Half-metallic ferromagnetism in chalcopyrite type compounds ZnMX2 (M=Sc, V, Mn, Fe; X = P, As)

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Half-Metallic Ferromagnetism in Chalcopyrite type Compounds $ZnMX_2$ (M = Sc, V, Mn, Fe; X = P, As)

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Abstract. Electronic structure and magnetic properties of $ZnMX_2$ (M = Sc, V, Mn and Fe; X= As and P) compounds in body centred tetragonal chalcopyrite structure have been investigated using first-principles calculations based on density functional theory (DFT) within the local spin density approximation (LSDA). The spin-polarized electronic band structure and density of states of all these compounds show that the spin-up electrons have metallic and the spin-down electrons have a semiconducting gap and the magnetic moment mainly originates from the strong spin polarization of 3*d* states of transition metal (M = Sc, V, Mn and Fe) atoms and *p*-like states of anion X (P and As) atoms.

Keywords: Half-metallicity, Transition metals, First principles study and Tight-binding linear muffin-tin orbital method
PACS: 31.15.ej, 61.50.Ah, 71.15.Mb, 72.25.Ba, 75.50.Cc.

INTRODUCTION

Half-metallic ferromagnetic (HMF) materials, which show metallic in one spin state and semiconductor in other direction exhibit a complete spin polarization (100%) at the Fermi level (E_F) and have large potential applications in spintronics as spin injection devices [1]. Half metallicity (HM) was first discovered by de Groot *et al* in half-Heusler alloy NiMnSb compound, based on his idea many HMF materials have been predicted theoretically and confirmed experimentally in different types of materials such as zinc-blende compounds, organic-inorganic hybrid compounds, pure organic compounds and transition metal oxides [2, 3]. However these materials need to have high Curie temperature and also good compatibility in structure while subjected to grow on a semiconductor substrate [3].

In 1966, Ohno *et al* observed ferromagnetism in Mn-doped GaAs at a Curie temperature of above 100 K [4]. Since then, transition metal doped semiconductors have been the subject of investigations for spintronics applications. Among the various materials that are being explored for spintronic device applications chalcopyrite structured materials are attractive due to their high Curie temperature, possibility of antiferromagnetism (AFM) and structural similarity with the conventional semiconductors. In this paper, the structural, electronic and magnetic properties of the $ZnMX_2$ (M = Sc, V, Mn, Fe; X = As; P) compounds are investigated using the first-principles calculations. These compounds crystallize in tetragonal body-centered chalcopyrite structure derived from full substitution of the group IV atoms of $ZnGeAs_2$ by transition (Sc, V, Mn and Fe) atoms. It is found that ferromagnetic (FM) state has lower energy than the non-magnetic (NM) state and the calculations show that $ZnVAs_2$ and $ZnMnAs_2$ are HMFs with half metallic gap of 0.013 eV and 0.39 eV and the other compounds exhibit HM property at their expanded volume.

COMPUTATIONAL METHOD AND CRYSTAL STRUCTURE

The ternary $ZnMX_2$ compounds crystallize in the chalcopyrite structure with a tetragonal space group $I\bar{4}2d$ (122), the primitive unit cell contains two formula units (eight atoms) and the atomic positions are Zn 4a (0, 0, 0), M 4b (0, 0, 1/2), X 8c (*u*, 1/4, 1/8) at the Wyckoff's positions respectively. The values of *u* for all the compounds are given in Table 1.

The electronic and magnetic properties of the $ZnMX_2$ compounds have been investigated in both FM and NM states through the first principles calculations using Andersen's tight-binding linear muffin-tin orbital (TB-LMTO) method within the atomic sphere approximation [5].

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The calculations are performed based on the density functional theory (DFT) within the framework of local spin density approximations (LSDA) without spin-orbit coupling. A mesh of 4 x 4 x 4 is taken in the irreducible wedge of Brillouin Zone for the ***k*-**point sampling. Exchange-correlation potential to both atomic and crystalline has been calculated by the von Barth-Hedin scheme.

