{r}) = v_{\text{3d}}(\mathbf{r} - \mathbf{a}_0) - v_{\text{3d}}(\mathbf{r} - \mathbf{a}_0) + U_c(\mathbf{r}) \) [24], whereas the potential of an interstitial impurity is \( H_{\text{imp}}(\mathbf{r} - \mathbf{a}_0) = v_{\text{3d}}(\mathbf{r} - \mathbf{a}_0) + U_c(\mathbf{r}) \). Here \( v_{\text{3d}}(\mathbf{r} - \mathbf{a}_0) \) is the potential of the host ion. Only substitutional impurities are discussed below since the obtained results can be easily extended to the latter case.

The Hamiltonian of the crystal structure with substitutional impurity in the second-quantized form can be expressed as \( H = H_1 + H_2 \), where \( H_1 = \hat{H}_0 + H_{\text{imp}} \) is the single-electron Hamiltonian in the basis \( \{d_{m\sigma \lambda \pm}, \phi^\dagger_{\mu \lambda \pm}, \phi_{\mu \lambda \pm}\} \), which includes localized 3d states \( d_{m\sigma \lambda \pm} \). The term \( H_2 \) contains interactions between single-electron states. The only interaction included in the Anderson model is the Coulomb repulsion between electrons with the same \( m \) but opposite \( \sigma \). \( H_2 = U_{\text{eff}} \sum_{m\sigma \lambda \pm} \hat{n}_{m\sigma \lambda \pm} \hat{n}_{m\sigma \lambda \mp} \). Besides \( H_{\text{QD}}, H_{\text{hyb}} \) and \( H_d = \sum_{m\lambda \sigma} d_{m\lambda \sigma \pm}^{\dagger} d_{m\lambda \sigma \mp} \), the Hamiltonian \( H_1 \) contains the scattering term

\[
H_{\text{scat}} = \sum_{\mu \neq \mu', \nu \neq \nu', \lambda \neq \lambda'} (U_{\nu \lambda \mu' \lambda'} c_{\nu \lambda}^{\dagger} c_{\nu' \lambda'} + U_{\mu \lambda \nu' \lambda'} b_{\mu \lambda}^{\dagger} b_{\nu' \lambda'} + \text{h.c.})
\]

usually omitted in the canonical Anderson model. Here

\[
U_{\nu \lambda \mu' \lambda'} = \langle \nu \lambda \mu' \lambda' \vert H_{\text{imp}} \vert \nu' \lambda' \mu' \lambda \rangle.
\]

The Bloch wavefunctions \( \Psi_{\nu \lambda \sigma}^{\text{3d}} \), where \( \Psi_{\nu \lambda \sigma} \) can be either \( \chi_{\nu \lambda} \), \( Y_{\nu \lambda \sigma} \), or \( S_{\nu \lambda \sigma} \), are not orthogonal to \( d_{m\sigma \lambda \pm} \) at \( k = 0 \). As a result anticommutators \( \{d_{m\lambda \sigma \pm}, c_{\nu \lambda}^{\dagger}\} \neq 0 \) and \( \{d_{m\lambda \sigma \pm}, b_{\mu \lambda}^{\dagger}\} \neq 0 \) because slowly varying envelopes \( \chi_{\nu \lambda \sigma}^{\text{3d}}(\mathbf{r}) \) can always be expressed as \( \sum_{k} A(k)e^{ik \cdot \mathbf{r}} \). We assume, however, that overlap integrals are negligible because we are interested in band states near \( k = 0 \).

To account for the sp–d Coulomb interaction between band and five 3d electrons the terms originating from \( \sum_{m\sigma \lambda \pm} c_{\nu \lambda}^{\dagger} c_{\nu \lambda} + b_{\mu \lambda}^{\dagger} b_{\mu \lambda} \) should be added to \( H_2 \). The potential \( U_c(\mathbf{r}) \) tends to compensate changes in electron density caused by the presence of the impurity and leads to the screening of the interaction between band and 3d electrons. Within the framework of linear response theory \( H_{\text{imp}}(\mathbf{q}) = \)
1/ε_{eff}(\mathbf{q}) (u_3(\mathbf{q}) - u_2(\mathbf{q}))$, where $\hat{H}_{\text{imp}}(\mathbf{q})$, $u_2(\mathbf{q})$ and $u_3(\mathbf{q})$ are Fourier transforms of $H_{\text{imp}}(\mathbf{r})$, $u_2(\mathbf{r} - \mathbf{a}_0)$ and $u_3(\mathbf{r} - \mathbf{a}_0)$, respectively [26]. Similarly, the screened Coulomb interaction between band and the th 3d electron is

$$v_{sc}(\mathbf{r} - \mathbf{r}_i) = \frac{4 \pi e^2}{(2\pi)^3} \int \frac{e^{i\mathbf{q}(\mathbf{r} - \mathbf{r}_i)}}{\epsilon_{\text{eff}}(\mathbf{q}) q^2} \, d^3 q.$$  (8)

This expression is appropriate for the Coulomb processes of non-radiative recombination that are characterized by small transferred quasi-momentum $q_{\parallel} \simeq 1/D$, $q_z \simeq 1/L$. Here $D$ and $L$ are characteristic lengths of QDs in the lateral and $0z$ direction, respectively. Quasi-momenta within this range participate in the formation of e–h states, which justifies the use of the linear response approach [26]. Since the transferred energy $E_0 \simeq 2.15$ eV satisfies condition $E_0 \simeq E_k \gg \hbar \omega_F$, the inert ionic system of the crystal does not contribute to the dielectric function so that the effective dielectric function is determined by band electrons. The processes caused by the long-range Coulomb interaction are characterized by $q \simeq 0$ so that for the Coulomb processes $\epsilon_{\text{eff}}(\mathbf{q} \simeq 0) \simeq \epsilon_{\infty}$.

Contrary to the Coulomb processes exchange ones are characterized by a small interaction radius so that the contribution of the processes with large transferred quasi-momenta can be negligible. The explicit form of the screened Coulomb interaction is not required for the future analysis of the exchange mechanism so that the expression $v_{sc}(\mathbf{r}_1 - \mathbf{r}_2)$ is used in this case.

The Coulomb interaction between band and 3d electrons $V_{sc} = \sum_{i=1}^{5} v_{sc}(\mathbf{r} - \mathbf{r}_i)$ generates many terms of the form $V_{i,j,k,l,m,n} a_i a_j a_k a_l$, where $a_i$ can be either of $a^\dagger_{msz}(a)_{msz}$, $a^\dagger_{msz}(c)_{msz}$, $b^\dagger_{ij}(b_{ij})$. The terms containing only 3d or band electron operators, i.e. those that do not couple 3d and band states, are not considered here since the effect of these terms are already accounted for in $H_{\text{Mn}}$ and $H_{\text{QD}}$.

The other terms which appeared because of $H_{\text{imp}} + V_{sc}$ are analyzed by means of the approach developed in [27]. The analysis shows that some terms originating from $V_{sc}$ are already included in $H_0$.

At distances $|\mathbf{r} - \mathbf{a}_0| \gg a_b$, where $a_b$ is the atomic Bohr radius, $v_{sc}(\mathbf{r} - \mathbf{r}_i) \approx v_{sc}(\mathbf{r} - \mathbf{a}_0)$, so that the term

$$\sum_{msz, m'sz} V_{p,msz,m'sz} a^\dagger_{msz} a^\dagger_{m'sz}$$  (9)

tends to compensate $\sum_{p,q} U_{p,q} a^\dagger_{p,q} a^\dagger_{p,q} = \sum_{p,q} \langle a_p | H_{\text{imp}}(\mathbf{r} - \mathbf{a}_0) | a_q \rangle a^\dagger_{p,q} a^\dagger_{p,q}$, which can be expressed as $\sum_{p,q} \langle a_p | Z_{Mn} e^2/\epsilon_{\infty} | \mathbf{r} - \mathbf{a}_0 \rangle | a_q \rangle a^\dagger_{p,q} a^\dagger_{p,q}$, where $Z_{Mn}$ is the net core charge that includes the Mn$^{2+}$ ion nuclear charge and the charge of completely filled atomic shells. The expectation value $\langle \sum_{msz} n_{msz} - Z_{Mn} \rangle$ is zero for an isoelectronic substitutional impurity [27]. The short-range difference between these potentials contributes to the potential scattering $\hat{H}_{\text{scat}}$ and energies of the 3d and band states.

