FIRST-PRINCIPLES STUDY OF ELECTRONIC AND MAGNETIC PROPERTIES OF DEFECTED ZnSe

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Electronic and magnetic properties of defected ZnSe 32- and 96-atom supercell systems were investigated from the first-principles study. We obtained that the presence of one, two, and three Zn vacancies defects lead to the magnetization of ZnSe with ~2 μ_B total magnetic moment and main contribution to magnetization of systems come from host Se atoms. The ferromagnetic alignment in the Zn vacany defected ZnSe supercell systems show semiconducting nature.

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1. INTRODUCTION

Transition-metal doped ZnSe supercell systems have revealed its potential for technical application. ZnSe is ideally appropriate for the fabrication of photodetectors, CO_2 laser focusing lenses, sensors, solar cells, and other photovoltaic applications [1]. This material can be applied for the production of optoelectronic devices such as light emitters and detectors [2-5]. The Zn(Fe)Se has been applied to the laser gain medium in mid-IR laser [6].

DMSs based on II-VI group compounds have been attracting great interest as promising materials for new spin electronic devices, because these compounds show ferromagnetic (FM) phase, who's Curie temperature, depends on the carrier concentration [7]. For industrial applications of DMSs room temperature, ferromagnetism is strongly required. Doping of TMs in nonmagnetic wurtzite ZnSe semiconductor is very impotant to make this material multifunctional. These materials have attracted a lot of attention as materials for spintronic applications because of their half-metallic ferromagnetic (HMFM) behaviors.

Investigations show that numerous research works devoted investigation of electronic and magnetic properties of defected zinc-blende ZnSe systems. Rai *et al* [8] studied 5 Zn vacancies in the monolayer hexagonal ZnSe 18-atom supercell modeled by 3×3×1 transferred based on the DFT. They reported that the Zn vacancy makes the FM state of ZnSe.

2. CALCULATION METHOD

The calculations were carried out for the ZnSe systems with 32 and 96 atoms by the DFT method within Local Spin Density Approximation (LSDA) implemented Atomistix ToolKit code within incorporated Mulliken population analysis. The interactions between the electrons and ions, and exchange-correlation were described by the Fritz-Haber-Institute ion pseudopotentials and the Perdew Zunger (PZ) functional, respectively. The Kohn-Sham wave functions expanded in a linear combination of atomic orbitals with a kinetic energy cutoff of 75 Ha. When calculating structural and electronic properties for pure compound, the primitive cell of ZnSe wurtzite containing 2 Zn and 2 Se atoms and the atomic positions are optimized until the force and stress on each atom converges to less than 0.001 eV/Å and 0.001 eV/Å^3, respectively. The supercells containing dopant atoms and vacancies were optimized with force and stress tolerances of 0.01 eV/Å and 0.01 eV/Å^3, respectively. The reciprocal space integration was performed with 5×5×5 (for supercells) and 7×7×7 (for bulk structure) Monkhorst-Pack *k*-point sampling and a standard electron temperature of 300 *K*.

The 12 electrons for Zn [Ar] +3d^{10}4s^2 and 6 electrons for Se [Ar] +4$s^2$4p^4 are treated as the valence electrons. The Hubbard *U* corrections took 4.5 eV for Zn 4*d*- and 3.5 eV for Se 4*p*-states.

RESULTS AND DISCUSSION

3.5 ZnSe supercell with Zn vacancy

ZnSe crystallizes in the wurtzite structure, a hexagonal analog of zinc blende lattice, with a space group P6$_3$mc with two formula units per unit cell. In this structure, each Zn atom is tetrahedrally coordinated with four other Se atoms and the atomic positions for zinc are (0, 0, 0) and (1/3, 2/3, 0.5), for selenium are (0, 0, 0.3408) and (1/3, 2/3, 0.8408) [38].

The first-principles computed Zn-Se and Zn-Zn (Se-Se) distances have been found equal to 2.39 and 3.9 Å, respectively. We get a structure with an average Zn-Se bond length of 2.39 Å and this value is in agreement with the reported results by Chen *et al* (theor.: 2.376 Å) [9] and Park *et al* (exp.: 2.20 Å) [10].

The magnetic properties of 32- and 96-atom supercells ZnSe wurtzite structure with vacancy defects at Zn sites (Figure 1). In this figure, the Zn vacancy-defect position is encircled. The studied structure is formed by the admixture of ionic and covalent bonds. One vacancy defect at the Zn site in systems creates the dangling of three Zn-Se covalent bonds and this fact will give three extra acceptors which will induce the spin magnetic moment at the nearest 4 Se atoms dangling bonding of Zn. Rai *et al* [8] and Chan *et al* [11] have reported a similar fact.

