THE MAGNETIC PROPERTIES OF ZnSe:TM (Cr, V): FIRST-PRINCIPLES STUDY

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Using spin polarized density functional theory with the local spin density approximation and Hubbard U corresctions, we have performed our simulations on ZnSe supercell compound, doped with 3d transition metals and vacancy positions. Investigation of electronic structures of $Zn_{1-x}TM_xSe$ systems show additionally peaks in the vicinity of Fermi level derived from TM^{2+} 3*d* orbitals. The computed spin moments for $TM_xZn_{1-x}Se$ alloys found of 3.0 μ_B for $V_xZn_{1-x}Se$, 4.0 μ_B for $Cr_xZn_{1-x}Se$ systems. The base contribution to the magnetization of systems comes from TM d-states. First-principles simulations of the total energies for ferromagnetic and antiferromagnetic phases show FM phase stability of $V_xZn_{1-x}Se$, $Cr_xZn_{1-x}Se$ systems.

Keywords: ZnSe:TM, ferromagnetic, antiferromagnetic, metallic, half-metallic
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1. INTRODUCTION

Nowadays, 3d metals (TM=Cr, V) doping II-VI group materials are useful semiconductor compounds for several applications [1, 2]. The recent progress of diluted magnetic compounds demonstrate magnificent physical and chemical properties, which have great potential for using in spintronics [3-4], because of their metallic and semi-metallic ferromagnetic (SMFM) phases with T_C > 300 K [5-6]. The previous study show that $Mn_xZn_{1-x}Se$ could be a utility material for spintronics, only if additional impurities are entered [7]. Refs. [8-9] found the chromium-doping in II-VI group compounds originate from ferromagnetic (FM) compounds at room temperature (RT). Ref. [10] reported results of experimental measurements for the $(V,Cr)_xZn_{1-x}Se$ with cubic structures and found antiferromagnetic (AFM) correlations occur in $Cr_xZn_{1-x}Se$ (with 0.15% and 4.5 % concentrations) below 60 K and in $V_xZn_{1-x}Se$ (with 10 % V) impurity ions dissolved in related structures. Ref. [11] reported SMFM behavior in $Cr_xZn_{1-x}Se$ systems, observed stability of the FM phase. 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 [12-14]. In Refs. [15-16] the authors reported that ZnSe:TM were appropriate for applications in spintronics and middle-IR lasing.

This work is dedicated to study of the magnetism in ZnSe:Cr and ZnSe:V by varying the impurity concentrations for the values x=12.5 %, 6.25 %, 3.125 %, 1.5625 %.

2. CALCULATION METHOD

The current simulations were done based on the Density Functional Theory (DFT). $TM_xZn_{1-x}Se$ systems were investigated under the same conditions (same supercells, same lattice parameters, same *k*-point sampling, etc.). The ferromagnetism in related supercell systems at different concentrations of impurities investigated within the Local Spin Density Approximation (LSDA) using Atomistic ToolKit (http://quantumwise.com/) simulations code. This is software for atomic-scale modeling and simulation of nanosystems. ATK combines DFT with non-equilibrium Green's functions for first-principles electronic structure, transport calculations of molecules, periodic systems etc. Two atoms of zinc were replaced by one Cr and one V atom, to obtain the ZnSe:Cr,V 32-atom co-doping system. The undoped ZnSe formed in wurtzite structure by two atoms with space group $P6_3mc$ [17]. Note that the investigated doped and co-doped supercells do not have appropriate hexagonal symmetry. In this study we present different configurations of Cr-, V-doped and co-doped ZnSe, which corresponds to different distances between TM ions.

The aim of the current study is to help the planner in the option of the candidate material for practical application. To accurate value of present results, it would be useful in future works, to solve the problem of DFT-LSDA which underestimates greatly the band gap by using the LSDA+U method.

3. RESULTS AND DISCUSSION

Electronic and Magnetic properties of ZnSe:Cr and ZnSe:V

In current work, have been investigated the electronic and magnetic properties of DMSs such as $Cr_xZn_{1-x}Se$ and $V_xZn_{1-x}Se$ in the wurtzite phase. For this to study the magnetic behavior of dopants, have been studied two Zn atoms of the 32-, 64-, 128- and

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256-atom supercells with Cr^{2+} and V^{2+} suitable to the impurity concentrations x=12.5 %, 6.25 %, 3.125 %, and 1.5625 %.