Similarly terms

$$\sum_{msz, m'sz} (V_{msz,m'sz} a^\dagger_{msz} a^\dagger_{m'sz} + \text{h.c.})$$  (10)

and

$$\sum_{\mu, \nu, \xi, \eta} (U_{\mu,\nu} a_{\mu} \epsilon_{\nu} + U_{\nu,\xi} a_{\nu} \epsilon_{\xi} + U_{\xi,\eta} a_{\xi} \epsilon_{\eta} + \text{h.c.})$$  (11)

effect of crystal ion potential on the sp–d mixing [27].

Similarly the term

$$\sum_{msz, m'sz} V_{p,msz,m'sz} a^\dagger_{msz} a^\dagger_{m'sz}$$  (13)

tends to compensate the contribution of $\sum_{msz, m'sz} U_{msz, m'sz} a^\dagger_{msz} a^\dagger_{m'sz}$ and the crystal ion core potential to energies of 3d and band states and the potential scattering of 3d states.

By taking into account the Coulomb interaction the Hamiltonian in (1) is transformed into

$$\hat{H} = \hat{H}_0 + \hat{H}_{\text{scat}} + \hat{U}_0,$$  (14)

where $\hat{U}_0$ contains terms generated by $V_{sc} + H_{\text{imp}}$ that are not included in $\hat{H}_0 + \hat{H}_{\text{scat}}$. They are responsible for various processes involving one, two or three 3d electrons and include those responsible for the non-radiative recombination.

The Hamiltonian in (14) can be rewritten in the familiar form [20, 28]

$$\hat{H} = \hat{H}_{\text{QD}} + \hat{H}_{\text{Mn}} + \hat{H}_{\text{int}},$$  (15)

where $\hat{H}_{\text{int}}$ is the interaction between the QD electron system and the Mn$^{2+}$ ion. The hybridization term $\hat{H}_{\text{hyb}}$ in (14) can be replaced by an effective scattering Hamiltonian [22, 29], so that $\hat{H}$ can be rewritten as

$$\hat{H} = \hat{H}_{\text{QD}} + \hat{H}_{\text{Mn}} + \hat{H}_{\text{scat}} + \hat{U}_0 + \sum_{I} \frac{\hat{H}_{\text{hyb}}|I\rangle \langle I| \hat{H}_{\text{hyb}}}{E_i - E_I},$$  (16)

where $E_i$ and $E_I$ are energies of the initial $|i\rangle$ and intermediate $|I\rangle$ states, respectively.

In addition to the terms $\hat{H}_{\text{eff}}$ and $\hat{H}_{\text{eff}}$ describing scattering of conduction and valence electrons on the 3d shell the effective Hamiltonian contains the term $\hat{H}_{\text{mix}}$ responsible for the mixed scattering.

As is shown in [22, 29] the Hamiltonian

$$\hat{H}_{\text{eff}} = \sum_{I} \frac{\hat{H}_{\text{pd}}|I\rangle \langle I| \hat{H}_{\text{pd}}}{E_i - E_I},$$  (17)

contains terms responsible for the potential scattering of valence electrons, a contribution to energy of the 3d level and terms of the p–d kinetic exchange that can be expressed in the Heisenberg form similar to $\hat{H}_x$ in (5) [22]. Analogous terms are contained in $\hat{H}_{\text{eff}}$.

The introduction of the effective Hamiltonian $\hat{H}_{\text{eff}}$ is justified in the ionic limit of the Anderson model [28]. It takes place when the broadening of the single-electron 3d states
due to their hybridization with delocalized band states (QD states do not contribute to the broadening) is smaller than the energy gaps between the ground $d^0$ and excited $d^2$ and $d^6$ configurations [28]. In this limit the ground and excited states of Mn$^{2+}$ ions are characterized by certain spins $S = 5/2$ or 3/2, which is obviously the case here.

The initial state, which we denote as $|d^6\text{eh}\rangle$, contains the Mn$^{2+}$ ion $d^5$ in the ground states and the e–h pair. Its energy is $E_i = E_0(5) - E_v + E_c$, where $E_0(n)$ is the energy of the $d^n$ configuration of the Mn$^{2+}$ ion, and $E_v$ and $E_c$ are energies of electron states at the bottom of the conduction and the top of the valence bands. Intermediate states $|I\rangle$ are of two kinds: $|I^+\rangle$ corresponding to the virtual absorption and $|I^-\rangle$ corresponding to the virtual emission of one electron. The dominant contribution to energy transfer comes from the virtual levels with minimal energy gaps $E_i - E^-$. The values of energy gaps $E_i - E^-$ are found in appendix B.

By using commutational relations and the fact that virtual levels involve only $d^0$ and $d^6$ configurations the term

$$\hat{H}_{\text{mix}} = \sum_{\mu\nu, ms z, \mu' ms' z'} \langle I|\hat{H}_{\text{sd}}|I\rangle|\hat{H}_{\text{sd}}|I\rangle$$

may be expressed as

$$\hat{H}_{\text{mix}} = \sum_{\mu\nu, ms z, \mu' ms' z'} (K_{\text{mix}} d_{\mu ms z}^\dagger d_{\mu' ms' z'} + K^+_{\text{mix}} d_{\mu ms z}^\dagger d_{\mu' ms' z'} + \text{h.c.),}$$

where the coefficients are

$$K_{\text{mix}} = -V_{\mu\nu, ms z, \mu' ms' z'}, V_{\mu\nu, ms z, \mu' ms' z'}$$

and $K^+_{\text{mix}} = K_{\text{mix}}^\dagger + K^+_{\text{mix}}^\dagger$. The second term in (19) leads to the interband potential scattering whereas the first one contributes to the non-radiative recombination as is shown in section 3.1.

The Hamiltonian given by (16) can be generalized to the case of many non-interacting Mn ions, which corresponds to the limit of small Mn content when the interaction between Mn ions can be omitted. The antiferromagnetic Mn–Mn coupling appears within the Anderson model in the fourth order of perturbation series and becomes important starting from $x \approx 0.05$. The Mn–Mn interaction leads to the formation of Mn–Mn pairs, triads and clusters. The antiferromagnetic Mn–Mn interaction leading to cluster formation affects the dynamics of energy migration between Mn ions. The influence of pairs and triads on energy transfer is considered in section 5. The discussion of the dynamics of Mn–Mn energy transfer is outside the scope of the current paper.

Thus, $\hat{H}_0 + \hat{H}_{\text{mix}}$ can be considered as a perturbation of the Hamiltonian

$$\hat{H}' = \hat{H}_0 + \hat{H}_{\text{mix}} + \hat{H}_{\text{ex}} + \hat{H}_{\text{sc}},$$

where $\hat{H}_{\text{ex}}$ is the sp–d kinetic exchange term. The potential scattering is dropped as it does not directly contribute to the non-radiative recombination.

The Coulomb and direct exchange interactions leading to the non-radiative recombination are contained in $\hat{U}_0$. In section 3.2 we consider contributions of $\hat{U}_0$ and $\hat{H}_{\text{mix}}$ to the recombination separately and estimate the relative efficiencies of the Coulomb and sp–d mechanisms.

