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Research paper

# Multiexponential dynamics of $Mn^{2+}(3d^5)$ excitation in manganese doped ZnCdS quantum dots: Stimulated emission band in femtosecond transient spectra reveals ultrafast nonradiative energy transfer to $Mn^{2+}(3d^5)$



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#### HIGHLIGHTS

- The stimulated emission (SE) of Mn<sup>2+</sup> was detected in Mn@ZnxCd1-xS the quantum dots.
- The excited Mn<sup>2+</sup> was detected at 120 fs time delay.
- $\bullet$  Energy transfer from exciton to  $\mathrm{Mn}^{2+}$  occurs in the femtosecond and picosecond scale.

#### ABSTRACT

Stimulated emission (SE)  ${}^{4}T_{1} \rightarrow {}^{6}A_{1}$  bands of  $Mn^{2+}(3d^{5})$  in  $Zn_{x}Cd_{1-x}S$  or  $Zn_{x}Cd_{1-x}S/ZnS$  quantum dots were detected in the femtosecond transient absorption spectra at a time delay of 120 fs. Multiexponential rise of SE( $Mn^{2+}$ ) amplitude due to nonradiative energy transfer to  $Mn^{2+}(3d^{5})$  occurs both in the femtosecond and picosecond time domain. Transient kinetics of SE( $Mn^{2+}$ ) band reveals the dynamics of energy transfer to  $Mn^{2+}(3d^{5})$  with time constants  $\tau_{1} \sim 400$ –600 fs,  $\tau_{2} \sim 4$ –6 ps and  $\tau_{3} \sim 87$ –112 ps. A possible mechanism of ultrafast energy transfer to the  $Mn^{2+}(3d^{5})$  center accompanied by spin-flip is discussed.

#### 1. Introduction

Since the first report by Bhagrava et al. [1] about luminescence enhancement and shortening of lifetimes of  $Mn^{2+}$  luminescence in  $Mn^{2+}$ @ZnS nanoparticles many works concerning to quantum dots (QDs) doped by metal ions were published [2–10]. The fundamental questions in these works were an energy transfer mechanism from an excited quantum dot to the dopant ion and the relaxation mechanism of the excited ion of the dopant atom [11,12]. Bhagrava et al. [1] suggested that a mixture of the electronic states of the ZnS QDs and the dstates of  $Mn^{2+}$  (3d<sup>5</sup>) promotes the transfer of exciton energy to  $Mn^{2+}$ (3d<sup>5</sup>) levels. Mixing of sp ZnS atomic level and  $Mn^{2+}$  (3d<sup>5</sup>) orbitals controls the spin-forbidden  ${}^{4}T_{1} \rightarrow {}^{6}A_{1}$  radiative transition in manganese. Later Chen et al. analyzed effect of crystal field and phonon coupling on  ${}^{4}T_{1} \rightarrow {}^{6}A_{1} Mn^{2+}$  emission in  $Mn^{2+}$ @ZnS QDs. [13] The excitation of  $Mn^{2+}$  (3d<sup>5</sup>) ions occurs due to nonradiative direct transfer from an edge exciton or transfer through intermediate states of traps [1–7,10,13–17]. Numerous works were dedicated to the study of the dynamics of the  $Mn^{2+}$  luminescence decay in QDs [1,4,6,7,10,14,16]. Only a few works are related to the dynamics investigations of the excitation of  $Mn^{2+}$  (3d<sup>5</sup>) ions [3,5,18,19].

In our letter, we report on the observation in the femtosecond transient absorption (TA) spectra a stimulated emission (SE) band which can be attributed to the  ${}^{4}T_{1} \rightarrow {}^{6}A_{1}$  radiative transition in  $Mn^{2+}$ ions that were embedded in  $Zn_{x}Cd_{1-x}S$  or  $Zn_{x}Cd_{1-x}S/ZnS$  core/shell QDs. The objective of the work is to determine the characteristic times of  $Mn^{2+}(3d^{5})$  excitation. We report about ultrafast formation of excited  $Mn^{2+}(3d^{5})$  accompanied by spin-flip due to the light absorption by band-edge exciton. Controlling the spin state of a magnetic  $Mn^{2+}$  ion using illumination opens up a unique opportunity to manipulate the photocatalytic and photoluminescent efficiency of a semiconductor nanostructure.

