Long-lived emission in Mn doped CdS, ZnS, and ZnSe diluted magnetic semiconductor quantum dots

Vitaly Proshchenko and Yuri Dahnovsky

Department of Physics and Astronomy/3905

1000 E. University Avenue

University of Wyoming

*Laramie, WY 82071**

(Dated: September 1, 2015)

Abstract

Slow luminescence is studied in Mn doped CdS, ZnS, and ZnSe quantum dots. Because of the high degeneracy of Mn d-orbitals, we employ the multi-determinant SAC-CI computational method to determine the spin-forbidden transition from the 4T_1 first excited to 6A_1 ground state. We find that the transition energies for each material are in the excellent agreement with the experimental data. The computations reveal that the absorption spectra are independent of the presence of Mn impurities in quantum dots. The calculations show that the Mn impurity levels are located inside the QD gaps and the slow emission energies are independent of QD sizes. These features allow us to conclude that there are two luminescence peaks in the spectrum with fast (the higher energy) and slow (the lower energy) relaxations. In experiments sometimes the fast luminescence band disappears. This effect depends on Mn concentrations and a doping method. For different QD crystal structures the Mn-S (Se) bond lengths can vary. Therefore we find that the slow luminescence energy is very sensitive to a bond length. Indeed if we change the Mn-S bond length by $0.1 \text{ \AA}$, the energy increases by 0.2 eV within the calculated range of bond lengths.

INTRODUCTION

Group II-VI compound semiconductor nanocrystals are the most attractive in the growing field of nanoscience because the absorption properties can be changed by the size of quantum dots. [1–8] The incorporation of Manganese atoms into semiconductor nanocrystals results in diluted magnetic semiconductors (DMS) that can exhibit simultaneously both a magnetic order and unusual optical properties. [9–19] Such interesting magneto-optical and magneto-electronic properties [20–35] can be due to the strong Mn-(sp-band) exchange interactions. Magnetic nanocrystals can be also efficient in nanospintronics [20] and may become a novel class of emissive materials. [17] It was experimentally demonstrated that Mn doping of ZnSe, ZnS, CdS and ZnTe nanocrystals leads to the appearance of a new emission line at lower energies. [9–19, 32, 35, 36] This emission that represents ${}^4T_1 \rightarrow {}^6A_1$ transition, is spin-forbidden and has a long life-time of 1.0-3.0 ms. The energy of the slow luminescence in II-VI compound semiconductors was found to be independent of a QD size. However, the emission energy of slow luminescence can vary due to the method of QD growth and the nature of attached ligands.[17, 18] Besides the slow relaxation photoluminescence (PL) line there is another peak, which corresponds to the fast interband emission. Sometimes this line disappears that can be due to the method of Mn doping. [13] To explain such unusual photoluminescence we theoretically study optical properties of CdS, ZnS and ZnSe quantum dots doped with an Mn impurity. In this research we place an Mn atom inside of a quantum dot as shown in Fig.1. The crystal field from a QD structure changes symmetry from the high spherical of 5-fold degenerate Manganese d-levels to the T_d symmetry in a QD crystal field. For the lower symmetry the 5-fold degenerate level splits into two levels where one of them, t_2 , is triply and the other, e , is doubly degenerate. In such a crystal field the ground state symmetry is 6A_1 and the excited states have the 4E , 4A_1 , 4T_2 and 4T_1 symmetries. The lowest energy excited state has the symmetry 4T_1 , from which the slow luminescence transition, ${}^4T_1 \rightarrow {}^6A_1$, takes place. This transition is spin-forbidden and only occurs due to small spin-orbit coupling for Mn atoms. Subsequently the slow relaxation time, 1.0-3.0 ms, can be explained by very small oscillator strengths, 10^{-6} smaller than for ordinary dipole transitions. Obviously such slow transitions cannot be observed in absorption spectra but can be detected in PL spectra only.

