HALF-METALLIC FERROMAGNETISM IN V-DOPED ZnSe: DFT STUDY

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The electronic and magnetic properties of V-doped ZnSe have been calculated within LSDA+U method. The ab-initio calculations are carried out using Atomistic ToolKit code, based on the density functional theory. The band structure and density of states calculations showed the half-metallic behavior for 12.5 %, 6.25 %, 3.125 %, 1.5625 % concentrations in ZnSe:V. The magnetic moment of $Zn_{1-x}V_xSe$ supercell is 3 μ_B. The defect formation energies were calculated and obtained that ferromagnetic phase is more stable than antiferromagnetic state. The Curie temperatures are estimated for $Zn_{1-x}V_xSe$ supercell for all studies concentrations. The results indicate that these materials are high Curie temperature DMSs. First-principles studies show that V-doped ZnSe are promising materials for spintronics.

Keywords: ZnSe:V, DMSs; ferromagnetic, half-metal
PACS: 61.43.Bn; 71.20.-b; 61.72.-y

1. INTRODUCTION

Diluted magnetic semiconductors known as semimagnetic compounds which a managed fraction of nonmagnetic cations are replaced by 3*d* transition metals (TMs). TM^{2+} magnetic ions doped II-VI semiconductor compounds are counted as promising optoelectronic materials in the mid-IR region, low energy optical phonon cut-off, and large emission cross-sections [1]. The development of Zn-based DMSs II-VI group show magnificent properties, which have huge opportunity to be applied in spintronics [2]. These materials have attracted a lot of attention as materials for spintronic applications [3] because of their half-metallic ferromagnetic behaviors at Curie temperatures higher than room temperature [4]. Maksimov *et al.* [5] experimentally studied the V-doped ZnSe cubic crystals and established that in $Zn_{1-x}V_xSe$ (x=10%) single crystal vanadium ions dissolved in zinc selenide in amounts corresponding to high doping levels.

Zinc selenide a semiconductor, can operate as a half-metallic compound and is a helpful material for optoelectronic and spintronic applications. Zinc selenide is a nonmagnetic material with a direct band gap of 2.70 eV and has great potential for a diversity of optical and electro-optical devices, such as short wavelength lasers, blue-green laser diodes, pure green light-emitting diodes, microwave and terahertz devices, solar cells and tunable mid-IR laser sources [6].

2. CALCULATION METHOD

The calculations were carried out based on the Density Functional Theory (DFT). The geometric model for ZnSe:V is built by replacing host Zn atoms with V. The ferromagnetism in investigated systems at various impurity concentrations have been investigated within the Local Spin Density Approximation (LSDA) as implemented in the Atomistic ToolKit software from Mulliken population analysis. Hubbard U semiempirical corrections (4.5 eV on *d*-states of Zn and 3.8 eV on *p*-states of Se) are used for correct band gap prognosis for bulk ZnSe [7]. The simulations are carried out for different supercells generated with the initial lattice parameters a=b=3.98 Å and c=6.53 Å [8]. One and two impurity atoms added at Zn cation sites in 32-, 64-, 128-, and 256-atom supercells to study the ferromagnetism of V-doped ZnSe. A *k*-sampling Monkhorst-Pack grids 5×5×5 and 3×3×3 used and all atomic positions have been geometry optimized. The valence electron configurations which included 12 electrons for Zn [Ar] $+3d^{10}\ 4s^2$, 6 electrons for Se [Ar] $+4s^2\ 4p^4$, and 5 electrons for V [Ar] $+3d^3\ 4s^2$ were taken into consideration.

3. RESULTS AND DISCUSSION

3.1 Vanadium-doped ZnSe

For this to study the magnetic behavior of dopants, have been studied two Zn atoms of the 32-, 64-, 128- and 256-atom supercells with V^{2+} suitable to the impurity concentrations x=12.5 %, 6.25 %, 3.125 %, and 1.5625 %. Spin-polarized simulations have been implemented using LSDA+U to study the electronic properties of the undoped and V^{2+} doped systems. Spin-polarized band structures and total density of states (TDOS) for undoped $Zn_{16}Se_{16}$ system are given in Fig. 1, correspondingly to the spin-up and spin-down states. The calculated band gap of undoped ZnSe 32-atom supercell is 2.7 eV which very closer to experimental results [9] and the spin-up and spin-down band structures are same.

The spin-polarized band diagrams and TDOS of $Zn_{1-x}V_xSe$ alloys with x=6.25 % concentration are illustrated in Fig. 2 and illustrate that the spin-up bands have a semi-metallic nature due to the top of valence band cutting the Fermi energy level with availability of a gap between the valence and conduction bands.

