The effect of spatial distribution of Zn vacancies in ZnS quantum dots on optical absorption spectra

Artem Pimachev, Vitaly Proshchenko, and Yuri Dahnovsky*

Department of Physics and Astronomy/3905

1000 E. University Avenue

University of Wyoming

Laramie, WY 82071, USA

Sabit Horoz

Department of Physics

University of Siirt

Siirt, 56100, Turkey

Omer Sahin

Department of Chemical Engineering

University of Siirt

Siirt, 56100, Turkey

(Dated: March 29, 2017)

Abstract

In this work we propose how to identify the location and spatial distribution of Zn vacancies in ZnS quantum dots (QDs). The experiments reveal a peak shift in absorption spectra towards the lower energies (about 0.1 eV) in the presence of Zn vacancies. To explain such a shift we computationally study the absorption spectra when Zn vacancies are localized in the core, on the surface, and both in the core and on the surface of a quantum dot. From the comparison with the experimental data we conclude that the most favorable configuration of the vacancies is an aggregation on a QD surface. We find that Zn vacancies localized in the core or uniformly distributed on the QD surface, do not explain the experimentally observed shift in the absorption curves.

Recently d^0 ferromagnetism in semiconductor materials has become attractive to investigators because of its high Curie temperature.¹⁻⁹ Much attention has been paid to metal oxide materials^{2,3,5-7} as well as II-IV type semiconductors such as ZnS quantum dots (QDs).¹⁰⁻¹⁶ ZnS compounds are useful materials for cathode ray tube, field emission display phosphors, electroluminescent devices, infrared windows²¹⁻²⁸ as well as good sensitizers for quantum dot sensitized solar cells.²⁹ These materials are d^0 ferromagnets (ferromagnets with no d electrons) that allow for the increase of a Curie temperature in nanoferromagnets. The magnetic moments and Curie temperatures in nanoferromagnets can be easily increased by varying two additional parameters, a vacancy concentration and QD size. Despite many theoretical and experimental investigations some fundamental microscopic mechanisms of ferromagnetism are still obscure. We do not know how Zn vacancies are distributed over a quantum dot, i. e., whether the vacancies are located in a QD core or on a QD surface. It is also unclear whether Zn vacancies are uniformly distributed or form a cluster (an aggregation). This is a very important problem that has to be understood because different Zn vacancy formations provide different values of a QD magnetic moment. For example, Zn vacancy clusters decrease the magnetization while the uniform distribution keeps higher magnetic moments.^{15,16}

In this work we both experimentally and theoretically study absorption spectra of ZnS QDs with and without Zn vacancies. Experimental absorption spectra in conjunction with electronic structure calculations allow us to identify the location and the nature of the distribution of Zn vacancies in a quantum dot.

Experiments. ZnS QDs are synthesized using co-precipitation (or wet chemical) method.¹⁵ In a typical wet chemical process the appropriate amount of aqueous solutions of $Zn(CH_3COO)_2 \cdot 2H_2O$ and Na_2S are placed into a beaker, then two milliliters of mercaptoethanol are added to the solution. Then, these two solutions are transferred into another beaker and stirred at room temperature for some time to have a homogeneous mixture. Then two milliliters of mercaptoethanol are again added into the mixture. The precipitated sample is filtered and the resultant particles are washed in water and ethanol. The final solution is dried in the oven. Then the obtained white powder is ground using a mortar to obtain ZnS nanocrystals. The structure and optical properties are studied by the x-ray diffraction (XRD) using a Rigaku X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda = 0.154059 \text{ nm}$) and

a VWR UV-3100PC, UV/Vis scanning spectrophotometer, respectively.