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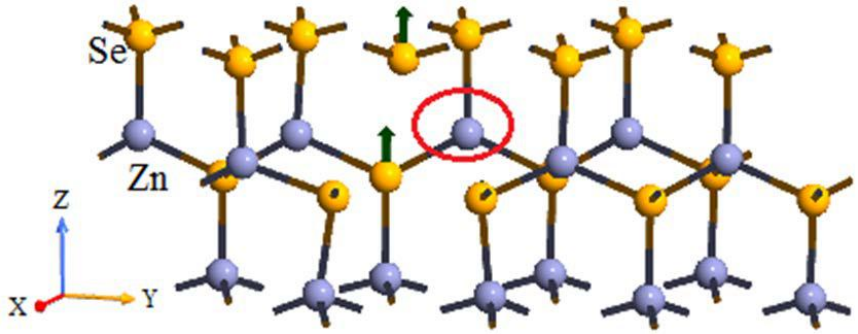

Fig. 1. The 32-atom ZnSe supercell structure and magnetization with one Zn vacancy-defected (Zn-gray, Se-yellow).

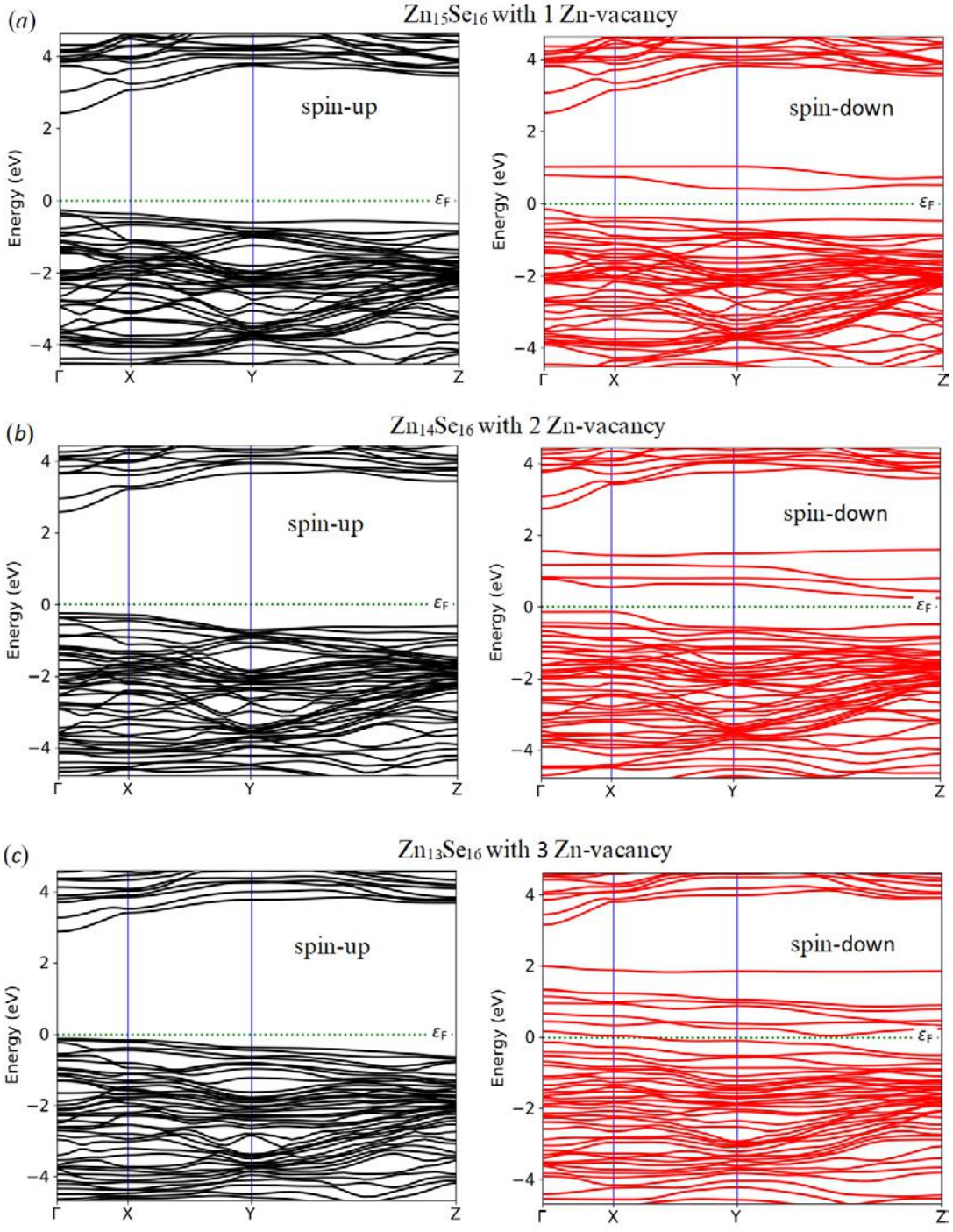

Fig. 2. The DFT-LSDA+U calculated electron band structures of $Zn_{15}Se_{16}$ (a), $Zn_{14}Se_{16}$ (b), and $Zn_{13}Se_{16}$ (*c*) systems with vacancy-defects at Zn sites: black-spin-up; red-spin-down states.