3. Mechanisms of non-radiative energy transfer to 3d shell

3.1. Non-radiative recombination due to Coulomb interaction

The non-radiative recombination due to the Coulomb interaction is usually considered as a transition of the first order [7, 8, 25]. The only term in $\hat{U}_0$ leading to such a transition is

$$\hat{V}_1 = \sum_{\mu\nu, ms z, \mu' ms' z'} (V_{\mu\nu, ms z, \mu' ms' z'} d_{\mu z}^\dagger e \mu_z d_{\mu' z'} + \text{h.c.),}$$

where $V_{\mu\nu, ms z, \mu' ms' z'} = (d_{\mu z}, \mu_z) |v_i| (d_{\mu' z'}, \nu_{z'})$ and $V_{\mu\nu, ms z, \mu' ms' z'} = (d_{\mu z}, \mu_z) |v_i| (d_{\mu' z'}, \nu_{z'})$.

Conversely to the potential scattering where the single-electron term $\hat{H}_{\text{imp}}$ tends to compensate the effect of the sp–d Coulomb potential, $\hat{H}_{\text{imp}}$ does not participate in the non-radiative recombination because matrix elements between initial and final states including different 3d configurations vanish.

The rate of resonant energy transfer from the photoexcited QD into the Mn$^{2+}$ 3d shell is given by Fermi’s golden rule:

$$R_{\text{nr}} = \frac{1}{\tau_{\text{nr}}} = \frac{2\pi}{\hbar} \frac{1}{N_i} \sum_{ij} |M_{ij}|^2 \delta(E_i - E_j),$$

where $N_i$ is the number of initial states [30].

The initial state of the system $|i(5/2, S_z, G)\rangle = 6\hat{A}_1(5/2, S_z)\psi_{ex}(G)|0\rangle$ consists of five 3d electrons and the e–h pair while the final state $|f(3/2, S_z)\rangle = 2\hat{T}_1(3/2, S_z)|0\rangle$ is the excited state of the Mn$^{2+}$ ion. Here $\psi_{ex}(G) = \psi_{ex}(G)|0\rangle$ is the exciton state, where $G$ denotes a set of quantum numbers characterizing it. In the absence of magnetic field $G$ is a representation of the symmetry group of the exciton state. For instance, it is $E$ for bright and $A_1$, $A_2$ for dark excitons in quantum dots and wells of D$_{2d}$ symmetry. The exciton creation operator $\psi_{ex}(G)$ is expressed via $c_{\mu z}$ and $b_{\mu z}$ operators. In a strong magnetic field $B \parallel 0z$ exciton states are characterized by $J_z$. Operators $\hat{T}_1(3/2, S_z)$ and $\hat{A}_1(5/2, S_z)$ are sums of products of five $d_{\mu z}$ operators. Wavefunctions of the many-electron $\hat{A}_1(5/2, S_z) = \hat{T}_1(3/2, S_z)|0\rangle$ and $\hat{A}_1(5/2, S_z) = 6\hat{A}_1(5/2, S_z)|0\rangle$ states in various approximations of the crystal field theory can be found in the literature [2, 20–23].

The matrix element of non-radiative recombination

$$M_{ij, S_z, S, G} = \langle f(3/2, S_z)|V_I|i(5/2, S_z, G)\rangle$$

reduces to a sum of Coulomb and exchange integrals. The Coulomb integrals lead to dipole–dipole energy transfer from QDs to Mn$^{2+}$ ions as is shown in appendix A. The anticommutation between 3d and band electrons does not affect Coulomb matrix elements so that energy transfer due to the Coulomb interaction can be understood as a result of emission and absorption of virtual
photons by QD states and Mn$^{2+}$ ions. The crystal media can screen this process but cannot interfere with it [31]. The dipole transition between $^4T_1(3/2)$ and $^6A_1(5/2)$ states is spin-forbidden and, therefore, admixing of Mn$^{2+}$ excited states with spin $3/2$ to $^6A_1(5/2)$ is required.

Robbins and Dean considered the dipole–dipole mechanism as the dominant one in non-radiative exciton decay accompanied by intratonic excitations [7]. A similar point of view is expressed in [25, 30, 32], where excitation of Er ions in Si accompanied by optically forbidden interconfigurational transitions of Er is considered. However, efficiency of the exchange mechanism can substantially exceed that of the Coulomb one when the latter is spin-forbidden, which is usual in atomic and molecular systems [33, 34]. Analyzing the process of de-excitation of Mn$^{2+}$ ions in the presence of free carriers, in other words, the reverse process with respect to the impact excitation (Auger process), Allen concluded that the Coulomb interaction underestimated it by as much as two orders of magnitude and, therefore, the main mechanism of energy transfer was related to the exchange interaction rather than the Coulomb one [8]. The idea about domination of the exchange mechanism in the excitation of Mn$^{2+}$ ions is widely accepted now [11, 35, 36]. The exchange mechanism of energy transfer in atomic and molecular systems is subject to the Wigner spin conservation rule, which states that it is allowed if the total spin of the interacting system is conserved [34].

The spin conservation rule was used by Nawrocki et al to derive selection rules for the exchange mechanism [11]. However, in order to apply it to the authors of [11] simplified the studied system so that they neglected any spin–orbit coupling in the system and consider the transition $^6T_1(3/2)\psi_e^r \rightarrow ^4T_1(3/2)\psi_e^r$ instead of exciton recombination. Exciton states in QDs are not completely characterized by spin due to the strong spin–orbit interaction in the valence band and e–h exchange interaction. However, spin selection rules for the exchange mechanism can be derived from the analysis of exciton and Mn$^{2+}$ spin functions.

The matrix element of the non-radiative recombination due to Coulomb interaction in the first-quantized form is

\[
M_{hi} = \langle f | V_{ei} | i \rangle,
\]

where $| i \rangle = | \hat{A}^4T_1(3/2, S_z)\psi_{ex} \rangle$, $| f \rangle = | \hat{A}^4T_1(3/2, S_z)\psi_0 \rangle$, $\psi_{ex}$ is the exciton many-electron function, $\psi_0$ is the ground state of the crystal and $\hat{A}$ is the antisymmetrization operator.

The exciton states are sums of products of spatial and spin functions corresponding to spins $s_{ex} = 0, 1$ and spin projections $s_{ex} = 0$ for bright and $s_{ex} = \pm 1$ for dark excitons because the wavefunctions of the bright exciton ground state can be expressed as $\psi_b^{s} (r_1, r_2) = F_{h0}(r_1)F_{0}(r_2)/\sqrt{2}((-X+Y)S_z \alpha_1 \beta_1 \pm (X-iy_1)S_z \beta_1 \alpha_2)$ which means that their contributions to energy transfer is small first of all because the matrix elements of perturbations $H_{max}$ and $V_{ei}$ are much smaller than the energy difference between any Mn$^{2+}$ configurations and e–h QD states. It is valid for the sp–d and Coulomb mechanisms as is shown in the appendices. It is natural to expect that this is also valid for the exchange mechanism.

The hybridization $H_{hyb}$ makes possible Coulomb processes via virtual states involving d$^4$ and d$^6$ configurations because of the second-order term:

\[
\sum_i \frac{|i| U_0 |I\rangle \langle I| H_{hyb} |I\rangle}{E_i - E_I} + \frac{|i| H_{hyb} |I\rangle \langle I| U_0 |I\rangle}{E_i - E_I},
\]

Its contribution to energy transfer is small first of all because the matrix elements $H_{hyb} u/(E_i - E_I)$ and $H_{hyb} u/(E_i - E_I)$ are much smaller than unity as is shown in appendix B. Besides, the Coulomb matrix elements between $|i\rangle |f\rangle$ and intermediate levels $|I\rangle$ involving d$^4$ and d$^6$ configurations with spin $S = 2$ are spin-forbidden.

