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**First principle calculations on structural, electronic and magnetic properties of
CdMAs₂ (M = Sc, Ti, V) chalcopyrites**

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Abstract

Structural, electronic and magnetic properties of ternary CdMAs₂ (M = Sc, Ti and V) compounds in the chalcopyrite structure have been studied using full-potential linearized augmented plane wave method (FPLAPW) based on density functional theory (DFT). We present a detailed study of electronic band structure, density of states and magnetic moment of all the three compounds within local spin density approximation (LDA) and generalized gradient approximation (GGA). CdMAs₂ compounds are derived from chalcopyrite structured CdGeAs₂ with the substitution of transition metal (TM) atoms at Ge site. Negative values of formation energy signify that these materials are stable in chalcopyrite structure. Spin-polarized calculations show that the substitution of TM atoms at the group IV site influences the appearance of ferromagnetic state (FM) in CdScAs₂ and CdVAs₂ compounds. FM in CdScAs₂ and CdVAs₂ compounds is mainly due to the strong spin polarization of 3d- states of M cations and 4p- states of As anion. CdVAs₂ also exhibit half metallic ferromagnetism (HMF) with an integer magnetic moment of 1.00 μ_B per formula unit. However, there is no effective spin-polarization of energy states at the Fermi level in CdTiAs₂ compound and shows a non-magnetic behaviour.

Keywords: First principles calculation, half-metallic ferromagnetism, heat of formation, Chalcopyrite crystals

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1. Introduction

Half-metallic ferromagnetic (HMF) materials with Curie temperature (T_C) above room temperature have attracted considerable research interest in spin-electronic devices due to the exhibition of 100 % spin-polarization around the Fermi level (E_F) in any one of the spin channel [1, 2]. So far in the literature, density functional theoretical (DFT) calculations on zinc blende (ZB) structured Ti-doped ZnS [3], Mn doped at the cation site of MnInAs and GaMnAs [4], V-doped BeX (X = S, Se, Te) [5], CrX (X = S, Se, Te) [6, 7], $Mg_{1-x}V_xY$ (Y = Se, Te) for $x = 0.25, 0.50, 0.75$ and 1.00 [8] and Sc, Ti, V, Mn and Cr-doped Wurtzite CdS [9] are found to exhibit HMF character. The appearance of half-metallic nature in the above said systems are due to the substitution of transition metal (TM) ions and small local magnetic moments are induced on the nonmagnetic ions with T_C up to 200 K [4, 10]. These materials have received greater attention in spintronic applications [1, 4, 9]. Since the T_C of above mentioned compounds does not exceed 200 K, [4] the use of III-V type magnetic semiconductors for practical applications is tedious nowadays. In general, for practical applications in spin based solid-state devices, materials that exhibit room temperature ferromagnetism (FM) are more preferred. Therefore, the exploration of materials that exhibit high carrier solubility with high T_C is needed.

Ternary II-IV- V_2 type semiconductors generally crystallize in the body-centered tetragonal chalcopyrite structure with the space group I-42d which can also be obtained by replacing group III and group V elements with group II and group IV elements column wise in III-V semiconducting compounds [11-14]. These materials are promising candidates for many technological applications like electronic, optical and magnetic properties. The possibility of using II-IV- V_2 materials in spintronics is due to replacing a small fraction of constituent atoms with TM ions such as Cr or Mn which leads to the strong spin splitting of energy levels around E_F due to *sp-d* exchange interaction with relatively high Curie temperatures [11, 12, 14-16]. The appearance of HMF depends on the concentration of magnetic ions and temperature. From the earlier experimental results, [17] the observation of room temperature FM with $T_C = 320$ K in Mn doped CdGeP₂ is mainly due to much high carrier solubility of Mn atom in CdGeP₂. Mn^{2+} can easily occupy the divalent Cd site without any sacrifice of electrical neutrality. However from band structure calculations the antiferromagnetic (AFM) phase is favored rather than FM phase due to higher concentration of Mn at the Cd site of $Cd_{1-x}Mn_xGeP_2$. First-principles calculation on V-doped MgSiN₂ at Si and Mg sites show more stable FM state than AFM [18]. From ab-initio calculations,