The obtained density of states showed hybridization between the Se *p*- and V *d*-states, which increased the antibonding state in the gap that stabilized the FM state associated to the double exchange mechanism. To understand the origin of the spin-polarized notion of

the density of states (DOS) in Fig. 3, we analyzed the partial DOS of investigated systems as presented in Fig. 4. These diagrams for both systems presented a similar behavior with high-spin state. They illustrate that the valence band formed mainly from Se *p*- and V *d*-states, which is close to the Fermi energy level, the DOS derived from 3*d*-states of impurity atom. At the Fermi level we have only up spin states, i.e., so called half-metallic situation is realized. From first-principles calculations found that the half-metallic state can be obtained in V-doped ZnSe systems: the dopant *p*- and *d*-states are partially occupied.

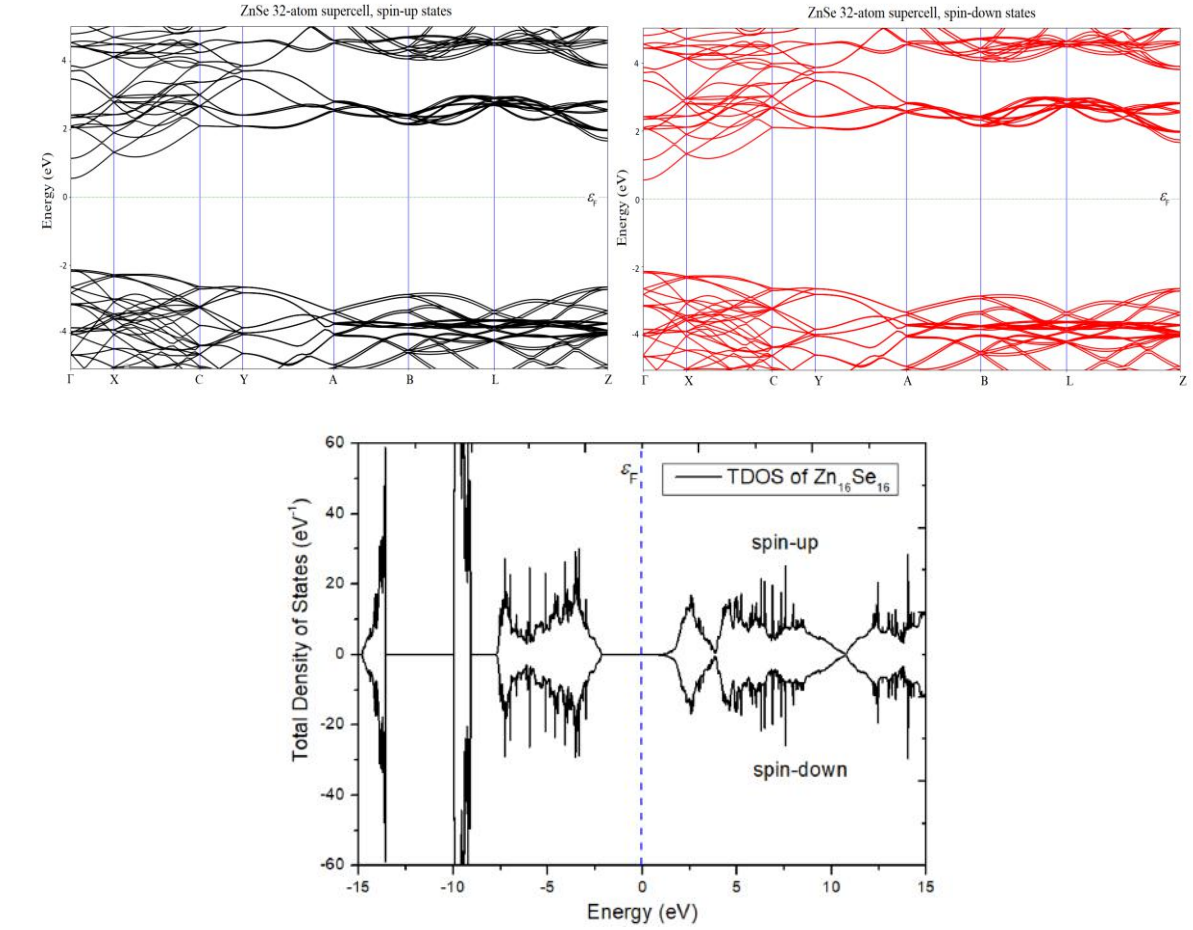

Fig.1. Spin-polarized band structures and TDOS for $Zn_{16}Se_{16}$ correspondingly to spin-up and spin-down states.