Figure .1 demonstrates the room temperature photoluminescence (PL) spectra with a Perkin-Elmer LS 50B, under 310 nm excitation, for ZnS QDs with Zn vacancies prepared by co-precipitation method. The broad green emission peak which is related to radiative recombination involving defect states due to absence of Zn vacancy, are located at about 523 nm for ZnS QDs with Zn vacancy. This result is consistent with the observations of Chen¹⁷. They concluded that Zn vacancies are introduced into ZnS QDs, which lead to the detected green emission from the ZnS QDs. Moreover, the PL spectra of ZnS QDs without Zn vacancies was obtained in our previous study¹⁸. In addition, it has been observed the blue broad emission at about 450 nm due to the Zn or S vacancies^{19,20}. In the experiment, we have prepare ZnS with Zn vacancies using the minimal amount of a Zn source. As the results of this approach the ZnS nanocrystals with Zn vacancies have been successfully synthesized. For the synthesis of pure ZnS nanocrystals 0.5 M of the 100 ml aqueous solutions of $Zn(CH_3COO) \cdot 2H_2O$ and 0.5 M of the 100 ml aqueous solutions of Na_2S are dissolved into two different beakers. Then these two solutions as cation and anion sources are placed into the third clean beaker and stirred for a certain time to get a ZnS homogeneous mixture at room temperature. While stirring the mercaptoethanol (2 ml) is added into the mixture. Then by filtering the precipitated sample has been separated from the solvent. De-ionized water and ethanol have been used to wash the obtained particles to eliminate the unwanted compounds. The obtained final solution has been heated in the oven up to 80 deg C . The ZnS nanoparticles have been obtained after grinding the powders in a mortar. For the synthesis of ZnS with Zn vacancies we have used the similar procedure where instead of using 0.5 M aqueous solutions of $Zn(CH_3COO) \cdot 2H_2O$, we have employed 0.2 M of $Zn(CH_3COO) \cdot 2H_2O$ aqueous solution.

Computations. For electronic-structure calculations of ZnS nanocrystals we use the Gaussian simulation package³⁰. The DFT method with the B3LYP exchange-correlation functional and LANL2dz basis set has been employed for the structure optimization. We have studied ZnS quantum dots of two different sizes, $Zn_{32}S_{32}$ and $Zn_{82}S_{82}$, with and without Zn vacancies. Then four Zn vacancies have been created in a QD core and on a QD surface. In addition we have calculated absorption spectra for uniformly distributed Zn vacancies over the nanocrystal and cluster formations located inside a QD and on a QD surface. The

FIG. 1: Room temperature photoluminescence (PL) spectra for ZnS QDs with Zn vacancies.

absorption spectra have been calculated within the TDDFT method for smaller QD sizes and the simplified time-dependent density functional theory (sTD-DFT) approach for the larger ones³¹. For sTD-DFT method we have chosen the BLYP functional. The choice of a functional has been determined to fit the experimental gaps.

Experimental results. To find the crystal structure of the material under study we provide the XRD pattern, which is shown in Fig. 2. The three peaks correspond to planes (111), (220), and (311), respectively. All nanocrystal diffraction peaks can be well identified as those of the ZnS cubic zinc-blende structure. The peak identification is consistent with the standard card (JCPD No. 65-9585). The average size for the QDs with and without vacancies is estimated to be 2.8 nm. The estimations are obtained from the full width at half-height of the diffraction peaks using the Debye- Scherrer formula. In order to determine the location of Zn vacancies in ZnS QDs we have created the samples with and without Zn vacancies. The estimated concentration of the vacancies is 12.4 %. The absorption spectra for ZnS quantum dots with and without vacancies are shown in Fig. 3. From this figure we observe that in the presence of the vacancies there is a shift in the absorption peak towards the red side of the spectrum (see the red curve). The shift in the absorption peak is about 11 nm or approximately 0.1 eV.

ZnS absorption spectra calculations. To understand the shift in the absorption peaks in ZnS quantum dots with and without Zn vacancies we consider the following plan: (a)

FIG. 2: XRD pattern for ZnS nanocrystals with and without vacancies. The blue and red curves correspond to the QDs without and with Zn vacancies. The three picks correspond to the (111), (220) and (311) planes, respectively.

FIG. 3: Absorption spectra for ZnS QDs with (the red curve) and without (the blue curve) vacancies. The dashed lines correspond to the absorption peak positions.

we calculate the absorption spectra for quantum dots of different sizes, (b) we place Zn vacancies in a QD core, on a surface, and both in a core and on a surface, and (c) we consider a uniform distribution and cluster (spot) formation.