A straightforward approach is to employ DFT or TDDFT for electronic structure calcu-

lations and optical spectra. The preliminary results reveal that these two methods provide unphysical data. In particular, five Mn d-orbitals are located deeply inside the valence band being half occupied what contradicts to the physical meaning of the ground state. This indicates that the basis wavefunction has to be multiconfigurational. Thus in this work we calculate the energy of ${}^4T_1 \rightarrow {}^6A_1$ transition employing the multiconfigurational Symmetry Adapted Cluster Configuration Interaction (SAC-CI) method, which we use because of the high degeneracy of Mn levels. The results are compared with experimental data.

FIG. 1: Optimized structures of $Cd_{81}Mn_1S_{82}$, $Zn_{81}Mn_1S_{82}$, and $Zn_{81}Mn_1Se_{82}$ quantum dots.

COMPUTATION DETAILS

In the present work we have performed all calculations within GAUSSIAN software [37]. We have studied the three types of semiconductor nanocrystals such as CdS, ZnS and ZnSe as shown in Fig. 1. For the starting geometry we have cut out the spherical quantum dots of three different sizes with 48, 64, and 164 numbers of atoms from the Würtzite crystal structures. Then these QD structures have been optimized by the DFT method with the B3LYP exchange-correlation functional using the LANL2dz basis set. Such an exchange-correlation functional and basis set are often used for electronic structure calculations of CdSe [6] and ZnSe, ZnS [38, 39] quantum dots. After that we have replaced one Cd or Zn atom by an Mn one in each quantum dot and then reoptimize all structures using the same method. All optical spectra have been calculated by TDDFT with the CAM-B3LYP exchange-correlation functional and the LANL2dz basis set for Zn, Cd, Se, and S atoms and the 6-31+G* basis set for Mn atoms. [40] The CAM-B3LYP exchange-correlation functional provides the best fit to the CIS(D) calculations of the optical spectra. The detailed procedure

FIG. 2: (Upper figure) Schematic representation of photoemission from the excited to ground state in a Mn doped quantum dot. (Bottom figure) Transition ${}^4T_1 \rightarrow {}^6A_1$ between the first excited to ground state in the tetrahedral ligand field.

was discussed in Ref. [21] The choice of the most reliable basis set is based on the two criteria: (1) the shortest time of calculations and (2) the best match with the results found with the largest basis set cc-pVDZ. We have found that the best basis sets are LANL2dz and 6-31+G*.

To calculate ${}^4T_1 \rightarrow {}^6A_1$ transition in an Mn ion it is important to take into account the high degeneracy of Mn states. In this work we use a multiconfigurational (multideterminant) basis set. With such a basis set, the calculations, in general, take long computational times and large memory for reasonable quantum dot sizes. To solve the problem we have decided to cut out small fragments, MnS_4 and $MnSe_4$, from Mn doped quantum dots for each type keeping the crystal field symmetry. The geometries of the fragments remain the same as in quantum dots (see Fig.3). Then we use the *Symmetry Adapted Cluster/Configuration Interaction* (SAC-CI) method from the GAUSSIAN software. [37] This method allows for the

correct treatment of the high degenerate states in an Mn atom. For the faster calculations we have modified the fragment geometries with the T_d symmetry. We believe that such a procedure does not significantly change the results because of small energies differences between the levels in each energy group shown in Fig. 3. For the SAC-CI calculations, we include all orbitals into the active space.

FIG. 3: MnS_4 fragment cut out from $Cd_{31}Mn_1S_{32}$ quantum dot (the left). The single electron energy levels for the same fragment (the right) are presented with their energy differences.

RESULTS AND DISCUSSIONS

For the calculations we employ the two hypothesizes, (a) the optical absorption spectra are almost independent of the presence of an Mn impurity and (b) the slow luminescence is determined by MnS_4 and $MnSe_4$ fragments in a T_d crystal field. If hypothesis (a) is valid, then it means that Mn levels are inside the gap because they do not change the absorption spectrum. As soon as the Mn d-levels are located inside the gap the slow luminescence is only determined by the Mn atom surrounded by the nearest neighbor environment (hypothesis (b)). The fragments described above represent an Mn impurity with the environment determined the smallest number of S or Se atoms.