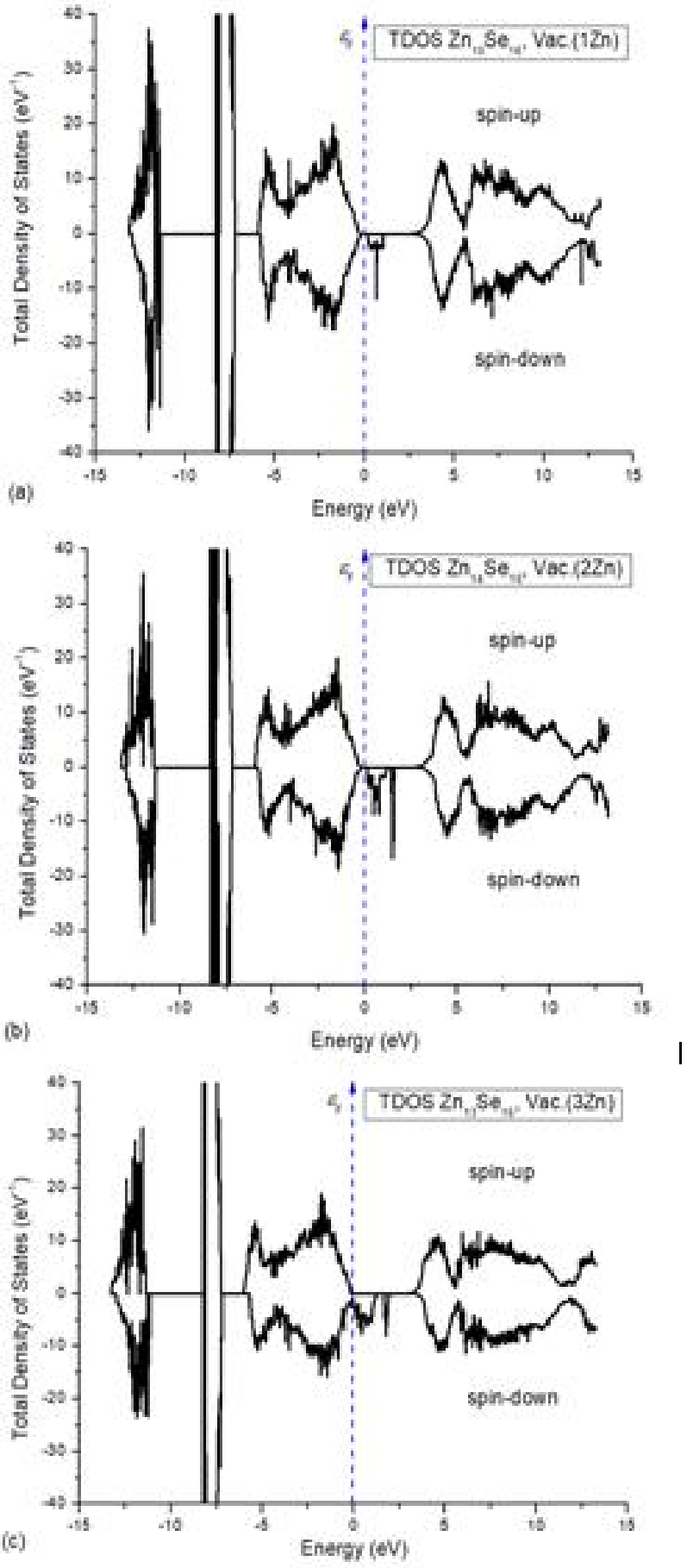

Fig. 3. The DFT-LSDA+U calculated the TDOS of $Zn_{15}Se_{16}$ (a), $Zn_{14}Se_{16}$ (b), and $Zn_{13}Se_{16}$ (c) systems with vacancy-defects at Zn sites.