The spin-polarized band diagrams and total density of states (TDOS) of $Zn_{1-x}Cr_xSe$ and $Zn_{1-x}V_xSe$ alloys with x=0.0625 concentration are illustrated in Figs. 1 and 2, respectively. These figures illustrate that the spin-up bands have a semi-metallic nature due to the top of valence band cutting the Fermi energy level (ε_F) with availability of a gap between the valence and conduction bands. Consequently, $Zn_{1-x}Cr_xSe$ and $Zn_{1-x}V_xSe$ alloys have a HMFM behavior for all the studied concentrations in ZnSe:Cr, ZnSe:V and ZnSe:Cr,V which are in agreement with reported results for ZnSe:TM zinc-blende structures [18]. The obtained density of states showed a hybridization between the Se *p*- and TM (Cr,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. 2, we analyzed the partial DOS of investigated systems as presented in Fig. 6. 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 Cr (or V) *d*-states, which is close to the Fermi energy level, the DOS derived from 3*d*-states of impurity atom.

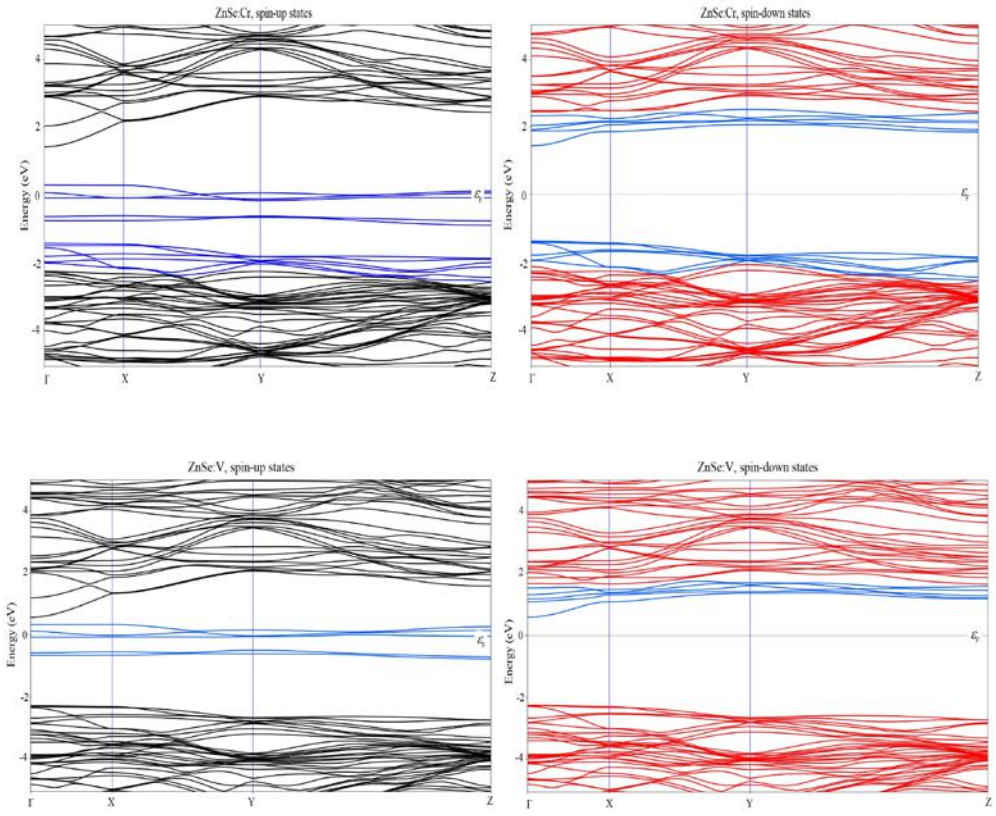

Fig. 1. Band structures for $Zn_{15}V_1Se_{16}$ and $Zn_{15}Cr_1Se_{16}$ correspondingly to spin-up and spin-down states.