Hypothesis (a). We prove that Manganese impurities at low concentrations do not affect the QD optical spectra. In Fig. 4 we demonstrate the absorption spectra calculated for (a) $Cd_{24}S_{24}$ and $Cd_{23}Mn_1S_{24}$; (b) $Zn_{24}S_{24}$ and $Zn_{23}Mn_1S_{24}$; (c) $Zn_{24}Se_{24}$ and $Zn_{23}Mn_1Se_{24}$ quantum dots. The black line represents the undoped QDs where the red line stands for the Mn doped QD. From the figures we see that the red lines completely match the black ones.

We can indirectly justify why the 6A_1 ground state for the fragment is very close to the top of the QD valence band. We would suggest two reasons: (a) if the 6A_1 level is located inside the gap, one could observe the absorption from the valence band to this 6A_1 level. However such an absorption peak has never been experimentally and theoretically found. (b) If the 6A_1 level were deeply embedded into the valence band, it would indirectly contradict to our scheme, which provides the slow luminescence energy matching the experimental values as discussed below. In this hypothesis we have assumed that optical spectra are independent of Mn impurities. There is also the experimental evidence in ZnTe nanocrystals where the absorption remains the same in QDs with and without Mn atoms. [36] Therefore, this proof allows us to use the results from the band gap calculations for undoped medium/large nanocrystals in the effective-mass approximation. [41–44] It should be noted that the values of the calculated optical gaps are lower than the experimental band gap values of crystals. Such a discrepancy should not confuse us because we would like only to prove that the absorption spectra are independent of an Mn impurity not paying attention to the absolute value of the gaps.

Hypothesis (b). As soon as hypothesis (a) is proved we conclude that the Mn impurities determine the slow luminescence from the gap. This feature allow us to simplify the problem and select the smallest fragments in the crystal fields determined by the QD geometries. All the fragments with different geometries have approximately the same T_d symmetry (see Fig.3), and thus the transitions for all fragments take place from Mn^{2+} excited 4T_1 to 6A_1 ground states. For the calculation of the Mn emission energy we use the multiconfigurational SAC-CI method, which allows us to classify the electronic states according to the T_d symmetry to make the calculations much faster. As shown in Fig.3 the fragment levels are grouped around two well separated values of energy with the small discrepancies. These two groups of levels can be transformed into the two levels with t_2 and e single electron configurations where t_2 is triply and e is doubly degenerate. In Fig. 3 the fragment describes $CdMnS$ quantum dot, however similar picture is true for $ZnMnS$ and $ZnMnSe$ as well. The calculated ${}^4T_1 \rightarrow {}^6A_1$ transition energies for different quantum dots are presented in Table I. We see from the table that the Mn-S and Mn-Se bond lengths are slightly different and might affect the PL energies shown in the third column. The calculated transition energies are very close to the experimental values. [16, 18, 19] Such an excellent match additionally proves that hypothesis (a) is true. There is another interesting feature seen from the table: there

FIG. 4: Absorption spectra for (a) $Cd_{24}S_{24}$ and $Cd_{23}Mn_1S_{24}$; (b) $Zn_{24}S_{24}$ and $Zn_{23}Mn_1S_{24}$; (c) $Zn_{24}Se_{24}$ and $Zn_{23}Mn_1Se_{24}$ quantum dots. The transitions with the spin-flip do not contribute because they are spin forbidden.

<i>QD</i>	<i>Mn – S(Se) bond length, Å</i>	${}^4T_1 \rightarrow {}^6A_1$, <i>eV</i>	<i>Exp. energy, eV</i>
<i>CdS</i>	2.42	2.52	2.58[19]
<i>ZnS</i>	2.39	2.43	2.43[18]
<i>ZnSe</i>	2.56	2.24	2.23[16]

TABLE I: SAC-CI calculations of ${}^4T_1 \rightarrow {}^6A_1$ transition energies for CdS, ZnS, and ZnSe quantum dots.

are two groups of quantum dots in which the transition energies are close to each other. CdS and ZnS make up group 1 while ZnSe and CdSe [20, 21] determine group 2. Indeed, the transition energies for CdS and ZnS are 2.52 *eV* and 2.43 *eV* which are very close to each other because the bond lengths (column two) are also very close. For CdSe and ZnSe the energies are also very close for the same reason. The calculated transition energy for CdSe was found to be equal to 2.3 *eV* in Ref. [21] and is not discussed in this research.