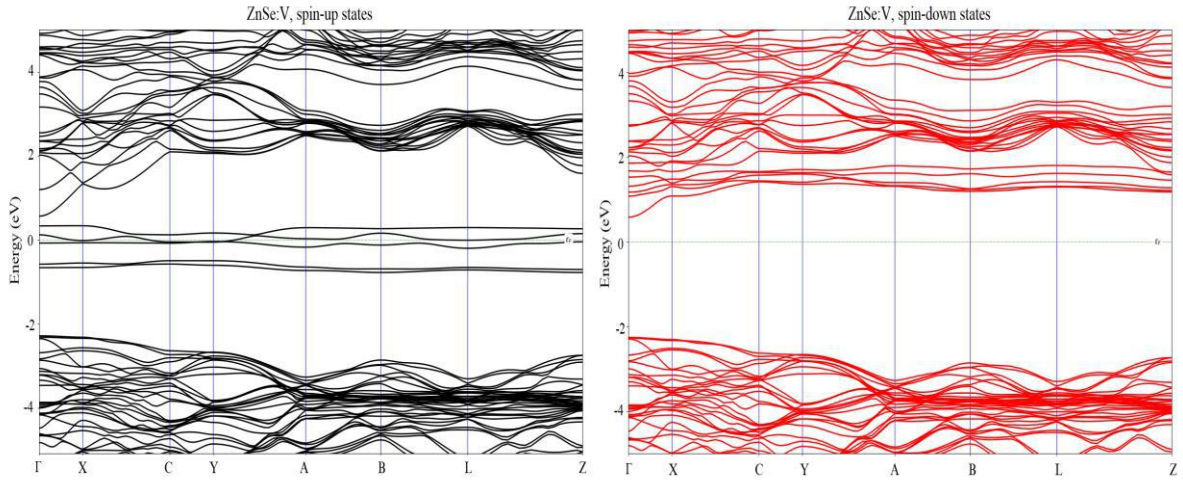

Fig. 2. Spin-polarized band structures for $Zn_{15}V_1Se_{16}$ correspondingly to spin-up and spin-down states.

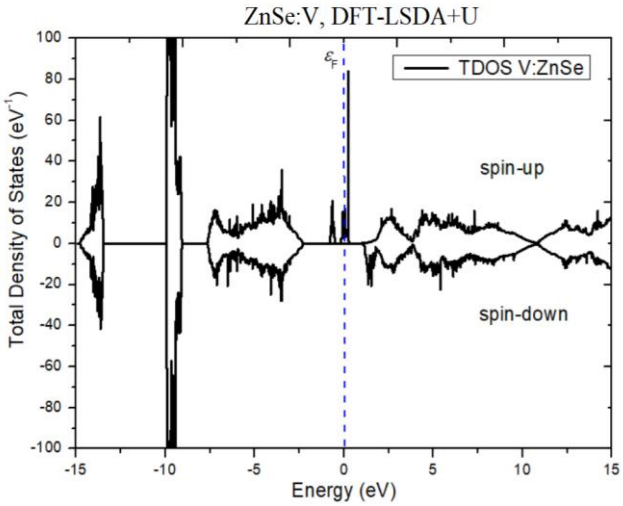

Fig. 3. Total DOS for $Zn_{15}V_1Se_{16}$ with LSDA+U.