Mahadevan and Zunger (2004) proved that the stable FM state can be achieved with $T_c = 355$ K with the substitution of Mn at the Ge site in CdGeP_2 forming holes and it is also easy to fabricate experimentally by molecular beam epitaxial method. Also these materials have high carrier concentration (accepting higher concentration) for TM atoms with the appearance of stable FM when TM atoms are substituted at the cation sites rather the binary III-V semiconductors [14, 15]. Thus, instead of TM doped III-V and II-IV dilute magnetic semiconductors with low solubility of magnetic ions, the TM doped or replaced chalcopyrite (II-IV-V₂) semiconductors [14-17] attract attention in the recent research field of spintronics due to the appearance of ferromagnetism above room temperature

On considering the theoretical predictions and experimental synthesis of MnGeP_2 and MnGeAs_2 materials in the chalcopyrite structure exhibiting room temperature FM with $T_c = 320$ K and 340 K respectively [11] and other theoretical predictions [19-21], here we report the results of CdMAs_2 ($M = \text{Sc, Ti and V}$) compounds in the chalcopyrite phase by replacing the Ge atom by M atoms systematically in CdGeAs_2 . Since, TM impurities introduce deep levels in the band gap of the semiconductor as a result attractive electronic and magnetic properties occur in these chalcopyrites. For the investigation purpose, we used FP-LAPW method with two different correlation functional, namely LSDA and GGA.

2. Method of calculation and crystal structure

2.1 Computation details

First principle calculations have been carried by FP-LAPW method as implemented in WIEN2k code [25-27] to calculate the structural, electronic and magnetic properties of CdMAs_2 compounds. LSDA given by J.P. Perdew, Y. Wang and GGA by Perdew et al (1996) are used [28, 29]. In this method a muffin-tin type of potential is applied to the crystal potential, where the crystal potential is assumed to be spherically symmetric within the muffin-tin sphere and constant in the interstitial region. The core electrons in the atomic sphere region are treated fully relativistically and self consistently in the spherical approximation and the valence electrons in the interstitial region are treated self consistently in the semi-relativistic approximation. The crystal potential, electronic wave functions, charge density are expanded with spherical harmonics inside the atomic sphere region expanding upto $l_{max} = 10$ and in interstitial region a plane wave Fourier series is used with a cut-off of $K_{max} = 7.0$ / RMT. The atomic sphere radii chosen are 2.12, 2.18, 2.23, 2.24 and 2.09 for Cd, Sc, Ti, V and As respectively. The charge density is Fourier expanded upto $G_{max} = 12$. From the relaxed geometry the electronic structure, electronic charge density and the

magnetic properties can be determined. We used a $\mathbf{k}$ mesh of $8 \times 8 \times 4$ for $\mathbf{k}$ -points integration in the irreducible wedge of the Brillouin zone. The total energy convergence of crystal's to a value of less than 0.01 mRy is achieved by the method of iteration.

2.2. Chalcopyrite Crystal structure

CdGeAs₂ semiconductor crystallize in chalcopyrite structure with body-centred tetragonal lattice (space group I-42d) [30, 31] and the Wyckoff's positions of the atoms are Cd = $4a$ (0, 0, 0), Ge = $4b$ (0, 0, 1/2) and As = $8d$ (u , 1/4, 1/8) with two molecules per unit cell. Ternary CdMAs₂ (M = Sc, Ti and V) belongs to II–IV–V₂ type semiconductor which are obtained by replacing Ge in CdGeAs₂ with $3d$ TM elements Sc, Ti and V. Since, the ionic, [31] atomic radii and electronegativities of M (Sc, Ti and V) are comparable to Ge, the same chalcopyrite crystal structure is retained for all CdMAs₂ compounds. In the crystal structure (Fig. 1) each As anion is coordinated with two Cd and two M/Ge cations, whereas each cation is tetrahedrally coordinated by four As anions and the anions are slightly displaced from their ideal tetrahedral site. The unit cell is tetragonally distorted with $\eta = c/2a = 1$. This tetragonal distortion can be characterized by the internal parameter u (anion displacement) leading to two unequal anion–cation bond lengths, which means the anions are closer to one pair of cations than to the other.

3. Results and discussion

3.1. Structural properties

3.1.1. Energy volume curve

CdMAs₂ compounds crystallize in the hypothetical chalcopyrite structure (body centered tetragonal phase) with the space group no 122 (I-42d). The complete crystal structure can be described using three lattice parameters: the unit cell lattice parameters a and c and one internal parameter u . Full structural optimization has been carried for all the three compounds in both LDA and GGA approximations and the calculated total energy as a function of lattice parameter is shown in Fig. 2. The optimized lattice parameters a , c and internal parameter u values (corresponding to the position of free energy minimum) of the unit cell of all the compounds are listed in Table 1 with other available results [29,30].