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#### 2. Experimental

#### 2.1. Materials

Zinc acetate dihydrate (Zn(OAc)<sub>2</sub>2H<sub>2</sub>O, 98%), cyclohexane (99+%, for spectroscopy), 1-octadecene (ODE, 90%, tech.,), tetramethylammonium hydroxide (TMAH, 25 wt% in methanol), manganese(II) chloride (MnCl<sub>2</sub>, anhydrous, 99%), CdO (99.5%), oleic acid (HOl, 90%, tech.), oleylamine (OlAm, C18 80–90%) cadmium acetate dihydrate (Cd(OAc)<sub>2</sub>2H<sub>2</sub>O,  $\geq$  98%), stearic acid (HSt, 95%) were purchased from Merck. Sulfur (reagent grade, 100 mesh) was purchased from Sigma-Oldrich. Reagents were used as received.

## 2.2. Synthesis of ZnxCd1-xS, Mn@ZnxCd1-xS and Mn@ZnxCd1-xS/ZnS QDs

Three types of QDs doped and undoped by  $Mn^{2+}$  (ZnxCd1-xS, Mn@ ZnxCd1-xS and Mn@ZnxCd1-xS/ZnS QDs) were synthesized under argon atmosphere at 310 °C. Synthesis details are present in supporting information (SI 1).

#### 2.3. Physical, optical measurements

*Transient absorption spectra* (TA) was measured by the femtosecond pump-probe technique with supercontinuum probe. The femtosecond pump pulse of 250 nJ energy, 30 fs time duration, 445 nm wavelength was used to excite the QD1 and QD2 samples. Femtosecond pulse with 405 nm wavelength was used to pump QD3 sample. Measurements were carried out in flow optical cell with length of 300  $\mu$ m at temperature of 278 K. The cyclohexane QD colloid solution was refreshed between incident laser pulses by a pump. The pump and probe light spots had the diameter of 300 and 120  $\mu$ m, respectively. The TA spectra were corrected to account for the group delay dispersion of the supercontinuum. The experimental setup's parameters were described previously [20,21].

*Transmission electron microscopy* (TEM) images were obtained using a LEO 912 AB OMEGA (Karl Zeiss) microscope with accelerating voltage of 100 kV.

*Elemental microanalysis* was performed by micro-Kjeldahl digestion (acid mineralization) with subsequent analysis by atomic absorption spectrometry on the spectrometer KVANT-2AT.

Absorption spectra of QDs colloids were measured using "Shimadzu UV-3600 Plus" spectrophotometer. Steady-state fluorescence work was performed on a "Shimadzu" spectrofluorometer. Rhodamine 6 g and Coumarin 6 dyes were used as standard solutions for determining the quantum yield in accordance with protocols.

#### 3. Results and discussion

#### 3.1. Composition and properties of $Mn@Zn_xCd_{1-x}S$ QDs

The QD samples are named as QD1, QD2, QD3. Sample QD1 didn't contain  $Mn^{2+}$  ions and had chemical composition -  $Zn_{0.37}Cd_{0.63}S$ . The composition of QD2 sample was Mn@Zn<sub>0.45</sub>Cd<sub>0.55</sub>S, the atomic ration of Mn/Cd was equal to 0.009. The sample QD3 was synthesized as Mn@ Zn<sub>0.91</sub>Cd<sub>0.09</sub>S/ZnS core/shell structure with ZnS shell. The atomic ration of Mn/Cd was equal to 0.067 for QD3. Diameters (D) of quantum dots were determined form the analysis of TEM images: D  $(QD1) = 4.7 \pm 1.0 \text{ nm}, D(QD2) = 4.4 \pm 1.2 \text{ nm}, D$ (QD3) = 7.6  $\pm$  0.9 nm. D(QD3 core) was estimated as 3.8  $\pm$  0.9 nm (SI 2). X-ray diffraction analysis revealed extended reflection peaks associated with the nanoscale sizes of the QDs. ZnS shell thickness was estimated as 4 layers of ZnS on the basis of X-ray diffraction and TEM data. The average number of Mn<sup>2+</sup> per quantum dots was determined as  $< N_{Mn} > = 2.2$  for QD2 and  $< N_{Mn} > = 10.7$  for QD3. According to the Poisson statistics  $Pi = (\langle N_{Mn} \rangle^{i}/i!)exp(-\langle N_{Mn} \rangle)$ , the fraction of empty quantum dots P<sub>0</sub> is equal to 0.11 for QD2.