As soon as the Mn slow luminescence energy is independent of a QD size, we plot the graphs in Fig. 5 where one curve represents the size-gap dependence calculated in the effective-mass approximation with no Mn impurity (solid line) [41–44] and the Mn slow luminescence transition energy (dashed line) of Mn doped (a) *CdS* (b) *ZnS* and (c) *ZnSe* quantum dots. For all cases the transition energy line never crosses the conduction band curve. This means that there are always two PL peaks, one is because of the fast luminescence from the conduction to valence bands (high energy) and the second is because of the slow luminescence due to the Mn ${}^4T_1 \rightarrow {}^6A_1$ transition. Sometimes the first peak is not well pronounced in some experiments. This depends on the concentration of Mn impurities inside of quantum dots that determined by a doping method. [13] As described above we have optimized the quantum dots from a Würtzite crystal structure. However there might be other crystal structures such as Zinc-Blended, for example. Therefore, the length between Mn and S(Se) atoms can be different. That is why we study how the slow luminescence transition depends on Mn-S(Se) bond lengths. The results are presented in Fig. 6. As shown in the figure the transition energy is very sensitive to the bond length change especially for Mn-S. Indeed if the bond length is changed by 0.1 Å, the energy increases by 0.2 *eV* within the calculated range of bond lengths.

FIG. 5: Size optical gap dependence calculated in the effective-mass approximation (solid line) [41–44] and the Mn slow luminescence transition energy (dashed line) for different sizes of Mn doped (a) *CdS* (b) *ZnS* and (c) *ZnSe* quantum dots.

FIG. 6: the Mn ${}^4T_1 \rightarrow {}^6A_1$ transition energy dependence of the Mn-S (red line) and Mn-Se (blue line) bond lengths.

CONCLUSION

Slow luminescence in quantum dots doped by Mn impurities has been studied for different materials such as CdS, ZnS, and ZnSe. Slow luminescence takes place from the Mn 4T_1 first excited to 6A_1 ground state. This transition is spin-forbidden but nevertheless it takes place because of the small spin-orbit coupling. The total luminescence has two bands, one is at higher energies with the fast relaxation and the second is at smaller energy with the slow relaxation (1.0 - 3.0 ms). The latter band describes the transition from the Mn 4T_1 excited state. The calculations of such systems can be complicated because of the high degeneracy of Mn d-states. The DFT and TDDFT calculations based on a single determinant basis wavefunction approach provide the unphysical results. However this problem can be resolved by employing a multi-determinant basis set and using the ab initio SAC-CI method. For such a large basis set the computations for the whole Mn doped quantum dot are restricted by time and memory. For this reason we have cut the smaller fragments out of the middle of quantum dots with the Würtzite crystal structure. The cut-out fragments consist of one Mn atom surrounded by four S (or Se) atoms with the same geometry as in the quantum dot

(see Fig.3). In Ref. [21] we studied the slow luminescence for Mn doped CdSe QDs where an Mn atom was placed in the middle and on the surface of a QD. In that investigation we found that the slow luminescence energy matches the experimental value only if an Mn impurity is located in the middle of a QD. Such an analogy makes us sure that a similar picture is true for CdS, ZnS and ZnSe QDs. The calculated and experimental energies of the $^4T_1 \rightarrow ^6A_1$ transitions for each material type are presented in Table I. From this table we see the excellent agreement between the computed and experimental energy values. There are also two groups of quantum dots, in which the transition energies are close to each other. CdS and ZnS with energies 2.52 eV and 2.43 eV make up group 1 and ZnSe and CdSe with energies 2.23 eV and 2.3 eV, [21] determine group 2. We have also shown that the QD energy gaps and the Mn slow luminescence energies are independent of a QD size in the presence of Mn impurities (see Fig. 4). These properties were experimentally confirmed for Mn doped ZnTe QDs measurements. [36] It should be noted that the values of the calculated optical gaps are lower than the experimental band gap values of crystals. Such a discrepancy should not confuse us because we would like only to prove that the absorption spectra are independent of an Mn impurity not paying attention to the absolute value of the gaps. Thus these two properties allow us to employ the effective-mass approximation for the size-gap dependences for pure (without an Mn impurity) quantum dots. In Fig. 5 the 4T_1 level never crosses the gap curve and therefore we should observe two distinct luminescence lines with the fast and slow relaxations. However in some experiments the fast luminescence line can be weak because of the value of Mn concentration and doping procedure. [13] In this work we have chosen the approximate Wurtzite crystal structure for all quantum dots. However, it is not the only possible QD crystal structure. Thus we have additionally studied how the slow luminescence energies depend on the length of Mn-S (Se) bond (this imitates a different QD crystal structure). The results are depicted in Fig. 5 where the energy is very sensitive to the bond length. Indeed if we change the Mn-S bond length by 0.1 Å, the energy increases by 0.2 eV within the calculated range of bond lengths. If the concentration of Mn impurities increases, the slow luminescence becomes fast because the optical transitions in a cluster with two or more Mn atoms are now spin allowed. At higher concentration the interaction between two impurities is important to determine the magnetic ordering in a nanocrystal. As shown in Refs. [33, 34, 45] the sp-d hybridization determines the magnetic ordering that can be changed from ferromagnetic at small distances to antiferromagnetic at

