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Optical spectra of CdMnSe of nano-ferro- and antiferro- magnets

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Abstract

We study optical transitions in CdSe quantum dots doped by Mn atoms. For low concentrations the transitions are spin-forbidden. Nevertheless, strong light absorption was experimentally found. To explain this effect we propose a new mechanism that includes two or more Mn atoms closely placed to each other containing the electrons with the opposite spin projections. In this case there a spin-flip is unnecessary. In addition we study absorption from quantum dots containing two Mn atoms with different multiplicities. We find that the strongest absorption from the gap is for an antiferromagnetic arrangement. The obtained results confirm the experimental concentration dependencies.

Transition-metal doped semiconductor nanocrystals have recently attracted more and more interest in various fields such as spintronics, solar cells, and optics and nanoelectronics of low dimensional materials.[1–11] Some unusual optical properties were observed in such systems. Indeed photoluminescence and absorption can be substantially altered by the presence of a Manganese impurity leading to tunable, dual luminescence in $Cd_{n-x}Mn_xSe_n$ quantum dots (QDs).[6,7,12] Another attractive feature is the additional absorption in a gap range and also the effect of gap narrowing.[3] In the latter case the additional absorption due to the presence of Mn impurities was found indirectly through the measurements of photocurrent depending on light absorption in solar cells sensitized by CdMnSe QDs. In these experiments the photocurrent increases by a factor of 3.5 for higher absorption energies.[3] In another type of experimental observations, Minh and co-workers[4] found that at low Mn concentrations the paramagnetic arrangement is favorable, then for higher Mn doping concentrations the antiferromagnetic coupling became more pronounced decreasing the total magnetic moment. Electronic levels of an Mn atom with the spherical symmetry are altered by a crystal field from a CdSe environment. If an Mn atom is placed somewhere in the middle of a QD, the crystal field has T_d symmetry.[6,7,12] In the case of an impurity location on a CdSe surface, symmetry is C_{3v}.[12] As shown in Fig. 1a the five-fold degenerate atomic energy level for *5d* electrons is split by a T_d crystal field in two degenerate single electron levels, where one level is doubly and the other is triply degenerate. The ground electronic state has $^6A_1$ symmetry while the excited state has $^4T_1$ symmetry. The multiplicities of both states are different and therefore, the electronic transition is spin-forbidden. This is the main reason why the relaxation of the second luminescence is very slow, with the relaxation time of *0.1-1.0 ms*.[6,7] However, the transition still takes place because of small spin-orbit interaction. Such slow relaxation indicates negligible oscillator strengths that are 10^6 lesser than the oscillator strengths for the fast luminescence. Apparently we would not expect any absorption from these levels located inside the gap. However additional absorption was experimentally found.[3,4] To understand a mechanism of such absorption using first-principle electronic structure calculations is the main goal of this research. We explain why the absorption from the gap levels is not forbidden by spin and therefore it increases the absorption coefficient in the gap range of the spectrum. We also consider an Mn concentration dependence of light absorption.

Electronic structure calculations have been successful in explanation of various photo-