Fig. 1. Absorption, PL and PLE spectra of ZnxCd1-xS and ZnxCd1-xS/ZnS quantum dots with and without  $Mn^{2+}$ . A, QD1,  $Zn_{0.37}Cd_{0.63}S$ . 1, absorption; 2, PL, excitation at 360 nm; 3, second-d derivative of absorption spectrum. Insert,  $50 \times$  expanded graph of PL spectrum. B, QD2, Mn@  $Zn_{0.45}Cd_{0.55}S$ ,  $< N_{Mn} > = 2.2$ . 1, absorption; 2, PLE of 590 nm band; 3, second-d derivative of absorption spectrum; 4, second-derivative of PLE spectrum; 5, PL, excitation at 360 nm; 6, second-derivative of PL spectrum of 590 nm band. C, QD3, Mn@  $Zn_{0.9}Cd_{0.09}S$ ,  $< N_{Mn} > = 10.7$ . 1, absorption; 2, PLE of 590 nm band; 3, second-d derivative of absorption spectrum; 4, second-derivative of PLE spectrum; 5, PL, excitation at 360 nm; 6, second-derivative of PLE spectrum; 5, PL, excitation at 360 nm; 6, second-derivative of PLE spectrum of 590 nm band; 3, second-derivative of absorption spectrum; 4, second-derivative of PLE spectrum of 590 nm band.

Fig. 1 shows absorption, photoluminescence (PL) and photoluminescence excitation (PLE) spectra. Absorption and PLEX spectra in the form of the second derivative reveal exciton peaks. The band-edge exciton peak at 454 nm was detected for QD1 sample, at 430 nm for QD2 and at 402 nm for QD3. An increase in the ratio of Cd/Zn leads to a shift of the peak to the red region of the spectrum [22]. QD1 sample shows narrow strong PL at 462 nm and weak wide band at 566 nm. The A narrow PL band at a wavelength of 462 nm may can be attributed to the PL of band-edge exciton, and wide band at 566 nm possibly corresponds to the PL of trap states. The quantum yield of QD1 PL at 462 nm is  $\sim$ 35%, and for the weak band at 566 nm, 0.83%. PL spectra of QD2 and QD3 reveal strong and rather wide PL bands close to 590 nm. The emission band of ~570–590 nm was attributed to  ${}^{4}T_{1} \rightarrow$  $^{6}A_{1}$  transition of Mn<sup>2+</sup> ions in nanoparticles [1-7,10,13,14,16]. The PLE spectra of Mn<sup>2+</sup> PL resemble the shape of the absorption spectra, but a quantitative decrease in the PLE curve with respect to absorption line is observed in the short-wave region. Similar effect was reported in the case of PL of edge exciton PL. The decrease in the quantum yield

#### Table 1

The parameters of the decomposition of the Mn<sup>2+</sup> PL band into Gaussian peaks.

QD2			QD3	QD3		
Peak (eV)	Amplitude (%)	Width (meV)	Peak (eV)	Amplitude (%)	Width (meV)	
1.900(652 nm)	1.2	38.14	1.897(653 nm)	5.09	43.92	
1.958(633 nm)	2.3	32.95	1.950(635 nm)	4.66	33.71	
2.039(608 nm)	6.6	42.48	2.032(610 nm)	5.12	40.97	
2.097(591 nm)	17	71.33	2.070(599 nm)	55.7	73.87	
2.169(571 nm)	71	71.08	2.157(574 nm)	29.3	61.54	
2.370(523 nm)	1.4	60.48	2.299(539 nm)	0.2	21.91	