3.2. Non-radiative recombination due to sp–d mixing

The sp–d mixing is responsible for the non-radiative recombination that can be understood as a result of successive hopping of the electron (hole) and hole (electron) in the 3d shell. The hopping of a valence electron in and out of the 3d shell is the reason for the kinetic p–d exchange interaction. The hopping of conduction electrons becomes possible because of the admixture of valence band states to conduction ones as $k \neq 0$. It is responsible for the reduction of the s–d exchange interaction reported in [18]. The sp–d mechanism
was proposed by Schmitt-Rink et al. as a mechanism of excitation of rare-earth ions incorporated into a semiconductor matrix [38]. It is related to the term
\[ \hat{H}_{\text{mix}} = \sum_{m_\alpha, \nu m, \mu_\nu, \nu' \mu, \nu'' \mu'} (K_{\text{mix}} d_{m_\alpha \nu}^\dagger d_{m' \nu'}^\dagger \epsilon_{\nu' \mu'} + \text{h.c.}) \]  

(25)

The p–d coupling coefficient for the valence electron ground state, \( \nu = 0 \), is
\[ V_{\text{pd}, m_\alpha, 0 \nu} = \frac{F_{\text{coul}}(a_0) (d_{m_\alpha}^\dagger \hat{U}_{\text{e} c} Z_{m_\alpha}) d_{m_\alpha} \delta_{\nu, 0}}{\nu_0^\dagger} \]

at the k point close to the center of the Brillouin zone. Coefficients \( V_{\text{pd}, m_\alpha, 0 \nu} \) and \( V_{\text{pd}, 0 \nu, m_\alpha} \) are related to the p–d hopping amplitude \( V_{pd}^0 \) as is shown in appendix B.

The matrix element of recombination of the bright exciton \( |4s (S_\gamma) T_\gamma \rangle \rightarrow |4s (S_\gamma') \rangle \) calculated in appendix B is
\[ M_{\text{mix}} = \alpha(S_\gamma) 16 \frac{F_{\text{coul}}(a_0) F_{\text{coul}}(a_0)}{N_0} V_{pd}^0 \delta_{S_\gamma, S_\gamma'} \]

(26)

(27)

where \( \alpha(S_\gamma) \) are certain coefficients found in appendix B. The factor \( \sqrt{v/2} \) appears because of admixing of valence band states to conduction ones. It is important that such a transition conserves the \( \text{Mn}^{2+} \) ion spin projection \( S_\gamma = S_\gamma' \).

The \( \nu \) exchange constant appearing in the hh exchange Hamiltonian \( \hat{H}_\nu = -\beta/3 |S\rangle \langle S| (r - a_0) \) is given by the expression
\[ \beta = -\frac{32}{5} \frac{1}{N_0} V_{pd}^{0.5} \left( \frac{1}{U_{\text{eff}} + \epsilon_d} + \frac{1}{E_e - \epsilon_d} \right) \]  

(28)

This expression is obtained by neglecting the crystal field splitting of \( \text{Mn}^{2+} \) states [14, 20]. This result is reproduced with due regard for crystal field splitting of the initial state [22]. It is natural to expect that neglecting the crystal field splitting in the matrix element \( M_{\text{mix}} \) in (27) also does not noticeably affect the result. The physical meaning of the sp–d mechanism is illustrated in figure 1. The process of kinetic p–d exchange interaction is shown in figure 2 for comparison.

The sp–d mechanism of non-radiative recombination can be much more effective than that due to the Coulomb interaction. Estimates presented in appendices A and B provide the ratio of recombination rates of the Coulomb and sp–d mechanisms for CdMnSe/ZnSe QDs averaged over the distribution of Mn ions \( \bar{R}_{\text{Coul}} / \bar{R}_{\text{mix}} \approx 10^{-2} \). The envelope \( F_{\text{coul}}(r) \) reaches a maximum at the center of the QDs, whereas \( F_{\text{coul}}(r) \) reaches a maximum at the QDs’ boundaries [17]. Therefore the ratio \( R_{\text{Coul}} / R_{\text{mix}} \) depends on the distribution of Mn ions within the e–h pair localization volume. The ratio \( R_{\text{Coul}} / R_{\text{mix}} \) is expected to be larger than \( \bar{R}_{\text{Coul}} / \bar{R}_{\text{mix}} \) in CdMnSe/ZnSe and smaller in CdSe/ZnMnSe QDs.

Although the sp–d mechanism was proposed for excitation of rare-earth ions in a semiconductor [38] it better matches our case. For instance, 4f orbitals of Er ions in Si are located much below the top of the valence band (~10 eV) [32], which results in weak p–f and s–f hybridizations. Besides, 4f orbitals are closely located to the ion core so that their interaction with band electrons is weak. In contrast, the 3d level lies at 3.4 eV below the top of the valence band [14, 15] and resonantly mixes with valence band states.

The dipole–dipole mechanism is an analogue of the Förster mechanism of energy transfer between atoms or molecules whereas the exchange-mediated mechanism is similar to the Dexter one [34]. The mechanism related to the sp–d mixing can also be associated with the Dexter mechanism, where \( \hat{H}_{\text{mix}} \) plays the role of the effective exchange interaction.
The contribution of the direct exchange mechanism to the non-radiative recombination can hardly be estimated in a simple manner so that the relative contributions of $M_{ex}$ and $M_{mix}$ are unknown. However, both mechanisms lead to spin-dependent energy transfer. Possible manifestations of such a process are discussed in section 5.

It is worth noting that the sp–d mechanism can contribute to the impact excitation of Mn$^{2+}$ ions. The excitation via either intra- or interband electronic transitions is possible [25, 38]. The impact excitation by means of the intraband transition becomes allowed when the energy of an optically or electrically excited electron with respect to the bottom of the conduction band exceeds $2.15$ eV. The impact excitation can be understood as a result of capture of such an excited conduction electron on the 3d shell because of the s–d mixing with successive escape of one of the 3d electrons with opposite spin also into the conduction band. Ayling and Allen state, however, that the efficiency of excitation of Mn$^{2+}$ via interband transitions is much larger than that via intraband ones [8, 39].

**4. Phonon-assisted processes and energy transfer into upper Mn$^{2+}$ excited states**

The resonant processes discussed above assume equality of the e–h pair transition energy and the energy of intraband excitation $E_0 \simeq 2.15$ eV. Experiments show that the photoluminescence quenches even when the transition energy of the ground state of e–h pairs in QDs substantially exceeds $E_0$ [2, 3]. There are two mechanisms which allow such processes: the phonon-assisted recombination and the non-radiative transition in upper Mn$^{2+}$ states.

The model of phonon-assisted energy transfer from a semiconductor crystal to rare-earth impurities is proposed by Yassievich et al [25]. It is based on the single configurational coordinate scheme describing the electron–phonon interaction of impurity electrons with a phonon mode of the crystal. According to the model nonresonant energy transfer is possible due to emission of multiple phonons. The probability of the phonon-assisted transition is given by

$$R_{nr}^p = \frac{2\pi}{\hbar} \frac{1}{N_i} \sum_{N_{ph}} |M_{ph}|^2 I(N_{ph}) \delta(E_g - E_0 - N_{ph} \hbar \omega_{ph}),$$

where $N_{ph} = (E_g - E_0)/\hbar \omega_{ph}$. At low temperatures, $k_B T < \hbar \omega_{ph}$, the coefficient $I(N_{ph}) \simeq (S_{HI})^{N_{ph}} e^{-N_{ph} / T} / N_i!$, where $S_{HI}$ is the Huang–Rhys factor, which determines the strength of electron–phonon coupling [19]. According to the recipe of [25] summation over $N_{ph}$ is replaced by integration and leads to the expression

$$R_{nr}^p(K_u) = \frac{1}{\tau_{nr}} = \frac{2\pi}{\hbar} \frac{1}{N_i} \sum_{N_{ph}} |M_{ph}|^2.$$  

The probability $R_{nr}^p(K_u)$ has the maximum at $K_u = S_{HI}$ at large coupling strength $S_{HI} > 1$ and quickly decreases with $K_u$. The upper limit of the efficiency of the phonon-assisted recombination can be estimated by the summation over all $K_u$.