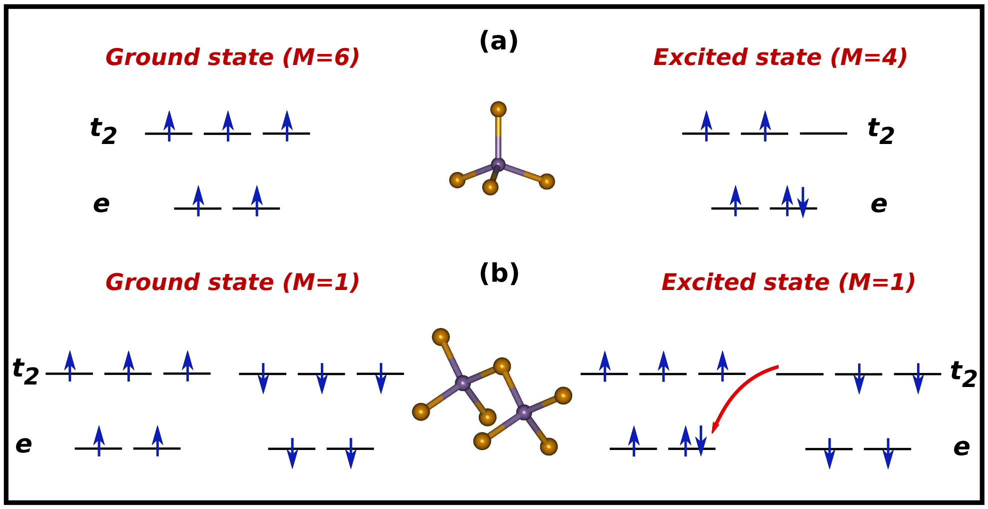

FIG. 1: Spherically symmetric five-fold degenerate level is split in two degenerate levels in the tetrahedral ligand field. (a) Light transition takes place with a spin-flip for a single Mn impurity. (b) For two Mn atoms no spin-flip occurs in optical transition. The two inserts stand for the fragments with (a) a single Mn atom in a T_d crystal field and (b) two Mn atoms in a C_{2v} crystal field. The spin arrangement is shown for the antiferromagnetic order only.

voltaic effects in quantum dots and rods.[13–45] The latter approach has some advantages because it provides besides energy levels, matrix elements, wave functions, and various constants that can be used for the evaluation of different time-dependent processes.[13,32–37,46,47] In this research we study CdSe QDs of different sizes with and without Mn impurities. All calculations have been performed within Gaussian software[48]. For the calculations we have used three different QD sizes with and without Mn atoms, such as $Cd_{10}Se_{10}$, $Cd_{16}Se_{16}$, $Cd_{32}Se_{32}$, $Cd_9Mn_1Se_{10}$, $Cd_{15}Mn_1Se_{16}$, $Cd_{31}Mn_1Se_{32}$, $Cd_{30}Mn_2Se_{32}$, and $Cd_{28}Mn_4Se_{32}$. We have also calculated optical spectra of different multiplicities for $Cd_{30}Mn_2Se_{32}$ quantum dot. QDs are cut out from the Würtzite bulk and then optimized with and without Mn impurities by the DFT method using a B3LYP exchange-correlation functional and LANL2dz basis set. To find QD optical spectra we have employed the TDDFT method. The exchange-correlation functional has been chosen to fit the optical spectrum obtained within the ab initio CISD method. We have found that the best functional is CAM-B3LYP. The choice of the most reliable basis set is based on the two following criteria: (a) the shortest time of calculations and (b) the best match with the results found with the larger basis sets. To find the best basis set we have checked first the following basis sets: LANL2dz, cc-pVDZ-pp, cc-pVTZ-pp, and cc-pVQZ-pp for Cd and Se atoms and 6-31+G* and 6-311+G* for Mn atoms. The computations have been performed for a small cluster, $Cd_2Mn_2Se_4$. The absorption spectra calculated by TDDFT are presented in Figs. 2a and 2b. In Fig. 2a we plot three different spectra where we use the following basis sets: (i) LANL2dz for Cd and Se atoms and 6-31+G* for an Mn atom (the black line); (ii) cc-pVDZ-pp for Cd and Se atoms and 6-31+G* for an Mn atom (the red line), and (iii) cc-pVDZ-pp for Cd and Se atoms and 6-311+G* (the blue line). All curves have the small deviations from the largest basis set calculations (the blue line), which is lesser than $0.1\,eV$. Then we have calculated the absorption spectra for the same cluster using cc-pVDZ-pp, cc-pVTZ-pp, and cc-pVQZ-pp for Cd and Se atoms and 6-311+G* for Mn atoms and compare the computational results. As shown in Fig. 2b the results are indistinguishable. Thus we conclude that the best selection for a basis set satisfying the criteria mentioned above is case (i) where we choose LANL2dz for Cd and Se atoms and 6-31+G* for an Mn atom with the accuracy lesser than $0.1\,eV$. We have also been aware of spin contamination in open shell TDDFT calculations. The spin contamination was very small (less than 10%) for the allowed transitions and for the forbidden transition it has been larger than the allowed spin contaminations. The latter transitions do not contribute to the absorption spectra.

We have found that the best functional and basis set are CAM-B3LYP and LANL2dz, respectively. For Mn doped CdSe QD calculations we have used a 6-31+G* basis set for Mn atoms while the basis set for Cd and Se atoms has remained unchanged. The exchange-correlation functional has been chosen also a CAM-B3LYP and unrestricted CAM-B3LYP in the case of Mn doping.