larger distances obey RKKY mechanism. [45]

This work was supported by a grant No. DEFG02-10ER46728 from the Department of Energy to the University of Wyoming and the University of Wyoming School of Energy Resources through its Graduate Assistantship program.

* Electronic address: yurid@uwyo.edu

- [1] A. V. Akimov, A. J. Neukirch, O. V. Prezhdo, Chem. Rev. 113 (2013) 4496.
- [2] R. Rossetti, J. L. Ellison, J. M. Gibson, L. E. Brus, L. E. J. Chem. Phys. 80 (1984) 4464.
- [3] S. Kilina, D. Kilin, V. V. Prezhdo, O. V. Prezhdo, J. Phys. Chem. C 115 (2011) 2164 .
- [4] O.V. Prezhdo, Acc. Chem. Res. 42 (2009) 2005.
- [5] S. V. Kilina, D. S. Kilin, O. V. Prezhdo, ACS Nano 3 (2009) 93.
- [6] S. V. Kilina, S. Ivanov, V. I. Klimov, S. Tretiak, S., J. Am. Chem. Soc. 31 (2009) 7717 .
- [7] V. Proshchenko, Yu. Dahnovsky, Chem. Phys. Lett. 595-596 (2014) 250.
- [8] V. Proshchenko, Yu. Dahnovsky, Phys. Chem. Chem. Phys. 16 (2014) 7555.
- [9] A. Nag, S. Sapra, C. Nagamani, A. Sharma, N. Pradhan, S. V. Bhat, and D. D. Sarma, Chem. Matter. 19 (2007) 3252-3259.
- [10] D. M. Hoffman, B. K. Meyer, A. I. Ekimov, I. A. Merkulov, Al. L. Efros, M. Rosen, G. Couino, T. Gacoin, J. P. Boilot, Solid State Commun. 114 (2000) 547-550.
- [11] B. B. Srivastava, S. Jana, N. S. Karan, S. Paria, N. R. Jana, D. D. Sarma, and N. Pradhan, J. Phys. Chem. Lett. 1 (2010) 1454-1458.
- [12] R. N. Bhargava, D. Gallagher, X. Hong, A. Nurmikko, Phys. Rev. Lett. 72 (1994) 416.
- [13] A. A. Bol, A. Meijerink, Phys. Rev. B 58 (1998) R15997.
- [14] J. F. Suyver, S. F. Wuister, J. J. Kelly, A. Meijerink, Phys. Chem. Chem. Phys. 2 (2000) 5445.
- [15] D. J. Norris, N. Yao, F. T. Charnock, T. A. Kennedy, Nano. Lett. 1 (2001) 3-7.
- [16] D. W. Lamger and, H. J. Richter, Phys. Rev. 146 (1966) 554.
- [17] N. Pradhan, X. Peng, J. Am. Chem. Soc. 129 (2007) 3339.
- [18] M. A. Malik, P. O'Brien and N. Revaprasadu, J. Matter. Chem. 11 (2001) 2382.
- [19] S. Salimian, S. F. Shayesteh, J. Supercond. Nov. Magn. 25 (2012) 2009.
- [20] R. Beaulae, P. L. Arecher, S. T. Ochsenein, D. R. Gamelein, Adv. Func. Mater. 18 (2008) 3873.