To obtain accurate band gap value, we first have been calculated the band structure of for ZnSe bulk structure and obtained the band gap of 2.7 eV [12, 13]. This value is very close with experimental results. The first-principles calculated band gap and magnetic moment results for vacancy-defected ZnSe systems for spin-up and spin-down states are presented in Table 1. Zn vacancy case increases the spin-up band gap, but decreases the spin-down band gap of $Zn_{1-x}Se$ systems, dependent on the number of vacancies. In this case, due to the presence of one (or two and or three) zinc vacancy-defect the total magnetic moment of the system is about ~2 μ_B (main contributions to the magnetization including 2.288 μ_B (2.34 μ_B) from 16 Se (or 48 Se) and -0.289 μ_B (-0.352 μ_B) from 15 Zn (or 47 Zn) atoms).

Table 1.

The band gap and magnetic moment results of vacancy-defected ZnSe for spin-up and spin-down states.

Supercell	Band gap, eV		μ_B per Vac.(Zn)
	Spin-up	Spin-down	
$Zn_{15}Se_{16}$	2.68	1.5	1.999
$Zn_{14}Se_{16}$	2.8	1.18	1.999
$Zn_{13}Se_{16}$	3.0	1.16	2.01
$Zn_{47}Se_{48}$	2.70	1.5	1.988

The values of total magnetic moments for ZnSe 32-atom supercells with one (1.99 μ_B; 1.83 μ_B), two ((1.99; 1.97 μ_B), and three Zn vacancy-defects (2.01 μ_B; 1.72 μ_B) calculated from Mulliken Population analyses well agree with the known theoretical results reported by Rai *et al* [8]. The positive contributions to magnetization from Se (2.288 μ_B) and smaller negative contributions from Zn atoms (-0.289 μ_B) of supercell.

Figures 2 and 3 show band structures and TDOS for Zn vacancy defected $Zn_{1-x}Se$ (x=1, 2, 3) systems. As seen in figure 8, the TDOS of major- and minor-spin states are not symmetric, because Zn vacancy-defects in ZnSe systems lead to the ferromagnetic spin ordering. DFT calculations revealed that present Zn vacancy cases increase the spin-up band gap, but decrease the spin-down band gap of $Zn_{1-x}Se$ systems, dependent on the number of vacancies.

DFT-LSDA+U calculations revealed that the availability of one Zn defect into the ZnSe supercell is the most effective for strengthening the magnetization. Thus, the shift of the moment of the system due to one Zn vacancy side is (1.6 ÷ 1.9) μ_B depending on the chosen location of the defect.

CONCLUSION

In summary, the spin-polarized electronic properties of ZnSe with Zn vacancy are studied by DFT within the LSDA+U method. The investigations performed for 32- and 96-atom ZnSe supercell systems show that Zn vacancy lead to a ferromagnetic spin ordering. The existence of defects in the structure affects the magnetization of the supercell with ~2 μ_B total magnetic moment. Our calculation revealed that in the Zn vacancy case, increases the spin-up band gap, but decreases the spin-down band gap of $Zn_{1-x}Se$ systems, dependent on the number of vacancies. The Zn vacancy is the most efficient for enhancing supercell magnetization.

[1] *G.F. Neumark, R.M. Park, J.M. Depuydt,* Physics Today, 1994, v.47, p.26.

[2] *B.I. Adetunji, P.O. Adebamboand G. A. Adebayo*, J. Alloys Compd., 2012, v.513, p.294.

[3] *M. A. Haase, J. Qiu, J.M. De Puydt and H. Cheng*, Appl. Phys. Lett., 1991, v.59, p.1271.

[4] *D.B. Eason, et al.,* Appl. Phys. Lett., 1995, v.66, p.115.

[5] *A.F. Gochuyeva, Kh.Kh. Hashimov, I. Y. Bayramov,* Chalcogenide Letters, 2023, v.20, p.285.

[6] *S.B. Mirov, et al.*, OSA Proc. Adv. Solid-State Lasers, AM4A., 2014, v.6, p.16.

[7] *G.A. Medvedkin, et al.*, Jpn. J. Appl. Phys., 2000, v.39, p. L949.

[8] *D.P. Rai, et al.*, Vacuum, 2020, v.182, p.109597.

[9] *X.L. Chen, et al.,* RSC Adv., 2015, v.5, p.106227.

[10] *H. Park, H. Chung and W. Kim*, Mater. Lett., 2013, v.99, p.172.

[11] *J.A. Chan, L. Stephan, A. Zunger*, Phys. Rev. Lett., 2009, v.103, p.016404.

[12] *V.N. Jafarova*, Intern. J. Modern Phys. B, 2022, v.36, p.2250156.

[13] *V.N. Jafarova, H.S. Orudzhev*, Sol. State Commun., 2021, v.325, p.114166.

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