In Fig. 4 we present the absorption spectra for ZnS quantum dots with and without Zn vacancies. The size of a QD with no vacancies is chosen to be $Zn_{82}S_{82}$. For the QD with Zn vacancies we consider only a $Zn_{78}S_{82}$ quantum dot, i.e., there are four Zn vacancies. In this figure the vacancies form a cluster. From the two absorption spectra we find the peak shift towards the blue side if the vacancies are present. Thus we conclude that the choice of the vacancy distribution does not fit the experimental data. The uniform distribution of the Zn vacancies in a QD core is difficult to generate because of a small QD size (some vacancies have to be on the surface). We later discuss a special case where the vacancies are

FIG. 4: Absorption spectra for ZnS quantum dots with (the black curve) and without (the red curve) Zn vacancies. The Zn vacancies are located in the middle of a quantum dot as a small cluster.

simultaneously distributed both in a QD core and on a surface.

We consider four vacancies placed on a QD surface as an aggregation (a spot). The calculated absorption spectra are presented in Fig. 5. The peak shift is now towards the

FIG. 5: Absorption spectra for ZnS quantum dots with (the black curve) and without (the red curve) Zn vacancies. The Zn vacancies are placed on a QD surface as a spot.

red side of the spectrum. The value of the shift is about 0.1 eV , which perfectly explains the experimental dependencies presented in Fig. 2. From the calculations we can also find some additional information on a QD surface vacancy distribution. In this case we uniformly distribute all four Zn vacancies over the surface. The absorption spectra are presented in Fig. 5 where we see the blue shift in the absorption peak, which does not explain the experimental dependencies presented in Fig. 3. Thus we conclude that the assumption based on the uniform surface distribution of Zn vacancies is not supported by the experiential observations.

Furthermore we have also considered the case where the distribution of Zn vacancies is both in the QD core and on the QD surface. The computational absorption spectra are

FIG. 6: Absorption spectra for ZnS quantum dots with (the black curve) and without (the red curve) Zn vacancies. The Zn vacancies are uniformly distributed over the QD surface.

shown in Fig. 7. In this case we do not find any peak shift in the presence of Zn vacancies. Thus there is only one choice remains where the Zn vacancies are located on the QD surface

FIG. 7: Absorption spectra for ZnS quantum dots with (the black curve) and without (the red curve) Zn vacancies. The Zn vacancies are located both in the QD core and on the QD surface.

as a spot.

In addition, we have also studied small quantum dots, $Zn_{32}S_{32}$, with and without Zn vacancies. The spectra exhibit similar dependencies. We do not present the computational results because of similarity to the absorption spectra of the larger quantum dots, which are more relevant to the experimental conditions.

Conclusions. In this work we have experimentally and theoretically studied the location and spatial distribution of Zn vacancies in a ZnS quantum dot. We have found that in the presence of Zn vacancies the absorption peak shifts (about 0.1 eV) towards the red side of the spectrum as shown in Fig. 3. To explain the experimental data we have computationally considered different locations of Zn vacancies: in a QD core, on a surface, and both core + surface. The computational results are presented in Figs. 4, 6, and 7, respectively. From the

comparison of the calculated absorption spectra with the experimental data we conclude that the Zn vacancies are located on the QD surface as a spot. The uniform distribution of Zn vacancies over the QD surface does not exhibit any peak shift contradicting the experimental dependencies (see Figs. 3 and 6). Thus from the analysis of the experimental absorption spectra in conjunction with the electronic structure calculations we are able to identify the location of Zn vacancies in a quantum dot. We find that the Zn vacancies are located on the QD surface as a spot rather than being uniformly distributed over the surface.

I. ACKNOWLEDGMENTS

This work was supported by a grant (No. DEFG02-10ER46728) from the Department of Energy to the University of Wyoming.