The single configurational coordinate picture is often used for the analysis of temperature dependence of PL lines of Mn$^{2+}$ internal transitions and the Stokes shift between Mn$^{2+}$ absorption and emission spectra [24, 35, 40]. The structures under study are characterized by a more than 200 meV wide Mn$^{2+}$ PL line [2] that can be attributed to a strong interaction of the 3d shell with crystal vibrations ($S_{HI} \gg 1$). Assuming that the energy of the vibrational mode is of order $\hbar \omega_{LO}$ one obtains from (30) $\tau_{nr} \simeq 10^{-11}$ s for a Cd$\delta$Mn$\beta$Se$\alpha$Zn$\gamma$Se QD with reasonable values of $D \simeq 35$ Å and $L \simeq 12$ Å.

Although this value of $\tau_{nr}$ is not far from the measured PL decay times $\tau_0 = 20–80$ ps of CdMnSe/ZnSe QDs with close parameters at $B = 0$ T [41], small intensities of the longitudinal optical phonon (LO-phonon) replicas of Mn$^{2+}$ PL lines in DMS materials indicate weak coupling between the 3d shell and LO phonons [42]. Similarly these structures are characterized by a weak vibronic interaction [24]. In this case recombination processes into upper excited Mn$^{2+}$ states can dominate because non-radiative energy transfer is possible not only into the lower excited state $^2T_1$ but also into other excited states $^4T_2, ^4E_1, ^4A_1$ located 0.2–0.7 eV above $^2T_1$. The large inhomogeneous broadening of Mn$^{2+}$ PL lines makes non-radiative transitions possible for a wide range of energies higher than 2.15 eV. The excited $^2T_1, ^4T_2, ^4A_1, ^4E$ states have spins $S = 3/2$, so that relaxation into the $^4T_1$ state is expected to be very fast.

**5. Spin-dependent selection rules and increase in PL intensity in magnetic field**

The strong increase in PL intensity of an ensemble of Cd(Mn)Se/Zn(Mn)Se QDs in the magnetic field $B \parallel 0z$ is explained as a result of suppression of the exciton non-radiative recombination because of depopulation of $A_1(5/2, S_z)$ states with $S_z > -5/2$ [4, 11]. The results of section 3 reveal that the Coulomb process is allowed for $S_z = \pm 5/2$ and it does not contribute to the increase in PL intensity.

The exchange and sp–d mechanisms lead to conservation of the total spin projection $S_z + s_{ex,z} = $ const. Recombination of bright excitons ($s_{ex,z} = 0$) requires $\Delta S_z = 0$, whereas the recombination of dark excitons ($s_{ex,z} = \pm 1$) is possible when $\Delta S_z = \mp 1$.

The selection rules predict that the non-radiative recombination of bright excitons involving $S_z = 5/2$ is spin-forbidden, whereas it is allowed for the dark exciton with $J_z = 2$ ($s_{ex,z} = 1$) and forbidden for that with $J_z = -2$ ($s_{ex,z} = -1$). The strong increase in PL intensity requires slow relaxation of bright excitons to $J_z = 2$ dark states. Phonon-assisted recombination and energy transfer into upper excited Mn$^{2+}$ levels do not break the rules.

However, the selection rules are not valid for e–h complexes formed by hole states with a large admixture of lh states, which is the case for bulk DMS materials of cubic symmetry. In contrast, the selection rules should be valid for highly anisotropic crystals of wurtzite structure such as CdMnS, which is in agreement with the results of photoreflectance measurements reported by Nawrocki et al [11].

Recent studies of the optically detected magnetic resonance give additional arguments in support of spin-dependent energy transfer from an ensemble of CdMnSe/ZnSe
QDs to Mn$^{2+}$ ions and its dependence on the direction of the magnetic field [43].

The observed increase in QD PL intensity indicates that spin-dependent sp–d and exchange mechanisms dominate over the Coulomb one. This assumption correctly explains the magnetic field and temperature dependence of the PL intensity of a QD ensemble. The following empirical expression is found to fit the experimentally observed increase in PL intensity with magnetic field $B \parallel oz: I(B) = \frac{A}{(1 + C p(B/T))},$ where $p(B/T) \simeq \alpha + \beta e^{-E(B)/k_B T},$ and $\alpha, \beta, A$ and $C$ are constants [2, 4]. This well-known expression describes the temperature dependence of the interband PL intensity in the presence of non-radiative recombination centers. The magnetic-field-dependent activation energy is $\Delta E(B) = \Delta_{eh} + \Delta_{Mn},$ where $\Delta_{eh} = \mu_B (g_e + g_h) B$ is the energy of Zeeman splitting of e–h states. The parameter $\alpha$ is the probability of non-radiative recombination independent of magnetic field while $\beta$ is the probability of non-radiative recombination involving the $S_c = -3/2$ level [2, 4, 11]. Results of [2] indicate that the ratio $I(B)/I(0) \simeq (1 + \beta/\alpha)$ can reach $10^3$ in high magnetic fields $\Delta E(B)/k_B T > 1$ [2], which is possible if $\beta \ll \alpha$ and the relaxation of the bright excitons into lower dark states is slow.

Since the radiative lifetime of the $^4T_1(3/2) \rightarrow ^6A_1(5/2)$ transition is substantially longer than the time of non-radiative recombination, fast saturation of $I(B)$ is expected because only a few tens of Mn$^{2+}$ ions can interact with the localized e–h pair. The derivation of $I(B)$ implies, however, that the reservoir of Mn$^{2+}$ ions is infinite. This fact can be related to the fast energy diffusion within an ensemble of Mn$^{2+}$ ions [42]. The dependence $I(B)$ very well describes experimental results [2, 4, 6], which supports the assumption.

The QDs considered in [2, 4] are assumed to be neutral; meanwhile a considerable amount of QDs in the ensemble can be negatively charged due to an n-type background doping almost always present in II–VI materials. The selection rules predict that $X^–j_z = \pm 3/2$ states are involved in non-radiative recombination at $B = 0$. In a magnetic field $B \parallel oz,$ which polarizes both trion and Mn$^{2+}$ states, only the $j_z = +3/2$ trion participates in the non-radiative recombination whereas the $j_z = -3/2$ trion does not.

At an Mn content of $x = 1–2\%$ the lower $X^–j_z = 3/2$ state in magnetic field $B \parallel oz$ is that with $j_z = 3/2$ [13]. Negatively charged QDs do not lead to an increase in PL intensity when the relaxation from the $j_z = -3/2$ to the $j_z = 3/2$ state is fast.

However, measurements of $X^–$ trions in individual CdSe/ZnSe/ZnMnSe QDs reported in [13] show a surprising increase in the intensity of the upper $\sigma^–$ component of the trion PL in magnetic field $B \parallel oz$. This result can be understood on the grounds of the proposed model if the relaxation $j_z = -3/2$ to $j_z = 3/2$ is slow. The two-level model, which takes into account the non-radiative recombination, relates the time of non-radiative recombination $\tau_{nr}$ to the time of spin relaxation $\tau_{s}$ from the upper trion state: $\tau_{nr}(B) < \tau_{s}/(1-e^{-\Delta_{Mn}/k_B T}),$ where $\Delta_{Mn} = \mu_B M_B B$ is the Zeeman splitting of the nearest Mn levels. This is probably because the relaxation $-3/2 \rightarrow 3/2$ requires changes $\Delta j_z = 3$ so that it can be slow in QDs under study because of strong lh–lh splitting and the splitting of Mn$^{2+}$ spin states in a magnetic field. Negatively charged Mn$^{2+}$ ions, therefore, can contribute to the increase in $I(B)$.