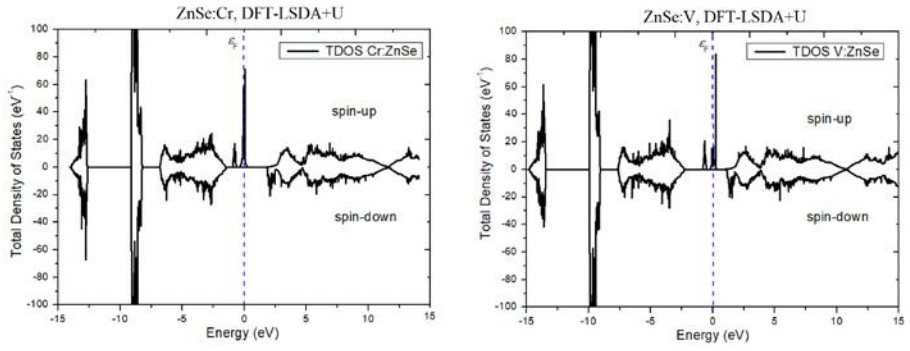

Fig. 2. Total DOSs for $Zn_{15}Cr_1Se_{16}$ and $Zn_{15}V_1Se_{16}$ with LSDA+U.

The spin-up HM gaps ranging from 1÷1.2 eV and 1.5÷1.8 eV for $Zn_{1-x}Cr_xSe$ and $Zn_{1-x}V_xSe$ systems at impurity atom concentrations x=12.5 %; 6.25 %; 3.125 %; 1.5625%, respectively. First-principles spin-polarized electronic structures and DOS calculations show that the Cr- and V-doped ZnSe are high-spin and half-metallic materials.

The magnetic moments for Cr and V dopants, and its neighboring host atoms have been calculated in detail using DFT-LSDA+U method. The Cr-Cr and V-V bond lengths and the total energy differences beetween disorder local moment (DLM) and ferromagnetic (FM) alignments $\Delta E=E_{DLM}-E_{FM}$ for different ZnSe:TM systems are shown in Table 1 and 2, respectively.

Table 1.

The Cr-Cr bond lengths and the total energy differences beetween DLM and FM alignments for different ZnSe:Cr systems using LSDA+U.

System	d_{Cr-Cr} [Å]	E_{DLM} [eV]	E_{FM} [eV]	ΔE [eV]
$Zn_{14}Cr_2Se_{16}$	7.96	-29436.83042	-29436.93222	0.1018
$Zn_{30}Cr_2Se_{32}$	9.50	-61067.72531	-61067.73679	0.01148
$Zn_{62}Cr_2Se_{64}$	17.21	-124329.62225	-124329.62264	0.00039
$Zn_{126}Cr_2Se_{128}$	43.17	-250853.38407	-250853.38436	0.00029

Table 2.

The V-V bond lengths and the total energy differences beetween DLM and FM alignments for different ZnSe:V systems using LSDA+U.

System	d_{V-V} [Å]	E_{DLM} [eV]	E_{FM} [eV]	ΔE [eV]
$Zn_{14}V_2Se_{16}$	7.96	-29219.57379	-29219.70519	0.1314
$Zn_{30}V_2Se_{32}$	9.50	-60850.47995	-60850.48887	0.00892
$Zn_{62}V_2Se_{64}$	17.21	-124112.35753	-124112.35800	0.00047
$Zn_{126}V_2Se_{128}$	43.17	-250636.02571	-250635.96228	-0.06343

The value of computed magnetic moment per Cr is found to be 4.028 μ_B (main contribution from Cr *d*-states: 3.193 μ_B) for $Zn_{1-x}Cr_xSe$ system. Insignificant positive contribution to the magnetization of $Zn_{1-x}Cr_xSe$ from 15 Zn atoms (0.195 μ_B) and negative contribution from 16 Se atoms (-0.221 μ_B).

4. CONCLUSION

In order to promote suitable semiconductor materials for spintronics devices, this study aims to evaluate the magnetic properties of the cromium an vanadium-doped wurtzite zinc selenide. Using an accurate DFT-LSDA+U approach, have been explored the spin-polarized electronic and magnetic properties of $Zn_{1-x}Cr_xSe$ and $Zn_{1-x}V_xSe$ for x=12.5 %, 6.25 %, 3.125 %, and 1.5625 %. While the introduction of Cr^{2+} and V^{2+} ions in the doped and co-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 4.0 and 3.0 μ_B for $Zn_{1-x}Cr_xSe$ and $Zn_{1-x}V_xSe$, and the mainly contribution to the magnetization comes mostly from d-states of impurity atoms. Results of the energy differences between the DLM and the FM states for both systems nearly represent a stable FM state. The present of Zn vacancy in ZnSe:Cr and ZnSe:V systems affect the magnetization, where increases or reduces the total magnetic moment of the supercell and behaves half-metallic ferromagnetism, Cr or V based ZnSe seems to be potential candidates for spintronic applications.

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