was observed in the short-wave spectral area region. This effect was interpreted as the competition of "hot" exciton scavenging by QDs traps with radiative transition of PL. [23] PLE and absorption spectra in the form of the second derivative of are very similar. It that implies that the PL of Mn<sup>2+</sup> may can be constitutes excited form band-edge as well as form higher excitonic states (Fig. 1). In QD2 sample with < $N_{Mn} > = 2.2$  two PL bands was are observed. The narrow weak band was is detected at 432 nm. This band can correspond to the PL of bandedge exciton in Mn-free nanoparticles of QD2 sample. The effective quantum yield of  $Mn^2$  <sup>+</sup> luminescence in the QD2 sample was ~26%. Only one strong PL band was detected at ~590 nm with a quantum yield of 43% for QD3 sample (  $< N_{\rm Mn} >~=~10.7$  ). Second derivative of ~590 nm PL bands for QD2 and QD3 disclosed that these bands are inhomogeneous (Fig. 1B and 1C). The peaks positions in ~590 nm PL bands for QD2 and QD3 were revealed by the analysis of second and fourth derivatives of PL spectra and by the decomposition of PL bands into Gaussian peaks (SI. The parameters of the decomposition into Gaussian peaks are given in Table 1. The positions and widths of this peaks practically coincide for both samples QD2 and QD3. However, the amplitudes of the Gaussian peaks are significantly different for QD2 and QD3 and due to this shape of the  $\mathrm{Mn}^{2+}$  PL bands is somewhat different. Four bands were reported for Mn<sup>2+</sup> photoluminescence in ZnS and  $Zn_xCd_{1-x}S$  semiconductor [2,16]. These bands were associated with Mn<sup>2+</sup> at axially, hexagonal and cubic distorted sites. In our case six Gaussian peaks were distinguished in Mn<sup>2+</sup> PL band. Apparently, the additional peaks of  $Mn^{2+}$  PL may be associated with sites inherent only to QDs. The time resolved decay of Mn<sup>2+</sup> PL exhibited biexponential kinetics for QD2 sample  $\tau_1^{PL} = 5.5$  ns (83%),  $\tau_2^{PL} = 143$  ns (17%). The lifetime in core/shell  $Zn_{0.91}Cd_{0.09}S/ZnS$  QDs was higher than 100 µs. An increase in the PL lifetime due to the deposition of a ZnS shell on the  $Zn_xCd_{1-x}S$  QD core was explained by the passivation of surface traps [7].

#### 3.2. Femtosecond transient absorption spectra

Fig. 2 shows transient absorption (TA) spectra after femtosecond laser pump with wavelength corresponding to band-edge exciton transition. Fig. 2A shows the leading motive for the shape of the TA spectra for all QDs. Spectral features in femtosecond TA spectra of QDs were discussed in many works: the negative absorption band was registered in the band-edge excition region due to the bleach of exciton band (BL) and to the stimulated emission (SE) of exciton; the positive absorption peaks corresponding to excited state absorption (ESA) were attributed to multielectron interactions, e.g. biexciton transion; weak broadband absorption in the TA red side was attributed to trap states [20,24,25]. We are focused on the analysis of the spectral Region of Interest (ROI) in Fig. 2A corresponding to the spectral region of  $Mn^{2+}$  PL band.

Fig. 2B and C show TA spectra for short and long delays in ROI domain for QDs doped and undoped by  $Mn^{2+}$ . Negative peaks are observed in samples containing manganese (QD2 and QD3) against the background of positive absorption in the TA spectra. The sample QD1 without  $Mn^{2+}$  doesn't reveal a negative peak. Background as a positive



**Fig. 2.** Transient spectra after excitation of band-edge exciton by a 445 nm pump pulse for QD1, QD2 and 405 nm for QD3. A, transient spectra of QD2 sample. Time delay: 1, 100 fs; 2, 10 ps; 3, 450 ps. ROI is Region Of Interest. B, transient spectra of QD1, QD2 and QD3 samples at time delay of 120 fs. 1, QD1; 2, QD2; 3. QD3. Smoothed negative peaks are Gaussian fitting of SE bands. C, transient spectra of QD1, QD2 and QD3 samples at time delay of 450 ps (left y-axis). 1, QD1; 2, QD2; 3, QD3. Smoothed negative peaks are Gaussian fitting of SE bands. 4, QD3, stationary  $Mn^{2+}$  PL band (right y-axis).