In the Voigt geometry ($B \perp oz$) the magnetic field aligns Mn$^{2+}$ and electron spins opposite to the direction the field whereas hh hole moments remain directed along $oz$. In addition, all dark $|\pm 2|$ and bright $|\pm 1|$ exciton states mix at $B \perp oz$. According to the selection rules the non-radiative recombination of dark excitons $J_z = 2$ is allowed at any $B$ and, therefore, no increase in PL intensity is expected in the Voigt geometry, which is in agreement with the results presented in [2]. The non-radiative recombination of trions in the Voigt geometry is also allowed because of the mixing of $|\pm 3/2|$ states.

The Mn–Mn interaction has been omitted in the foregoing discussion; meanwhile it causes the formation of Mn clusters among which Mn–Mn pairs and triads are the most important [44]. The number of the pairs quickly increases with increase in Mn content and reaches a maximum at $x$ of several per cent. The pairs are characterized by the relatively large antiferromagnetic coupling energy, about 1 meV for nearest neighbors in CdMnSe and ZnMnSe [14], so that they remain coupled even at a high magnetic field of about 12 T. Such pairs do not participate in the Zeeman splitting of band states as the total spin of the pair is zero. In contrast, the pairs can participate in radiative and non-radiative recombinations as those processes involve excitation of individual Mn$^{2+}$ ions in the pairs. The Mn–Mn coupling energy is still too weak to modify or mix 3d$^5$ configurations of individual ions within the pair as the energy gap between 3d configurations is several electronvolts. Therefore, there are not many reasons to expect strong changes of either $R_{Coul}$ or the time of the intraionic optical transition $1/\tau_c$. There are no reasons to expect strong changes of $M_{mix}$ and $M_{ex}$ due to the formation of pairs and triads.

Experimental results reported in [44] revealed, however, a shorter PL lifetime of the d–d pair line than that of individual Mn$^{2+}$ ions. It can be assumed that the pair formation modifies the Mn$^{2+}$ ion’s environment and changes the covalent coupling strength, which, in turn, decreases $\tau_c$. Consequently, an increase of $R_{Coul}$ and the ratio $R_{Coul}/R_{max}$ with Mn$^{2+}$ content can be expected as $R_{max}$ linearly depends on $x$. The Mn–Mn pairs do not lead to the increase in $I(B)$, because the magnetic field does not align spins of coupled Mn$^{2+}$ ions. In contrast to the pairs, Mn–Mn–Mn triads are characterized by nonzero average spin and therefore can contribute to the increase in $I(B)$.

The sp–d and exchange mechanisms are short-range ones and they are effective within the e–h pair localization volume. In contrast, the dipole–dipole mechanism is a long-range one. It may be important in CdSe/ZnMnSe QDs and obscure spin-dependent effects. At distances between the CdSe/ZnMnSe QD edge and the Mn$^{3+}$ ion core $R_0$ much larger than the QD dimensions $M_{Coul}$ decreases as $R_0^{-6}$ [31, 33]. Thus, the ratio $R_{Coul}/R_{max}$ increases with $R_0$ and the dipole–dipole mechanism can dominate at large distances. Assuming that the energy transfer between Mn ions is fast one can expect a larger increase in $I(B)$ for CdMnSe/ZnSe neutral QDs with $x < 0.1$ and a smaller one for CdSe/ZnSe/ZnMnSe neutral QDs, which is in agreement with experimental results [2, 41]. At large
Appendix A. Matrix element of non-radiative recombination due to Coulomb interaction

The only term in $\hat{V}_0$ leading to the transition from the initial state $|f\rangle = \hat{T}_1(3/2, S_z)|0\rangle$ states in first order is

$$
\hat{V}_1 = \sum_{\mu \nu \mu', \nu'} \sum_{\mu m, \mu' m'} (V_{\mu \nu \mu', \nu'} d_{m \mu}^\dagger \psi_{\mu}\psi_{\mu'}) + h.c.,
$$

(A.1)

where $V_{\mu \nu \mu', \nu'}$ is parameterized as

$$
V_{\mu \mu', \nu \nu'} \approx \langle d_{m \mu} \psi_{\mu'} | d_{m' \nu} \psi_{\nu'} \rangle + \text{V}_{m, \mu, \nu}.
$$

The Coulomb operator can be rewritten as $\hat{V}_{\mu \nu} \equiv \sum_{\mu m, \nu m'} \sum_{\mu m, \nu m'} \psi_{\mu}^\dagger \psi_{\nu}^\dagger d_{m \mu} \psi_{\mu'} d_{m' \nu} + h.c.$ and the Coulomb matrix element $\langle f | \hat{V}_{\mu \nu} | i \rangle$ is equal to $e^2 / \epsilon_{\mu}$ $\langle f | \hat{d} | i \rangle$, where $\hat{d} = \sum_{\mu m, \nu m'} \sum_{\mu m, \nu m'} \psi_{\mu}^\dagger \psi_{\nu}^\dagger d_{m \mu} \psi_{\mu'} d_{m' \nu}$ is the operator of the intraband dipole transition and $\hat{\psi}_{\mu}$ is the operator of the intraatomic dipole transition and $\hat{\psi}_{\mu}$ is the operator of the intraband dipole transition and $\hat{\psi}_{\mu}$ is the operator of the intraband dipole transition and $\hat{\psi}_{\mu}$ is the operator of the intraband dipole transition and $\hat{\psi}_{\mu}$ is the operator of the intraband dipole transition and $\hat{\psi}_{\mu}$ is the operator of the intraband dipole transition and $\hat{\psi}_{\mu}$ is the operator of the intraband dipole transition.

The matrix element

$$
\langle \mu \nu | \hat{V}_{\mu \nu} | \nu \mu \rangle = \langle \mu | \hat{d} | \nu \rangle
$$

(A.4)

The wavefunctions of the ground state of the conduction electron, $\psi_0 = 0$, are $|\phi_0^k\rangle = \pm 1/2 = |r_1^k\rangle = |\mu \nu \rangle = \phi_{\mu \nu}^k(r) = F_{\mu \nu}(r)u_{\nu, \pm 1/2}(r) = \sum_k A_k(k) e^{i k r} u_{\nu, \pm 1/2}(r)$, where $u_{\nu, \pm 1/2}(r) = \mp (X + i Y)_{\pm 1/2}/\sqrt{2}$ are periodic parts

Acknowledgments

This work has been supported by the Russian Foundation for Basic Research, FCT project PTDS/FIS/72843/2006 and SANDiE Network of Excellence. The authors are grateful to I N Yassievich, S N Molotkov and V M Edel’stein for fruitful discussions and to S Diehm for reading the manuscript and supplying critical comments.
of the Bloch functions of conduction and valence electrons, respectively. Wavefunctions of the bright exciton are $$|\pm 1\rangle = c_{\pm 1/2} b_{\pm 3/2}(0)$$. The transition is spin and parity forbidden respectively. Wavefunctions of the bright exciton are

$$|\pm 1\rangle = c_{\pm 1/2} b_{\pm 3/2}(0)$$

which means that the Coulomb process reduces to the dipole–dipole transition. The transition is spin and parity forbidden.