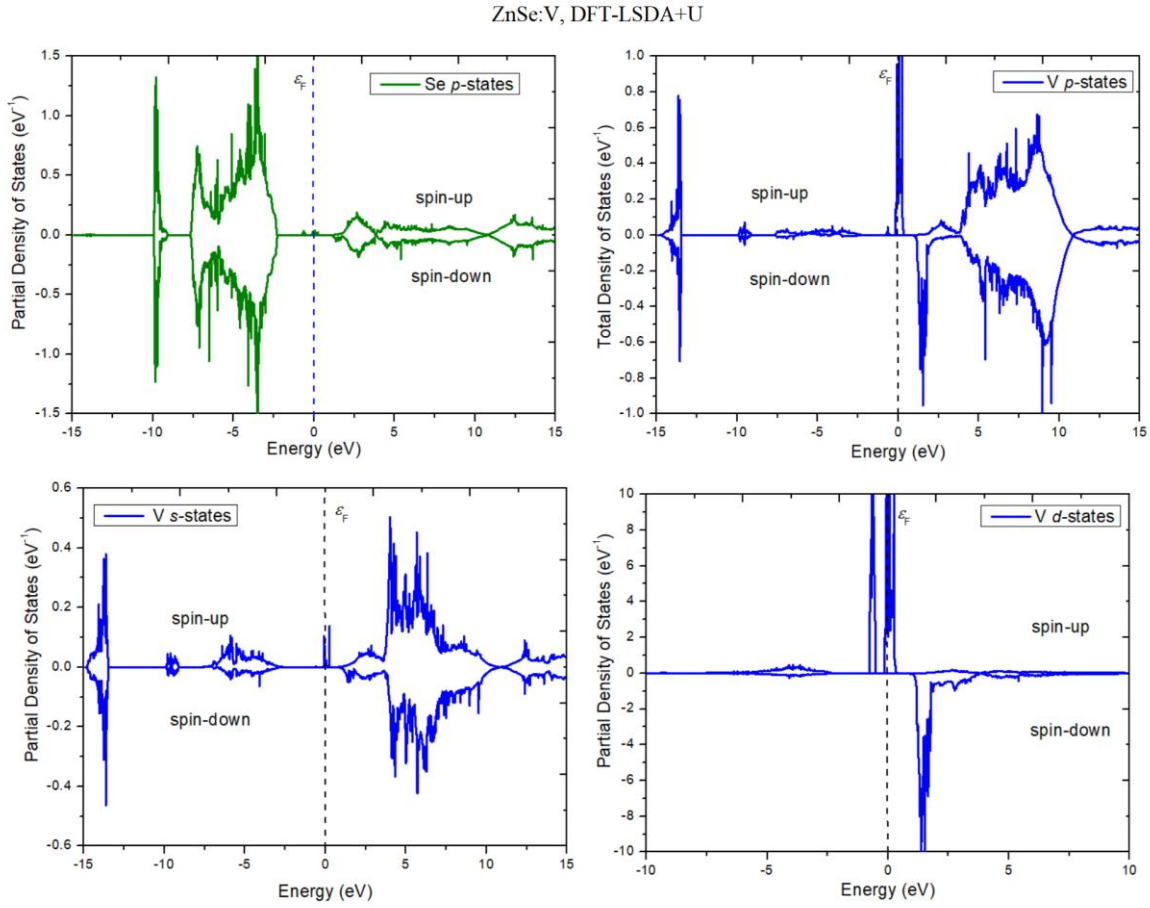

Fig. 4. Partial DOS for $Zn_{15}V_1Se_{16}$ with LSDA+U.

Table 1.

Bang gaps values for different V-ZnSe systems.

System	MP grid	IC [%]	Band gap [eV]	
			up	dn
$Zn_{15}V_1Se_{16}$	5×5×5	6.25	1.69	2.88
$Zn_{14}V_2Se_{16}$	5×5×5	12.5	1.84	3.00
$Zn_{30}V_2Se_{32}$	5×5×5	6.25	1.62	2.88
$Zn_{62}V_2Se_{64}$	3×3×3	3.125	1.53	2.79
$Zn_{126}V_2Se_{128}$	3×3×3	1.5625	1.45	2.744

First-principle computed spin-polarized electronic structures and DOS calculations show that the V-doped ZnSe materials are half-metallic, and this fact corresponding to reported result in Ref. [10]. First-principles computed value of electronic band gaps of V-doped 32-, 64-, 128-, and 256-atom supercells are listed in Table 1. Valence band edges are created due to hybridization between Se-3*p* and V 3*d* (spin-up) states, although the conduction band edges are the result of Zn-4*s* spin-down states. The magnetic moments for V dopants, and its neighboring host atoms have been calculated in detail using DFT-LSDA+U method. For recent simulations, the FM and AFM states of V doped ZnSe supercells can be described as $Zn_{1-x}V^{\uparrow}_{x/2}V^{\uparrow}_{x/2}Se$ and $Zn_{1-x}V^{\uparrow}_{x/2}V^{\downarrow}_{x/2}Se$, respectively.

The total energy differences beetween AFM and FM alignments show FM stability of ZnSe:V doped systems. Only the result of the total energy differences beetween AFM and FM alignments for $Zn_{126}V_2Se_{128}$ supercell show stability of AFM state.

The spin-polarization structure of $Zn_{15}V_1Se_{16}$ supercell is shown in Fig. 5. In this spin-polarization structure, the magnetic moments of atoms are indicated by black arrows, which these are significant values than other host atoms.