wide band apparently corresponds to traps ESA. Negative peaks suggest stimulated emission, and these SE bands are located in the spectral window of the  $Mn^{2+}$  transition. Fig. 2C demonstrates the PL band recorded by the steady-state fluorimeter for comparison with the SE band in TA spectra. A significant similarity may be noted between these SE and PL bands. This suggests that SE bands correspond to luminescent transition in  $Mn^{2+}$  centers. It should be especially noted that the SE ( $Mn^{2+}$ ) bands in samples QD2 and QD3 with manganese are recorded



Fig. 3. The map of transient absorption spectra in the region of  $Mn^{2+}$  PL. QD3 sample,  $Mn@~Zn_{0.91}Cd_{0.09}S, < N_{Mn} > ~=~10.7$ .

at short delay times (120 fs, Fig. 2B). TA spectra in the ROI were decomposed into SE peak and ESA. The SE(Mn<sup>2+</sup>) band was fitted by a Gaussian peak, as shown in Fig. 2B and C. ESA band in the ROI was treated as background. It was fitted by polynomial of the third order on a limited part of the spectrum in ROI. Fig. 3 gives an overall qualitative picture of the development of the SE(Mn<sup>2+</sup>) band. Figs. 2 and 3 suggest that SE (Mn<sup>2+</sup>) appears very fast on femtosecond time scale and then an additional increase in the amplitude of SE (Mn<sup>2+</sup>) occurs on the time scale from a picosecond to several hundred picoseconds. Fig. 4 shows a comparison of the transient curves of the BL<sub>exciton</sub> band decay and the kinetic curves of the rise SE (Mn<sup>2+</sup>) band. The satisfactory approximation of the BL<sub>exciton</sub> decay was achieved by 3-term exponential fits a<sub>1</sub>·exp( $-t/\tau_1$ ) + a<sub>2</sub>·exp( $-t/\tau_2$ ) + a<sub>3</sub>·exp( $-t/\tau_3$ ) + a<sub>4</sub>. Time constants and amplitudes are  $\tau_1 = 625$  fs, a<sub>1</sub> = 21.7%,  $\tau_2 = 4.41$  ps, a<sub>2</sub> = 28.9%,  $\tau_3 = 87.4$  ps, a<sub>3</sub> = 25.9%, a<sub>4</sub> = 23.5% for QD2 sample, < N<sub>Mn</sub> > = 2.2. Time constants and amplitudes are

#### Table 2

Time constants  $(\tau_i)$  and amplitudes in 3-term exponential fit of SE(Mn^{2+})  $b_i$  transient curves.

QD2, $< N_{Mn} > = 2$	2	QD3, $< N_{Mn} > =$	10.7
$\tau_1~=~625~fs$	$b_1 = 11.4\%$	$\tau_1 = 396 \text{ fs}$	$b_1 = 17\%$
$\tau_2 = 4.41 \text{ ps}$ $\tau_3 = 87.4 \text{ ps}$	$\begin{array}{l} b_2 \ = \ 8.55\% \\ b_3 \ = \ 15.4\% \\ b_4 \ = \ 64.9\% \end{array}$	$\begin{array}{l} \tau_2 \ = \ 6.1 \ ps \\ \tau_3 \ = \ 112 \ ps \end{array}$	$b_2 = 16\%$ $b_3 = 15\%$ $b_4 = 52\%$

 $\tau_1$  = 396 fs,  $a_1$  = 57%,  $\tau_2$  = 6.1 ps ps,  $a_2$  = 32%,  $\tau_3$  = 112 ps,  $a_3$  = 10%,  $a_4$  = 1