From the Fig. 2 it is observed that CdVAs₂ occurring the phase transition from FM to NM at the volume 1199.5890. However for CdScAs₂ and CdTiAs₂ we did not get any phase change. FM phase has lower total energy when compared to the NM phase and the calculated total energy difference ΔE ($\Delta E = E_{\text{NM}} - E_{\text{FM}}$) between the NM and FM phase is positive. It

signifies that the FM state is more stable than the NM state for CdScAs₂ and CdVAs₂ compounds which is given in **Table 1**. The calculated total energy difference ΔE between NM and FM phase is negative (**Table 1**) indicating that this compound is NM. Then the total energy volume relation is fitted to the Birch-Murnaghan's equation of state [32] to obtain the equilibrium lattice constant (a , c) and bulk modulus B_0 listed in **Table 1** along with other structural parameters. From **Table 1** it is observed that the anion displacement or internal parameter u varies from 0.265 to 0.306 and c/a ratio ranging from 1.87 ~ 2.00 leads to the small tetragonal distortion from the ideal ZB structure. It is clear from the table that the calculated structural parameters of CdGeAs₂ are in good agreement with other experimental and theoretical data [29,30]. By replacing the TM atoms in the host compound (CdGeAs₂) there is a decrease or increase in lattice parameters and the corresponding bulk moduli may increase or decrease.

3.1.2. Bond length

The anion-cation $R_{\text{Cd-As}}$ and $R_{\text{M-As}}$ bond lengths are calculated using the relations (1) and (2), and are given in **Table 1**.

$$R_{\text{Cd-As}} = a \left[u^2 + \frac{(1+\eta^2)}{16} \right]^{1/2} \quad (1)$$

$$R_{\text{M-As}} = a \left[\left(u - \frac{1}{2} \right)^2 + \frac{(1+\eta^2)}{16} \right]^{1/2} \quad (2)$$

The calculated bond lengths are shorter within GGA when compared to LDA scheme. Shorter bond length enhances the stiffness between the Cd, TM and As atoms and it increases the density of electrons in the valence region. For better understanding of the behaviour of electrons in the valence region, band structure, density of states and electron charge density of these compounds are computed.

3.1.3 Heat of formation

The heat of formation (ΔH) for all CdMAs₂ compounds is calculated using the expression.

$$\Delta H = \frac{1}{a+b+c} \left[E_{\text{Total}}^{\text{CdMAs}_2} - aE_{\text{Solid}}^{\text{Cd}} - bE_{\text{Solid}}^{\text{M}} - c2E_{\text{Solid}}^{\text{As}_2} \right] \quad (3)$$

where, $E_{tot}^{CdMAS_2}$ is the total energy of CdMAS₂ per molecule. CdE_{tot}^{Cd} , ME_{tot}^M and AsE_{tot}^{As} are the total energies of the constituent atoms in their respective ground state structures. The calculated heat of formation values are given in **Table 1** and are found to be negative and both the LSDA and GGA approximations indicates that all the compounds will be thermodynamically stable in the chalcopyrite structure.

3.2. Electronic properties

3.2.1 Electronic band structure

Electronic band structures of CdGeAs₂ and CdMAS₂ compounds are computed along the high symmetry directions of the first Brillouin zone at their equilibrium volume within LSDA and GGA approximations. CdGeAs₂ is found to be semiconducting with a band gap of 0.192 eV and 0.32 eV within LSDA and GGA scheme. The overall band structure profile is similar for all CdMAS₂ compounds in both the approximations, for illustration, the electronic band structures of CdMAS₂ (M = Sc, Ti, V) compounds under GGA-PBE approximation is shown in **Fig. 3**. The substitution of M (Sc, Ti, V) atoms at the Ge site of CdGeAs₂ semiconductor introduces *d*- states of M atoms at the E_F and these *d*- states split into '*t_{2g}*' and '*e_g*' as a result of crystal field resonance.