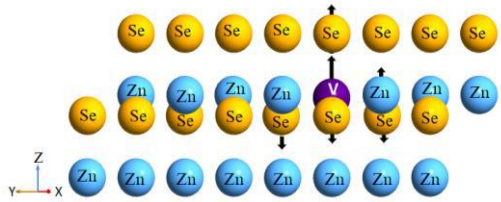

Fig. 5. The spin-polarization of $Zn_{15}V_1Se_{16}$ supercells.

The obtained values of total magnetic moments for ZnSe:V systems are 3.0 μ_B, respectively, which in a good agreement with the results of Ref. [11]. Khatta et al. [11] first-principles studied the magnetic properties of $Zn_{1-x}V_xSe$ ternary alloys (16-atom supercell) in zinc-blende phase and the obtained values of total magnetic moment is ranging from 2.78 to 3.0 μ_B, for different impurity atom concentrations (x=0.125÷0.875).

In the case of V-doping ZnSe the obtained value of magnetic moment per V, dopant atom is found to be 2.9 μ_B, which in good agreement reported result (2.84 μ_B) in Ref. [11]. The main contribution to the magnetization from d-states of V: 2.313 μ_B, the small positive and negative contribution from 15 Zn (0.216 μ_B) and 16 Se (-0.206 μ_B) atoms, respectively. First-principle calculations show that the FM phase in V-doped ZnSe systems is more stable than the AFM phase which is in agreement in Ref. [10].

3.2 FORMATION ENERGIES AND CURIE TEMPERATURES OF ZnSe:V

It is known that the stability of TM doped systems can be defined by the defect formation energy of structure. Formation energy calculations are performed for the fully relaxed different defected systems. The formation energy calculations were studied for enough large systems containing 32, 64, 128, and 256 atoms.

The formation energy of V^{2+} doped ZnSe systems is assigned as the energy needed to introduce such impurity in bulk ZnSe and can be calculated by the following expression [1]

$$E_{form.} = \frac{1}{N}\left[E_{tot.}(Zn_{1-x}V_xSe) - E_{tot.}(ZnSe) + n\cdot\mu_{Zn} - n\cdot\mu_V\right] \quad (1)$$

where N is the total number of atoms in supercell, $E_{tot.}(Zn_{1-x}V_xSe)$ and $E_{tot.}(ZnSe)$ are the total energies of doped and pure ZnSe systems having the same dimension to supercell, correspondingly. Terms n, μ_{Zn}, and μ_V are the number of doping atoms, the chemical potentials of Zn and V atoms, respectively.

The Curie temperatures of V-doped ZnSe systems are estimated by using the Heisenberg model in the Mean-Field Approximation (MFA) [6]

$$T_C = \frac{2}{3}\frac{\Delta E}{k_B x}, \quad (2)$$

where k_B and x are the Boltzmann constant and impurity atom concentration, respectively.

In this work, the defect formation energies and the Curie temperatures are estimated for different $Zn_{1-x}V_xSe$ systems using the reported results of energy difference between the AFM and FM alignments, and listed in Table 2.

Table 2.
The calculated values of formation energies, and the Curie temperatures for $Zn_{1-x}V_xSe$.

System	x, %	$E_{form.}$[eV]	T_C [K]
$Zn_{14}V_2Se_{16}$	12.5	75	4065
$Zn_{30}V_2Se_{32}$	6.25	37.5	552
$Zn_{62}V_2Se_{64}$	3.125	18.75	58

The obtained formation energy values of ZnSe:V are positive, indicating that it is hard to incorporate V atom to ZnSe, which agrees with known experimental results [12]. In Ref. [10] the authors have predicted a high Curie temperature for V-doped ZnSe systems, which are in agreement with results of current work. From Table 2, the Curie temperature is found to decrease with the decreasing of impurity atom concentrations for ZnSe:V and this material is suitable materials for application in spintronics.

4. CONCLUSION

In order to promote suitable semiconductor materials for spintronics devices, this study aims to evaluate the magnetic properties of the V-doped ZnSe. Using an accurate DFT-LSDA+U approach, have been explored the spin-polarized electronic and magnetic properties of $Zn_{1-x}V_xSe$ for x=12.5 %, 6.25 %, 3.125 %, and 1.5625 %. While the introduction of V^{2+} ions in the doped ZnSe systems change the TDOS and found the half-metallic ferromagnetic coupling. The obtained value of total magnetic moment has been found to be 3.0 μ_B for $Zn_{1-x}V_xSe$, and the mainly contribution to the

magnetization comes mostly from *d*-states of impurity atom. Results of the energy differences between the AFM and the FM states for both systems nearly represent a stable FM state.

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