% for QD3 sample,  $< N_{Mn} >~=~10.7.$  Multiexponential kinetics of excitonic decay is common for QDs in colloids and it was studied previously [26]. Multiexponential decay dynamics can be due to heterogeneity in size, shape, structure and surface within OD sample. Also, the dynamics of multiexponential decay can be due to populations of different states, which differ in the rate of radiative and nonradiative transitions. These states may be accessible to excitonic charge carriers. It is worth noting here that an increase in  $< N_{Mn} >$  leads to faster decay of BLexciton (Fig. 4A, Table 2). This suggests the quenching of QDs excitons by manganese ions and the kinetics of the SE band rise can be characterized by the same set of time constants as the BL<sub>exciton</sub> decay. SE (Mn<sup>2+</sup>) kinetics curves in Fig. 4B were fitted by 3-term exponential rise function  $b_1(1-\exp(-t/\tau_1)) + b_2(1-\exp(-t/\tau_2)) + b_3(1-\exp(-t/\tau_2))$  $\tau_3$ ) + b<sub>4</sub> with the fixed set of time constants determined by the fitting of  $BL_{exciton}$  decay. The  $b_i$  (i = 1, 2, 3, 4) amplitudes varied only (Table 2). Fig. 4B shows that the  $BL_{exciton}$  transients and SE (Mn<sup>2+</sup>) rise kinetics can be approximated by the same sets of time constants. It should be noted that in the kinetics of the decay of the exciton and SE  $(Mn^{2+})$  development, a fast kinetic component with a time constant of the femtosecond time interval is observed. Chen et al. [5] determined the time constant of  $\tau_{ET}$   $\sim$  60 ps for energy transfer from exciton to  $Mn^{2+}(3d^5)$  in CdS/ZnS QDs by using simple kinetic model taking into account the competition of exciton relaxation and trapping. Kanemitsu et al. [18] reported  $\tau_{\text{ET}}$  value of ~2 ns. Chung et al. [3] found a 700 ps rise time for  $Mn^{2+}(3d^5)$  emission in ZnS nanoparticles. Olano et al. [19] reported that the energy transfer could occur on the time scale of tens of ps in ZnSe QDs. So, the time constants of the relatively slow components of the kinetics of Mn<sup>2+</sup>(3d<sup>5</sup>) excitation found in the present work



Fig. 4. A, exciton BL band amplitude vs. time delay. 1, QD3 sample, < N<sub>Mn</sub> > = 10.7. 2, QD2 sample,  $< N_{Mn} > = 2.2$ . Smoothed solid lines are 3-term exponential curve-fitting functions  $a_1 \exp(-t/\tau_1)$  +  $a_2 \exp(-t/\tau_2) + a_3 \exp(-t/\tau_3) + a_4$ . The same set of time constants  $\tau_i$  is used in curve fitting function of SE amplitude dependence on time in subplot B. B. Dependence of the SE(Mn<sup>2</sup><sup>+</sup>) intensity on time in the form of the amplitude dependence of the fitting Gaussian peak vs. time delay. 1, QD3 "hourglass" markers. 2, QD2 sample, sample, "circle" markers. Solid lines are curve-fitting functions  $b_1(1-\exp(-t/\tau_1)) +$  $b_2(1-exp(-t/\tau_2)) + b_3(1-exp(-t/\tau_3)) +$  $b_4$  with the same set of time constants  $\tau_i$  as in subplot A. C. SE(Mn<sup>2</sup> +) versus time, position of the fitting Gaussian peak as a function of time. 1, QD3 sample, "square" markers. 2, QD2 sample, "circle" markers.



Scheme 1. Energy levels of  $Mn^{2+}(3d^5)$  in  $Zn_xC_{1-x}dS$  QDs.