First, we have calculated the optical spectrum of $Cd_{16}Se_{16}$ shown by the red line in Fig. 3. If an Mn atom is added to the QD replacing a Cd atom in the middle and at the surface of the QD, the spectra for both cases have remained unchanged. These spectra confirm the physical picture discussed above where the transitions between Mn levels inside the gap are forbidden by spin. Thus, we do not observe any significant changes in the absorption spectra for doped and undoped QDs. We have also calculated a larger QD, $Cd_{32}Se_{32}$ and $Cd_{31}Mn_1Se_{32}$ and have found no significant changes in the absorption spectra either (the results are not presented). However, the magnetic moment can be large due to the polarization of the Mn spins by the magnetic field at low Mn concentrations.[4]

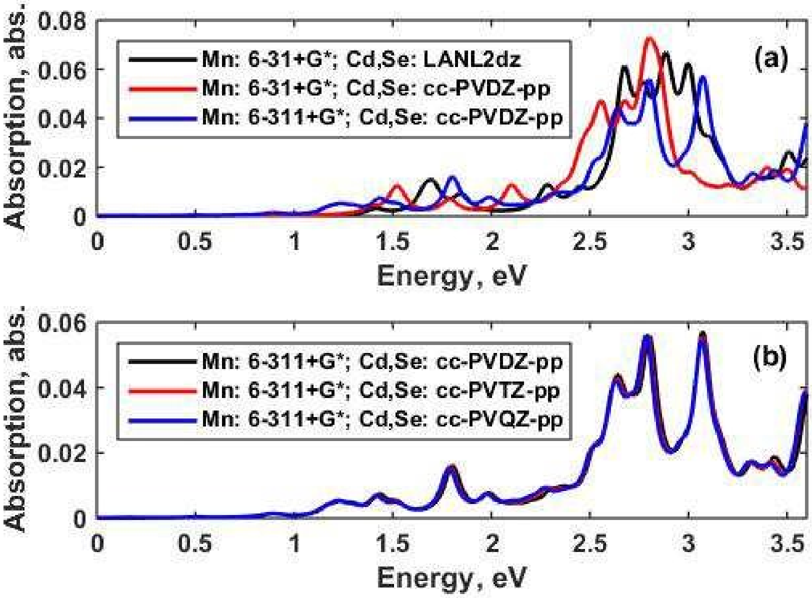

FIG. 2: Absorption spectra for $Cd_2Mn_2Se_4$ cluster calculated in TDDFT with the following basis sets: (a) (i) LANL2dz for Cd and Se atoms and 6-31+G* for an Mn atom (the black line); (ii) cc-pVDZ-pp for Cd and Se atoms and 6-31+G* for an Mn atom (the red line); and (iii) cc-pVDZ-pp for Cd and Se atoms and 6-311+G* (the blue line). (b) cc-pVDZ-pp, cc-pVTZ-pp, and cc-pVQZ-pp for Cd and Se atoms and 6-311+G* for Mn atoms.