TABLE 1. The internal parameter (u), equilibrium lattice constant (a), c/a ratio, Bulk modulus (B_0), total energy difference ($\Delta E = E_{NM} - E_{FM}$), partial and total magnetic moments (M), and half-metallic gap (E_{HM}) of $ZnMX_2$ compounds.

Compound	u	a (Å)	c/a ratio	B_0 (GPa)	ΔE (eV)	MZn (μ_B)	MC (μ_B)	MX_2 (μ_B)	M_{tot} (μ_B)	E_{HM} (eV)
$ZnGeAs_2$	0.210 (0.245)	5.867 (5.635)	1.976 (1.960)	64.1 (72.1)						
$ZnScP_2$	0.223	5.840	1.9760	72.6	1.022	0.076	0.243	0.679	0.99	
$ZnVP_2$	0.231	5.375	1.9761	92.7	0.1028	-0.009	1.109	-0.124	0.94	
$ZnMnP_2$	0.241	5.297	1.9759	84.7	0.3563	0.036	2.922	-0.120	2.84	
$ZnFeP_2$	0.216	5.391	1.9212	71.7	0.0294	0.031	2.762	-0.137	2.65	
$ZnScAs_2$	0.223	5.859	1.9754	61.6	0.00037	0.071	0.232	0.628	0.93	
$ZnVAs_2$	0.231	5.574	1.9759	80.9	0.2729	-0.017	1.218	-0.179	1.00	0.031
$ZnMnAs_2$	0.241	5.423	1.9761	71.6	5.906	-0.008	3.61	-0.583	3.00	0.392
$ZnFeAs_2$	0.216	5.591	1.9759	64.9	0.0626	0.049	2.798	-0.145	2.07	

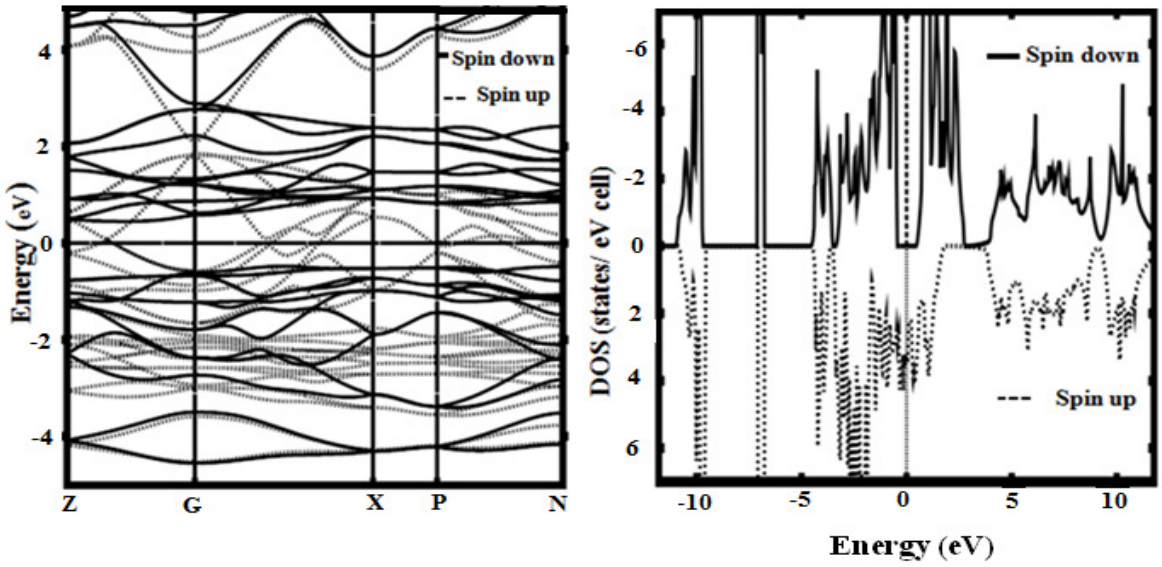

FIGURE 1. The spin-polarized electronic band structure and density of states of $ZnMnAs_2$.