 $\tau_2 \sim$  4–6 ps and  $\tau_3 \sim$  87–112 ps are consistent with the previous publications. The excitation dynamics of  $Mn^{2+}(3d^5)$  in femtosecond time domain is registered in the first time. The value of b4 amplitude gives an idea of the fraction of excited Mn<sup>2+</sup>, which are formed within  $\sim$ 120 fs. The b<sub>4</sub> amplitude is about 64% for QD3 and about 52% for QD2 of the total amplitude of SE (Mn<sup>2+</sup>) band in a finite time delay of ~400 ps. Fig. 4C demonstrates the spectral shift of peak position of Gaussian peak of  $SE(Mn^{2+})$  in time. It should be noted that the position of the SE(Mn<sup>2+</sup>) peak with an increase in the delay time shifts to the position of the maximum of the Mn<sup>2+</sup>PL band recorded stationary. Taking into account that the PL band of  $Mn^{2+}(3d^5)$  is inhomogeneous and consists at least of six components (SI3, Fig. SI 1, 2). It can be assumed that the SE( $Mn^{2+}$ ) spectral shift is due to different excitation dynamics of various Mn<sup>2+</sup>(3d<sup>5</sup>) centers. The appearance of the ultrafast component of the  $SE(Mn^{2+})$  band with a time of less than 120 fs is not obvious and requires additional hypotheses. PLE spectra manifest that the dominant Mn<sup>2+</sup>(3d<sup>5</sup>) excitation occurs due to the excitonic states quenching (Fig. 1B and C). Scheme 1 shows energy levels of  $Mn^{2+}(3d^5)$ in  $Zn_xCd_{1-x}S$  QDs. The position of the energy levels of  $Mn^{2+}(3d^5)$  relative to the energy levels of QDs is poorly known. The energy mismatch between the exciton energy and the energy of  ${}^{4}T_{1} \rightarrow {}^{6}A_{1}$  spin-flip transition is  $\delta_1 + \delta_2 = 0.78$  eV for QD2 and 0.98 eV for QD3 that is higher than energy of longitudinal optical phonon, e.g.  $\hbar\omega_{LO}$ = 350 cm<sup>-1</sup> (43.4 meV) for Mn:Zn. Ultrafast  $Mn^{2+}(3d^5)$  excitation with compensation for energy mismatch by emission of the cascade of single-phonon transitions seems unlikely [25,27]. Multiphonon processes [27] can be taken into account as efficient nonradiative decay mechanism because the electron-vibronic (Huang-Rhys) coupling in alloy is much larger than in pure semiconductor as was shown for  $Zn_{1-x}Cd_xSe$  alloys [28]. Fast excitation of  $Mn^{2+}(3d^5)$  ions implies not the only conservation of energy, but also the Wigner's rule of conservation of spin must be observed. It means that additional electronic transition possibly with participation of trap states can be involved in the mechanism of fast Mn<sup>2+</sup>(3d<sup>5</sup>) excitation to conserve the spin. Gamelin et al. [29] theoretically shown that Auger relaxation in  $Mn^{2+}(3d^5)$  doped semiconductors are primarily related to efficient sp-d exchange coupling and due to this the Auger relaxation in Mn<sup>2+</sup>(3d<sup>5</sup>) fall in the time window of 1–10 ps [29]. Strong sp-d coupling may be a reason of the observed fast  $Mn^{2+}(3d^5)$  excitation in the present study.

#### 4. Conclusions

SE bands in the femtosecond TA spectra were registered in the spectral region of  $Mn^{2+}(3d^5)$  PL for  $Mn@Zn_xCdS_{1-x}$  and  $Mn@Zn_xCdS_{1-x}/ZnS$  QDs. The SE bands can be assigned with  ${}^{4}T_{1} \rightarrow {}^{6}A_{1}$  radiative transition in excited  $Mn^{2+}(3d^5)$ . Transient curves of SE  $(Mn^{2+})$  reveal dynamics of  $Mn^{2+}(3d^5)$  excitation due to nonradiative

energy transfer from band-edge exciton.  $Mn^{2+}(3d^5)$  excitation was detected at the femtosecond time scale and at the scale of tens to hundreds picosecond. Strong sp-d coupling may be a reason of the observed fast  $Mn^{2+}(3d^5)$  excitation. The time constants of the relatively slow components of excited  $Mn^{2+}(3d^5)$  production found in the present work in the range from ~5 ps to ~100 ps are consistent with previous publications.

#### CRediT authorship contribution statement

Victor Nadtochenko: Supervision, Project administration, Conceptualization, Data curation, Writing - original draft, Writing review & editing. Andrei Kostrov: Methodology, Data curation. Andrei Titov: Methodology, Investigation, Resources. Arseniy Aybush: Software, Methodology, Investigation. Fedor Gostev: Software, Methodology, Investigation. Ivan Shelaev: Investigation, Resources, Data curation. Denis Shepel: Investigation, Data curation. Olga Antonova: Investigation, Methodology. Sergei Kochev: Methodology, Investigation. Yuriy Kabachii: Formal analysis, Investigation, Methodology.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cplett.2020.137160.

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