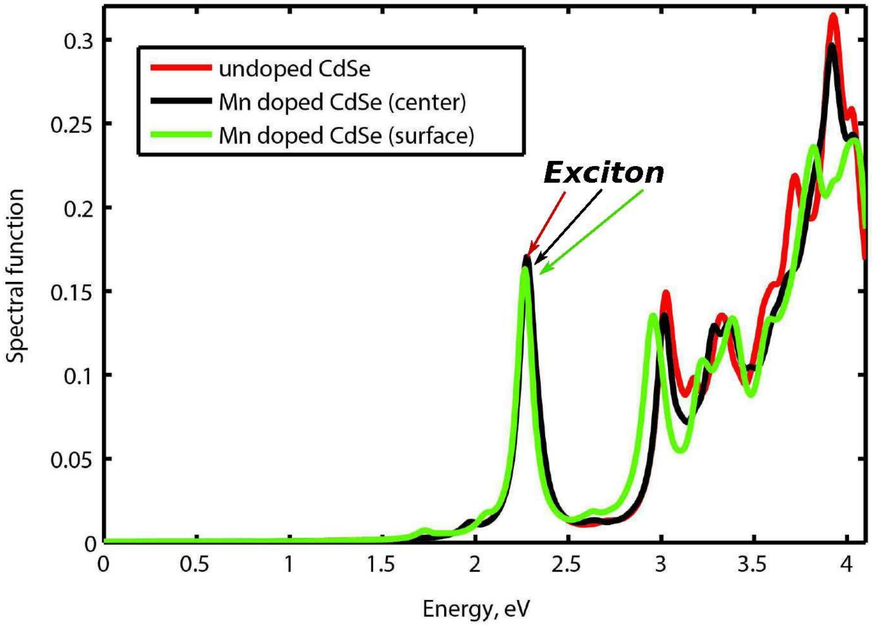

FIG. 3: Optical spectra for $Cd_{16}Se_{16}$ (red line) and $Cd_{15}Mn_1Se_{16}$. The black line denotes the optical spectrum with the Mn atom placed in the middle of QD. The green line stands for the Mn atom lying on the QD surface.

Since the presence of a single Manganese atom does not make any change in light absorption, we have also studied CdSe QDs doped by two Mn atoms in a close proximity. These two Mn atoms are arranged in an antiferromagnetic order with the total spin $S = 0$ and the multiplicity $M = 1$. In this case a spin-flip does not take place due to the optical absorption because the electron with the opposite spin already exists at the other Mn atom as shown in Fig. 1b. Now we do observe the significant enhancement of the absorption in the gap range of the spectrum as demonstrated in Fig. 4. In this figure we see the additional lines that we ascribe to the allowed transitions in a QD doped by two Mn atoms. There is some difference in absorption spectra between Mn placed in the middle and at the surface of the quantum dot. The absorption spectrum with the impurities place on the surface is more shifted to lower energies. The Mn atom placement is depicted in Fig. 5.

Then we have studied the concentration dependences of a Manganese impurity in a CdSe QD. In Fig. 6 we have presented the absorption spectrum with four Mn atoms in a close proximity that are placed in the middle and on the surface of a quantum dot. The geometric

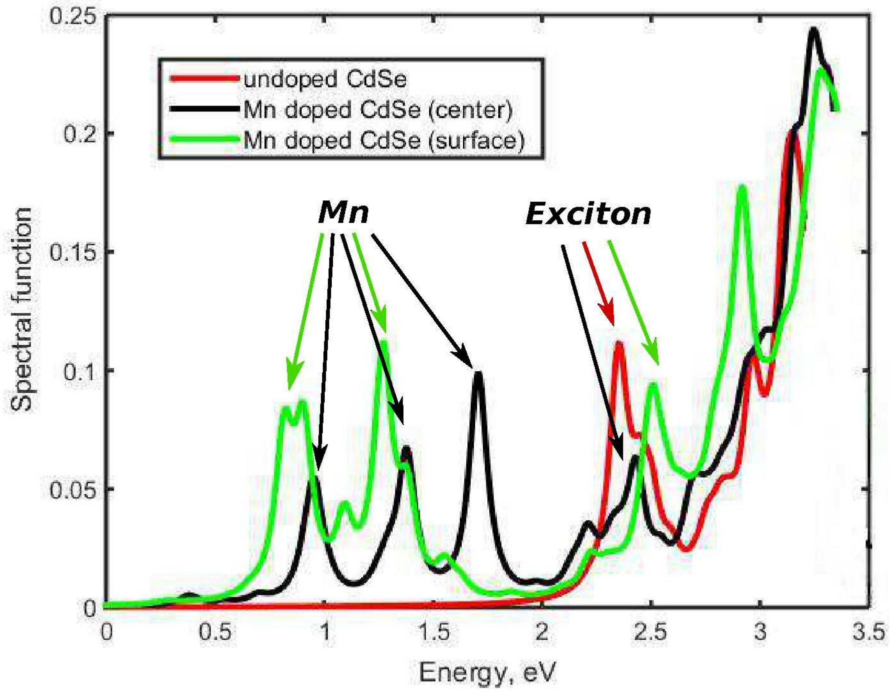

FIG. 4: Optical spectra for $Cd_{32}Se_{32}$ (red line) and $Cd_{30}Mn_2Se_{32}$. The black line denotes the optical spectrum with the two Mn atoms placed in the middle of QD. The green line stands for the two Mn atoms located on the QD surface.