$$\langle u_{\pm 1/2}\rangle = \langle u_{\pm 3/2}\rangle$$

Therefore, the matrix element $$M_{\text{Coul}}$$ becomes

$$M_{\text{Coul}} = \frac{4\pi e^2}{\epsilon_\infty} \sum_{k,k'} |d_{\pm 1/2} r_{\pm 3/2} (k) F_{\text{hho}}(a_0) F_{\text{th}}(a_0) d_{\pm 1/2} r_{\pm 3/2} (k)$$

which means that the Coulomb process reduces to the dipole–dipole energy transfer. The above result can be reproduced if the matrix element

$$M_{\text{Coul}} = \frac{4\pi e^2}{\epsilon_\infty} \sum_{k} |d_{\pm 1/2} r_{\pm 3/2} (k) F_{\text{hho}}(a_0) F_{\text{th}}(a_0) d_{\pm 1/2} r_{\pm 3/2} (k)$$

is considered, where $$V_{\text{coul}}(r_1, r_2, \cdots, r_9) = \sum_{i=1}^{9} v_{\text{coul}}(r_i - r_i)$$. Indeed, the matrix element of the transition

$$\langle 0\rangle A_1(1/2, 1/2) \psi_{\text{exc}}(J_z = \pm 1) \rightarrow T_{1/2}(3/2, 3/2)$$

can be expressed as

$$M_{\text{Coul}} = \frac{4\pi e^2}{\epsilon_\infty} \sum_{k} |d_{\pm 1/2} r_{\pm 3/2} (k) F_{\text{hho}}(a_0) F_{\text{th}}(a_0) d_{\pm 1/2} r_{\pm 3/2} (k)$$

where $$a_0$$ is the atomic Bohr radius and $$\lambda$$ enumerates the Mn$$^{2+}$$ ions. In derivation of this equation the relations $$r = i k p/m_0 V_{\text{coul}}$$ and $$P^2 = E_k = (\Delta/\epsilon_k/2/m_0)$$ are used, where $$m_0 = 0.1 m_0$$ is the conduction electron mass in CdSe or ZnSe [19]; $$\Delta$$ is the Kane constant. Since $$\Delta/E_k < 0.3$$ in ZnSe and CdSe crystals we assume that $$\Delta/E_k = 0$$.

After averaging over positions of the Mn$$^{2+}$$ ion, the rate becomes

$$R_{\text{Coul}} = \frac{2\pi}{h} \langle 4\pi^2 \rangle N_{\text{Mn}} \left( \frac{e^2}{\epsilon_\infty a_0} \right)^2 \frac{d^3 r}{V_{\text{coul}}} \delta(E_k - E_f) \left( \frac{d^3 r}{8m_0 a_0^2 E_k} \right)$$

where $$V_{\text{coul}}$$ is the effective volume of electron (hole) localization and coefficients

$$\eta_{\text{eb}} = \int_{V_{\text{coul}}} d^3 r |F_{\text{eb}}(r)|^2$$

characterize penetration of the electron (hole) wavefunction into the DMS layer.

The presented analysis generalizes the approach developed in [7, 8, 25], where the interconfigurational optical transitions are considered as single-electron ones.
Appendix B. Matrix element of non-radiative recombination due to sp–d hybridization

The Hamiltonian responsible for the non-radiative recombination via sp–d mixing is

$$\hat{H}_{mix} = \sum_{m,m',\alpha',\sigma_1,\sigma_2, i,j} (K_{mix} d_{m\sigma_1}^\dagger d_{m'\sigma_2}^\dagger b_{ij}^\dagger e_{\alpha_1\sigma_1} + \text{h.c.}) \tag{B.1}$$

where

$$K_{mix} = -V_{id} m_{\sigma_1} \langle \psi_{pd} \rangle_{m'\sigma_2} \left( \frac{1}{E_i - E^*} + \frac{1}{E_i - E^*} \right) \tag{B.2}$$

and $E_i$ is the energy of the initial state whereas $E^*$ and $E^*$ are the energies of intermediate states. For calculations of the matrix element we use wavefunctions of the ground and excited states in the spherical approximation similar to the approach of Schiffer in the calculation of the kinetic exchange constant [20]. We choose the initial state of the Mn$^{2+}$ ion to be $|A_1(5/2, -5/2)\rangle = \sum_{m=-2}^2 d_{m\sigma_1=1/2}^\dagger |0\rangle$. States with other spin projections can be obtained from this state by means of the step-up $\hat{S}_z = \sum_{m} d_{m1/2}^\dagger d_{m-1/2}$ and step-down $\hat{S}_z = \sum_{m} d_{m-1/2} d_{m1/2}$ spin operators: $|5/2, S_z\rangle = C_S \sqrt{5/2} S^z |0\rangle$ and $|3/2, S_z\rangle = C_{3/2} \sqrt{3/2} S^z |0\rangle$, where $C$ is the normalization constant. In particular, $C = 1/\sqrt{5}$ for $S_z = \pm 3/2$ and $C = 1/\sqrt{10}$ for $S_z = \pm 1/2$.

We assume here that Hund’s rules are valid. Thus, the final state is the $G^2(3/2)$ excited state of the Mn$^{2+}$ ion $|3/2, -3/2\rangle = d_{3/2}^\dagger d_{-3/2}^\dagger |0\rangle$. Creation and annihilation operators $d_{m\sigma_1}^\dagger, d_{m\sigma_1}$ satisfy standard commutativ relations. Although $\langle \psi_d | d_{m\sigma_1}^\dagger \rangle \neq 0$ and $\langle \psi_d | d_{m\sigma_1}\rangle \neq 0$, Kane basis functions are orthogonal to 3d states, so that the nonorthogonality effect is negligibly small.

The initial state for the recombination of a bright exciton $|1\rangle = c_{1/2}^\dagger b_{3/2}^\dagger |0\rangle$ is $|i\rangle = c_{1/2}^\dagger b_{1/2}^\dagger C_S \sqrt{5/2} S^z |0\rangle$, whereas the final state is $|f\rangle = d_{1/2}^\dagger d_{-1/2}^\dagger C_{3/2} \sqrt{3/2} S^z |0\rangle$. Matrix elements of the s–d coupling are $|V_{sd}\rangle = |V_{sd}\rangle = |V_{pd}\rangle \sqrt{7/2}$. Transitions involving the state $d_0$ are forbidden because they do not mix with valence band states, i.e. $V_{sd} = 0$.

By means of the relation $V_{pd} = 4V_{pd} \sqrt{N_0}$, where $V_{pd}$ is the hopping amplitude [14, 22], the matrix element of the transition $|A_1(\pm 3/2)J_z=1\rangle \to |T_1(\mp 3/2)\rangle$ is

$$M_{mix} = \alpha(\pm 3/2) \frac{16}{N_0} F_{e=0}(a_0) F_{\beta=0}(a_0) |V_{pd}|^2 \times \left( \frac{1}{U_{eff} + \epsilon_d - E_c} + \frac{1}{E_c - \epsilon_d} \right) \left( \frac{\gamma}{2} \right)^{1/2} \tag{B.3}$$

where $N_0$ is the number of unit cells per unit volume and $\alpha(\pm 3/2) = -1/\sqrt{5}$. By means of spin-up operators and wavefunctions of the initial and final states the coefficient $\alpha(\pm 1/2) = -\sqrt{3}\gamma/10$ for the transition $|A_1(\pm 1/2)J_z=1\rangle \to |T_1(\pm 1/2)\rangle$ can be found.

By using $\varphi_d^\dagger(\epsilon)$ for free electrons the coefficient $\gamma$ is evaluated as $\gamma \approx h^2/2m_e E_g L^2$. A smaller value $\gamma \approx h^2/2m_e E_g L^2 / (1 + h^2/2m_e E_g L^2)$ can be found for the symmetric quantum well of width $L$ with infinitely high barriers by using functions $\psi_{d1/2}^\dagger(\epsilon)$ presented in [17]. Since $E_1 = 5D - E_c + E_c, E_2 = 4eV_c + E_c$ and $U_{eff} = 7.0 eV$ then $E_1 - E_2 = -(E_c - \epsilon_d) \approx -3.5 eV$ and $E_1 - E_3 = -(U_{eff} + \epsilon_d - E_c) \approx -1.5 eV$. Values of $U_{eff}$, $E_c - \epsilon_d$ and $V_{pd}] \approx -0.6 eV$ are taken from [16].