* Electronic address: yurid@uwyo.edu

- ¹ M. Venkatesan, C. B. Fitzgerald, and J. M. D. Coey, *Nature* 430 (2004) 630.
- ² A. Sundaresan, R. Bhargavi, N. Rangarajan, U. Siddesh, and C. N. R. Rao, *Phys. Rev. B* 74 (2006) 161306(R).
- ³ D. Milivojevic, J. Blanus, V. Spasojevic, V. Kusigerski, B. Babic-Stojic, *Solid State Comm.* 141 (2007) 641.
- ⁴ Yu. Huang, W. Zhou, Pi.Wu, *Solid State Comm.* 183 (2014) 3134
- ⁵ N. H. Hong, J. Sakai, N. Poirot, and V. Brize, *Phys. Rev. B* 73 (2006) 132404.
- ⁶ H. Pan, J. B. Yi, L. Shen, R. O. Wu, J. H. Yang, J. Y. Lin, Y. P. Feng, J. Ding, L. H. Van, and J. H. Yin, *Phys. Rev. Lett.* 99 (2007) 127201.
- ⁷ D. Gao, G. Yang, J. Zhang, Z. Zhu, M. Si, and D. Xue, *Appl. Phys. Lett.* 99 (2011) 052502.
- ⁸ Z. Zhang, U. Schwingenschlogl, I. S. Roqan, *RSC Adv.* 4 (2014) 50759.
- ⁹ W. Adli, M. Ferhat, *Solid State Comm.* 189 (2014) 68.
- ¹⁰ G. Zhu, S. Zhang, Z. Xu, J. Ma, and X. Shen, *J. Am. Chem. Soc.* 133 (2011) 15605.
- ¹¹ W.-Z. Xiao, L.-L. Wang, O. Y. Rong, G. Xiao, and B. Meng, *J. Appl. Phys.* 115 (2014) 213905.
- ¹² S. Fang, Y. Bando, U. K. Gautam, T. Y. Zhai, H. B. Zeng, X. J. Xu, M. Y. Liao, and D. Golberg, *Crit. Rev. Solid State Mater. Sci.*, 34 (2009) 190.

- ¹³ W. Liu, N. Wang, R. M. Wang, S. Kumar, G. S. Duesberg, H. Z. Zhang, and K. Sun, *Nano Lett.* 11 (2011) 2983.
- ¹⁴ Y. P. Zhang, W. Liu, and R. M. Wang, *Nanoscale* 4 (2012) 2394.
- ¹⁵ V. Proshchenko, S. Horoz, J. Tang, and Yu. Dahnovsky, *J. Appl. Phys.* 119 (2016) 223901.
- ¹⁶ V. Proshchenko, A. Karanovich, and Yu. Dahnovsky, *J. Phys. Chem. C* 120 (2016) 11253.
- ¹⁷ H. Chen, Y. Hu, X. Zheng, *J. Mat. Scie.*, 46 (2011) 2715.
- ¹⁸ S. Horoz, B. Yakami, U. Poudyal, J. M. Pikal, W. Wang, J. Tang, *AIP Advances*, 6 (2016) 045119.
- ¹⁹ K. Sooklal, B. S. Cullum, S. M. Angel, and C. J. Murphy, *J. Phys. Chem.* 100 (1996) 4551.
- ²⁰ X. Zeng, J. Zhang, and F. Huang, *J. Appl. Phys.* 111 (2012) 123525.
- ²¹ K. Kuratani, K. Tatsumi, and N. Kuriyama, *Cryt. Growth Des.* 7 (2007) 1375.
- ²² P. Mcgeehin and A. Hooper, *J. Mater. Sci.* 2 (1977) 1.
- ²³ A. Clearfield, *Chem. Rev.* 88 (1988) 125.
- ²⁴ S. Barbato and J. Gautier, *Electrochim. Acta.* 46 (2001) 2767.
- ²⁵ A. E. Ringwood, S. E. Kesson, N. C. Ware, W. Hibberson, and A. Major, *Nature* 278 (1979) 219.
- ²⁶ H. Sato, T. Enoki, J. I. Yamaura, and N. Yamamoto, *Phys. Rev. B* 59 (1999) 12836.
- ²⁷ H. Sato, J. I. Yamaura, T. Enoki, and N. Yamamoto, *J. Alloys Compd.* 262 (1997) 443.
- ²⁸ S. Ishiwata, J. Bos, O. Huang, and R. J. Cava, *J. Phys.: Condens. Matter.* 18 (2006) 3745.
- ²⁹ S. Horoz, Q. Dai, F. S. Maloney, B. Yakami, J. M. Pikal, X. Zhang, J. Wang, W. Wang, and J. Tang, *Phys. Rev. Applied* 3 (2015) 024011.
- ³⁰ Gaussian 09, Revision A.1, M. J. Frisch, et al., Gaussian, Inc., Wallingford CT, 2009.
- ³¹ C. Bannwarth and S. Grimme, *Comput. Theor. Chem.* 1040-1041 (2014) 45-53.