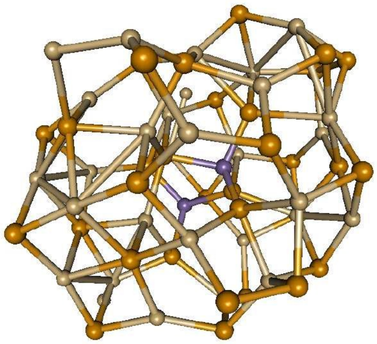

FIG. 5: Arrangement of two Mn atoms placed in the middle of a CdSe QD. The purple spheres represent the Mn atoms.

arrangement of the four Mn atoms is shown in Fig. 7.

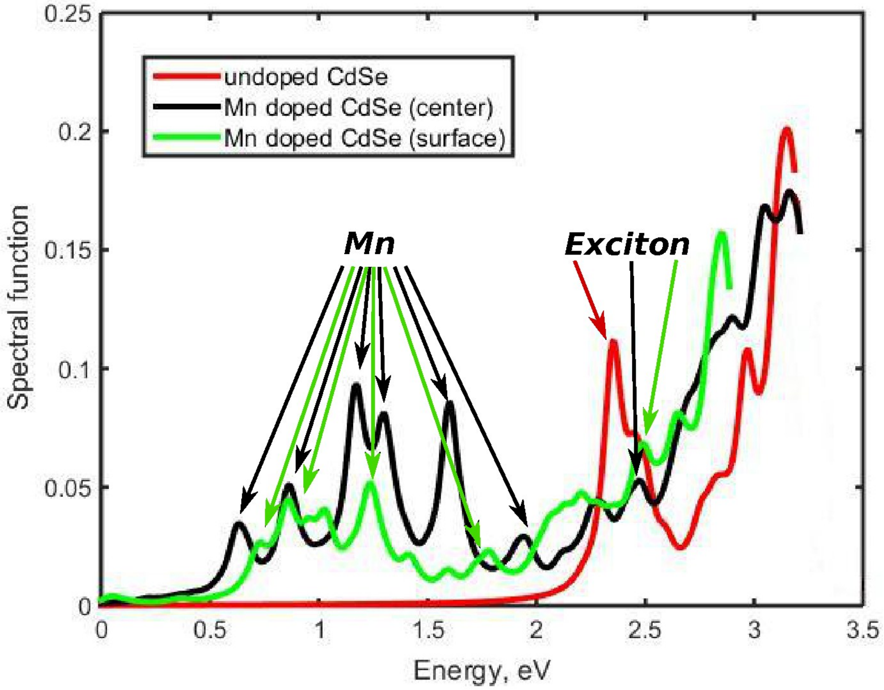

FIG. 6: Optical spectra for $Cd_{32}Se_{32}$ (red line) and $Cd_{28}Mn_4Se_{32}$. The black line denotes the optical spectrum with the four Mn atoms placed in the middle of QD. The green line stands for the four Mn atoms located on the QD surface.

As in the case with two Mn atoms we even find stronger absorption from the gap. As demonstrated in Fig. 6 there are more Mn peaks (energy levels) than in the case of two Mn atoms. For Mn atoms placed on the surface, the picture is qualitatively similar.

It is very important to study the dependence of the absorption spectra on an Mn-Mn multiplicity. In Fig. 8 we present the absorption spectra in $Cd_{30}Mn_2Se_{32}$ quantum dot. The strongest gap absorption takes place for $M = 1$ (the antiferromagnetic order). The other multiplicities reveal the similar spectra with the small absorption from the gap. The peak at $\hbar\omega = 2.1\ eV$ is present for all multiplicities and can be ascribed to the transitions from the Mn-Mn levels to the CdSe conduction band. The CdSe exciton peak remains almost unchanged but the absorption intensity varies for different multiplicities. We should also mention that the absorption spectrum for the transitions in the conduction band is slightly modified by the presence of the Mn atoms.