RESULTS AND DISCUSSION

The lattice constant and stability of all the compounds are performed for both spin polarized (FM) and unspin-polarised (NM) states. Since experimental lattice parameter a is not available, at each given volume, the internal parameter u and the c/a ratio, are determined by changing u and c/a to minimum total energy for both FM and NM states. The minimum total energy as a function of relative volume are fitted to Birch equation of states to obtain the ground state properties lattice parameter a and Bulk modulus B_0 [6].

Total energy difference between NM and FM states ($\Delta E = E_{NM} - E_{FM}$) are calculated for all the

compounds, the positive value of ΔE (+ΔE) indicates that the FM state is more favorable than the NM state. The total energy difference ΔE, internal parameter *u*, equilibrium lattice constant *a*, the *c/a* ratio and Bulk modulus B_0 are tabulated in Table 1 for stable FM state along with the available theoretical results of $ZnGeAs_2$ [7].

The $ZnMX_2$ (M = Sc, V, Mn, Fe; X = P, As) compounds in chalcopyrite structure show metallic nature from unspin-polarized electronic band structure calculations. In order to determine the magnetic property, spin-polarized band structure, total and partial densities of states (DOS) are performed for all the compounds. From spin-polarized calculations the exhibition of FM state can be seen from the exchange spin-splitting of energy states around the Fermi level. Also it has been observed that for $ZnVAs_2$ and $ZnMnAs_2$ compounds, there is an energy gap around the Fermi level in the majority-spin (spin-down) channel while the minority-spin (spin-up) channel is strongly metallic which confirms the existence of HMF nature with 100% spin-polarization around the Fermi level. The calculated majority spin-gap ($E_{g\uparrow}$) and non-zero value of HM gap (E_{HM}) reveal the existence of true HMF nature. For illustration, band structure and DOS of $ZnMnAs_2$ is shown in Fig. 1. From the band structure diagram, the spin-down channel show semiconducting nature with an indirect band gap of 1.025 eV and there is a small gap (HM) of 0.392 eV for spin-flip excitations from the bottom of conduction band to the Fermi level at equilibrium volume. The calculated total magnetic moment of $ZnMnAs_2$ is 3 μ_B/f.u. An integer magnetic moment is a characteristic feature of HMFs.

From the DOS and partial density of states, it is observed that the states near the Fermi level are due to the hybridization between Mn- 3*d* states and nearest neighbouring anion As 4*p*-like states with small contribution of Zn *4s*-like states. Since, Mn atom donates 4 electrons to saturate the bonding and occupies 4+ sites. Then the remaining unpaired 3*d* electrons are responsible for the integer magnetic moment of 3 μ_B/f.u. in spin-down states. The calculated magnetic moments of Zn, Mn and As are -0.008, 3.61 and -0.583 μ_B respectively. Zn and As atoms have induced spin magnetic moments antiparallel with the spin magnetic moments of Mn atoms. Similar property is observed for $ZnVAs_2$ compound with an integer magnetic moment of 1 μ_B/f.u. and a HM gap of 0.031eV. The total and partial magnetic moments of all the compounds with half metallic gap at their optimized equilibrium lattice constant are given in Table 1. Whereas, in other compounds $ZnMX_2$ (M = Sc, V, Mn, Fe; X = P, As) the valence state electrons crosses the E_F for both the spin states reveals metallic behavior at equilibrium lattice constant however exhibits HMFs at their expanded volume

CONCLUSION

To summarize, structural, electronic and magnetic properties of $ZnMX_2$ compounds (M = Sc, V, Mn, Fe; X = P, As) in body centered tetragonal chalcopyrite structure have been investigated using first-principles calculations within LSDA. From the calculations it is observed that the FM state is stable than NM state from minimum total energy calculations at their equilibrium condition. The spin-polarized band structure calculations show that these compounds exhibits stable half-metallic ferromagnetism and calculated magnetic moment of $ZnVAs_2$ and $ZnMnAs_2$ are 1μ_B and 3μ_B/f.u. with the HM gaps 0.031 eV and 0.392 eV and it mainly originates from hybridization of M-3*d* states and X-*p* like states.

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