- [21] V. Proshchenko, Yu. Dahnovsky, J. Phys. Chem. C 118 (2014) 28314.
- [22] P.V. Radovanovic, D. R. Gamelin, Proc. SPIE Int. Soc. Opt. Eng. 4809 (2002) 51.
- [23] D. A. Schwartz, N. S. Norberg, Q. R. Nguyen, J. M. Parker, D. R. Gamelin, Am. Chem. Soc. 125 (2003) 13205.
- [24] N. S. Norberg, K. R. Kittilstved, J. E. Amonette, R. K. Kukkadapu, D. A. Schwartz, D. R. Gamelin, J. Am. Chem. Soc. 126 (2004) 9387.
- [25] N. S. Norberg, D. R. Gamelin, J. Appl. Phys. 99 (2006) 08104.
- [26] N. S. Norberg, G. M. Dalpian, J. R. Chelikowsky, D. R.;Gamelin, Nano Lett. 6 (2006) 2887.
- [27] N. S. Norberg, G. L. Parks, G. M. Salley, D. R. Gamelin, J. Am. Chem. Soc. 128 (2006) 13195.
- [28] P. A. Archer, S. A. Santangelo, D. R. Gamelin, D.R. J. Am. Chem. Soc. 129 (2007) 9808.
- [29] P. I. Archer, S. A. Santangelo, D. R. Gamelin, Nano Lett. 7 (2007) 1037.
- [30] D. A. Bussian, S.A.; Crooker, M. Yin, M. Brynda, Al. L. Efros, V. Klimov, Nat. Mater. 8 (2009) 35.
- [31] J. K. Furdyna, J. Kossut, Eds.: Diluted Magnetic Semiconductors. In Semiconductors and Semimetals; R. K. Willardson and A. C. Beer, Eds. New York: Academic Press, (1988), v. 25.
- [32] R. Beaulac, Y. Feng, Joseph W. May, E. Badaeva, D. R. Gamelin, X. Li, Phys. Rev. B 84 (2011) 195324.
- [33] E. Badaeva, C. M. Isborn, Y. Feng, S. T. Ochsenbein, D. R. Gamelin, X. Li, J. Chem. Phys. C 113 (2009) 8710.
- [34] C. A. Johnson, A. Cohn, T. Kaspar, S. A. Chambers, G. M. Salley, D. R. Gamelin, Phys. Rev. B, 84 (2011) 125203.
- [35] V. A. Vlaskin, N. Jansen, J. van Rujssel, R. Beaulac, D. R. Gamelin, Nano Lett. 10 (2010) 3670.
- [36] J. Eilers, E. Groeneveld, C. de Mello Donega, A. Meijerink, J. Phys. Chem. Lett. 3 (2012) 1663.
- [37] Gaussian 09, Revision A.1, M. J. Frisch, et al., Gaussian, Inc., Wallingford CT (2009).
- [38] S. Xu, C. Wang, Y. Cui, J. Mol. Struct. 916 (2009) 168.
- [39] K. A. Nguen, R. Pachter, P. N. Day, J. Chem. Theory Comput. 9 (2013) 3581.
- [40] G. Accorsi, G. Verri, A. Acocella, F. Zerbetto, G. Lerario, G. Gigli, D. Saunders, R. Billinge, Chem Comm. 50 (2014) 15297.
- [41] A. L. Efros, A. L. Efros, Sov. Phys.-Semicond. 16 (1982) 772.

- [42] A. L. Efros, V. A. Kharchenko, M. Rosen, Solid State Commun. 93 (1995) 281.
- [43] A. D. Yoffe, Adv. Phys. 42 (1993) No.2, 173.
- [44] A. D. Yoffe, Adv. Phys. 50 (2001) No. 1, 1.
- [45] V. Proshchenko, Y. Dahnovsky, Phys. Status Solidi B, (2015), doi: 10.1002/pssb.201552246.

Graphical Abstract

First excited state

Ground state