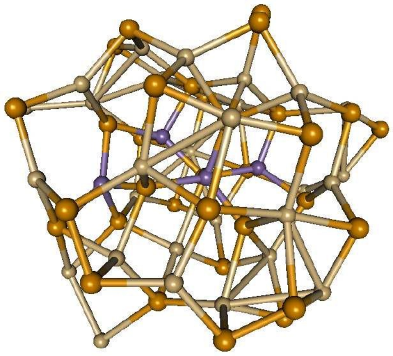

FIG. 7: Arrangement of four Mn atoms placed in the middle of a CdSe QD. The purple spheres represent the Mn atoms.

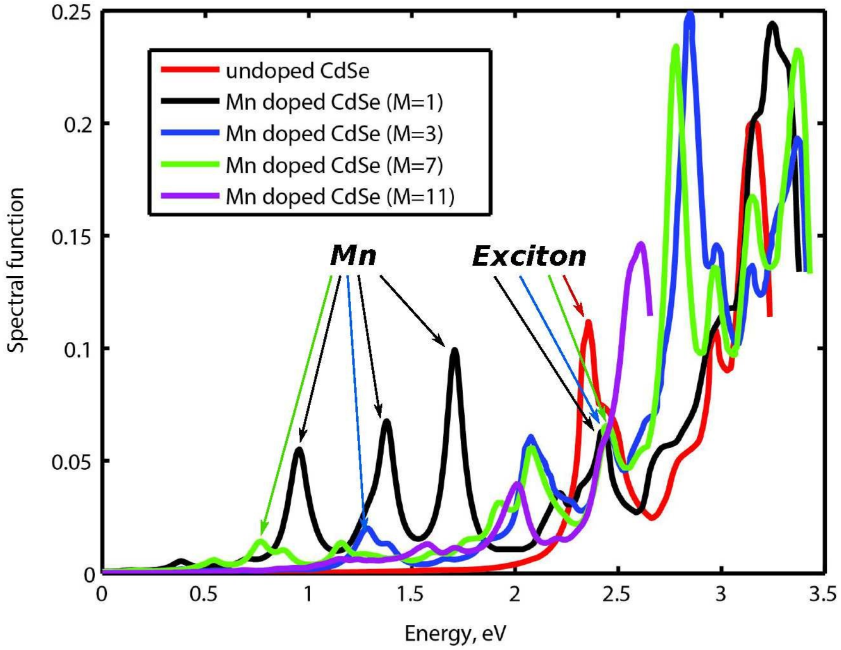

FIG. 8: Optical spectra for $Cd_{32}Se_{32}$ (red line) and $Cd_{30}Mn_2Se_{32}$ with different multiplicities. The black line corresponds to $M = 1$, the blue line stands for $M = 3$, the green line responds to $M = 7$, and the purple line denotes $M = 11$.

Thus, we conclude that despite the absence of the optical transitions in a CdSe QD with a single Mn atom or a low concentration, we have found the strong light absorption from the gap if two or more Mn atoms are close to each other. The mechanism of absorption can be explained by the presence of two or more atoms with an antiferromagnetic arrangement ($S = 0$). In this case a flip of the spin does not occur because the electron with the opposite spin already exists on the other Mn atom as schematically shown in Fig. 1b . In the case of a single Mn atom a transition does not take place because it is spin-forbidden (see Fig. 1a).[6,7,12] As shown in Figs. 4 and 6 we find the additional absorption from the gap, thereby effectively decreasing the gap as indirectly observed in Ref.[3] We have also studied the concentration dependence of an Mn impurity and found that the total absorption increases with the number of Mn atoms. It is also important to study the optical spectrum for two Mn atoms with different multiplicities. As demonstrated in Fig. 8 the largest gap absorption is for $M = 1$ (the antiferromagnetic order). The other multiplicities exhibit only slight absorption from the gap. Such a physical picture confirms the experimental dependences found in Ref.[4] where a strong magnetic moment was found for low concentration doping. For higher concentrations the presence of the antiferromagnetic Mn couples increases resulting in smaller total magnetic moment. Finally, we have proposed the new mechanism of light absorption from the gap in CdSe QDs doped by Mn atoms. Within this new mechanism the strongest absorption occurs only if two or more Mn atoms are present in a close proximity to each other with an antiferromagnetic arrangement. For small Mn concentrations the light transitions are forbidden by spin and are not pronounced in the absorption spectrum.

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