Taking into account equation (B.3) the probability of non-radiative recombination is as follows:

$$R_{mix} = \frac{1}{\tau_{mix}} = \frac{1}{N_1} \sum_{\alpha} \sum_{\epsilon} \frac{2\pi}{\hbar} |M_{mix, \alpha}|^2 \delta(E_i - E_f). \tag{B.4}$$

Here $\lambda$ enumerates the Mn$^{2+}$ ions. The recombination rate of the bright exciton averaged over the Mn$^{2+}$ ion distribution can be obtained in the manner described in appendix A.

The ratio of rates, corresponding to the Coulomb and sp–d mixing processes, is

$$R_{Coul}/R_{mix} = \frac{1}{2} \left( \frac{c_{eff}^2}{\epsilon_\alpha^2} \right)^2 \left( \frac{a_0^2}{\Omega_0} \right)^2 \left( \frac{\lambda}{\alpha_0} \right)^2 \lesssim 10^{-2} \tag{B.5}$$

where $U = 1/(\epsilon_d + U_{eff} - E_c) + 1/(E_c - \epsilon_d), \epsilon_\infty \approx 6$ and $\Omega_0$ is the volume of the unit cell.

The parameters of $U_{eff}$, $E_c - \epsilon_d$ and $V_{pd}$ are not independent but related to each other via the exchange constant $\beta$. These parameters are obtained by means of theoretical and numerical analysis of Zeeman splitting of band states and photoemission spectroscopy data [14]. The experimental results of Zeeman splitting as well as photoemission data are reported with an accuracy of two significant figures. The best correspondence between experimental and theoretical results is found with values $U_{eff} = 7.0 eV, E_c - \epsilon_d = 3.5 eV$ and $V_{pd} = 0.6 eV$ for CdMnSe [14, 16]. Taking into account the uncertainty of the parameter $\epsilon_d + U_{eff} - E_c$ related to the fact that $E_g$ depends on the Mn content and strain distribution within the sample we conclude that the accuracy of our estimate is better than an order of magnitude.

References

[1] Awschalom D D, Loss D and Samarth N 2002 Semiconductor Spintronics and Quantum Computations (Berlin: Springer)
[2] Chernenko A V, Dorozhkin P S, Kulakovskii V D, Brichkin A S, Ivanov S V and Toropov A A 2005 Phys. Rev. B 72 045302
[3] Kratzert P R, Puls J, Rabe M and Henneberger F 2001 Appl. Phys. Lett. 79 2814
[4] Kim C S, Kim M, Lee S, Kossut J, Furdy J K and Dobrowolska M 2000 J. Cryst. Growth 214/215 395
[5] Makowski S, Lee S, Furdy J K, Dobrowolska M, Prechal G, Hiijs W, Kossut J and Karczewski G 2002 Phys. Status Solidi b 229 469
[6] Lee S, Dobrowolska M and Furdyna J K 2005 Phys. Rev. B 72 075320
[7] Robbins D J and Dean P J 1978 Adv. Phys. 27 499
[8] Allen J W 1986 J. Phys. C: Solid State Phys. 19 6287
[9] Falk H, Hubner J, Klar P J and Heimbroidt W 2002 Phys. Status Solidi b 229 781
[10] Falk H, Hubner J, Klar P J and Heimbroidt W 2003 Phys. Rev. B 68 165203
[11] Nawrocki M, Rubo Yu G, Lascaray J P and Coquillat D 1995 Phys. Rev. B 52 R2241
[12] Chekhovich E A, Brichkin A S, Chernenko A V, Kulakovskii V D, Sedova I V, Sorokin S V and Ivanov S V 2007 Phys. Rev. B 76 165305
[13] Brichkin A S, Chernenko A V, Chekhovich E A, Dorozhkin P S, Kulakovskii V D, Ivanov S V and Toropov A A 2007 JETP 105 379
[14] Larson B E, Hass K C, Ehrenreich H and Carlsson A E 1988 Phys. Rev. B 37 4137
[15] Hass K C 1991 Semimagnetic Semiconductors and Diluted Magnetic Semiconductors ed M Averrois and M Balkanski (New York: Plenum)
[16] Young P M, Ehrenreich H, Hui P M and Hass K C 1991 Phys. Rev. B 43 2305
[17] Merkulov I A 2000 Phys. Solid State 42 132
[18] Merkulov I A, Yakovlev D R, Keller A, Ossau W, Geurts J, Waag A, Landwehr G, Karczewski G, Wojtowicz T and Kossut J 1999 Phys. Rev. Lett. 83 1431
[19] Abakumov V N, Perel V I and Yassievich I N 1991 Nonradiative Recombination in Semiconductors (Modern Problems in Condensed Matter Sciences) vol 33, ed V M Agranovich and A A Maradudin (Amsterdam: North-Holland)
[20] Schriffer J R 1967 J. Appl. Phys. 38 1143
[21] Griffith J S 1962 The Theory of Transition Metal Ions (Cambridge: Cambridge University Press)
[22] Bhattacharjee A K 1992 Phys. Rev. B 46 5266
[23] Blinowski J, Kacman P and Przybylinska H 1991 Solid State Commun. 79 1021
[24] Kikoin K A and Fleurov V N 1994 Transition Metal Impurities in Semiconductors. Electronic Structure and Physical Properties (Singapore: World Scientific)
[25] Yassievich I N and Kimerling L C 1993 Semicond. Sci. Technol. 8 718
[26] Pantelides S T 1978 Rev. Mod. Phys. 50 797
[27] Flerov W B and Elliott R J 1986 Phys. Rev. B 34 5525
[28] Hirst L L 1970 Phys. kondens. Mater. 11 255
[29] Hirst L L 1971 Z. Phys. 244 230
[30] Prokofiev A A, Moskalenko A S and Yassievich I N 2008 Mater. Sci. Eng. B 146 121
[31] Andrews D L and Bradshaw D S 2004 Eur. J. Phys. 25 845
[32] Yassievich I N, Bresler M S and Gusev O B 1997 J. Phys.: Condens. Matter 9 9415
[33] Agranovich V M and Galanin M D 1982 Electronic Excitation Energy Transfer in Condensed Matter (Amsterdam: North-Holland)
[34] Calvert J G and Pitts J J N 1966 Photochemistry (New York: Wiley) chapter 2
[35] Boulanger D, Parrot R and Cherfi Z 2004 Adv. Funct. Mater. 14 3873
[36] Abramishvili V G, Komarov A M, Ryabchenko S M and Semenov Yu G 1991 Solid State Commun. 78 1069
[37] Elliot J P and Dawber P G 1985 Symmetry in Physics vol 2 (Oxford: University Press) chapter 17
[38] Schmitt-Rink S, Varma C M and Levi A F J 1991 Phys. Rev. Lett. 66 2782
[39] Aying S G and Allen J W 1987 J. Phys. C: Solid State Phys. 20 4251
[40] Moriswaki M M, Becker W M, Gehrdt W and Galazhka R R 1982 Phys. Rev. B 26 3165
[41] Toropov A A, Sorokin S V, Kuritsyn K A, Ivanov S V, Pozina G, Bergman J P, Wargen Mt, Chen W M, Monemar B, Waag A, Yakovlev D R, Sas C, Ossau W and Landwehr G 2001 Physica E 10 362
[42] Agekyan V F 2002 Phys. Solid State 44 2013
[43] Baranov P G, Romanov N G, Tolmachev D O, Babunts R A, Namozov B B, Kusrayev Yu G, Sedova I V, Sorokin S V and Ivanov S V 2008 JETP Lett. 88 631
[44] Benecke C, Busse W, Gumlich H E and Pohl U W 1985 Phys. Status Solidi b 128 701
[45] Boulanger D, Parrot R and Cherfi Z 2004 Phys. Rev. B 70 075209