From the band structure of CdScAs₂ and CdVAs₂ we can notice that there is an effective spin-polarization of energy states around the E_F. The valence band maximum (VBM) is due to the hybridization of *d* (*t_{2g}*) states of cations (M) with anion (As) *-p* states forming *p-d* hybridized orbitals which leads to the high concentration of acceptor energy levels around the E_F. Band gap disappeared in CdScAs₂ and CdVAs₂ is due to the coupling and repulsion of magnetic *-3d* (*t_{2g}* and *e_g*) states of TM atoms and As *-4p* states in the VBM. However, in the case of CdTiAs₂ the valence band is well localized and the valence band maximum lies below the E_F. There is no spin polarization of energy states around the E_F and the compound is a non magnetic semiconductor with a band gap of 0.63 eV and 0.76 eV within GGA and LSDA scheme. In CdScAs₂, valence bands cross the E_F in both the spin-up (majority spin) and spin-down (minority spin) channels making it metallic. Whereas, in the case of CdVAs₂ the valence energy bands crosses the E_F in the spin-up channel and the energy bands are localized well below the E_F in the spin-down channel (i.e.) Top of the valence band are situated at Σ point and bottom of the conduction band fall at the Γ point resulting in an indirect band gap in the spin-down channel leads to the appearance of HMF in this compound. Half-metallic and spin-splitting gaps are listed in **Table. 2**.

3.2.2 Total and partial density of states

Total and partial density of states (PDOS) for CdMAs₂ (M = Sc, Ti and V) obtained using GGA-PBE are presented in Fig. 4. A common observation from the DOS and PDOS for CdScAs₂ and CdVAs₂ is, that the valence states of Cd *s*-, M (Sc and V)- *e_g*, *t_{2g}* and As *p*- are well hybridized and crosses the *E_F* in the majority spin channel whereas in the minority spin channel the behavior of valence states are different.

In Fig. 4 for the CdScAs₂ the spin-polarized states near the *E_F* is associated with Sc 3*d*- (*t_{2g}* and *e_g*) like states and 4*p*- like states of As anion with very small contribution of Cd *s*- like states and crosses the *E_F* exhibiting metallic nature in minority spin channel also. While in CdVAs₂ the *e_g* orbitals are well-localized since they are much lower in energy than the *t_{2g}* orbitals these states contributes to the occupied states, whereas the *t_{2g}* orbitals are strongly hybridized with the nearest-neighbour tetrahedrally coordinated As -4*p* states due to the strong electronegativity of As ion. The *t_{2g}* bonding state is located well inside the valence band leads to the appearance of indirect band gap at the bottom of the conduction band signifies the exhibition of HMF in CdVAs₂ compound. This strong *p*-*d* exchange coupling between band carriers and localized spins leads to the appearance of HMF. Thus the *p*-*d* electrons of As and V play the dominant role in the formation of the gap between valence and conduction band. The contribution of Cd -*s* states is very small near the *E_F*. Thus the spin polarization of energy states around the *E_F* and positive value of ΔE signifies the exhibition of stable FM in CdScAs₂ and CdVAs₂ compounds [22, 23]. Analysis of total and partial DOS of CdTiAs₂, shows that the top of the valence band is mostly contributed by As 4*p*-, *t_{2g}* of 3*d*- Ti and small contribution of Cd *s*- states, while the bottom of the conduction band is by both Ti 3*d*- states with Cd *s*- states. In this case the density is equally contributed by Cd, Ti and As in both the spin channels (i.e.) almost zero density of electrons at the Fermi level show that this is a nonmagnetic semiconducting material.

3.3 Magnetic properties

3.3.1 Total magnetic moment

The calculated total and local magnetic moments of the individual atoms and muffin tin spheres in the interstitial region of CdMAs₂ within LSDA and GGA are given in Table. 2. The results show that the total magnetic moments mainly originated from the unfilled 3*d*-states of M atoms. The total magnetic moments of the M atoms get reduced by the *p*-*d* hybridization from its free space charge value and it creates small local magnetic moments on the non-magnetic Cd and As sites. Thus the nature of interaction in these materials can be

described by the $sp-d$ exchange splitting. Since, the Sc has one unpaired $3d$ - electron the magnetic moment of Sc gets reduced in CdScAs_2 due to hybridization of tetragonally coordinated Sc $3d$ - and nearest neighbour As $4p$ - states it cannot create integer magnetic moment. In CdVAs_2 , V donates, four of its valence electrons to the majority spin band for the bond formation and the remaining one unpaired d electron is responsible for the total magnetic moment of $1.00 \mu_B$ in CdVAs_2 compound (Table 2). The integer value of the total magnetic moment is one of the significant feature of the half-metallic nature. However in CdTiAs_2 there is no spin polarization resulting in zero magnetic moment (Table 2) and this is due to absence of magnetic moment on each atomic site. Spin magnetic moments generated by As atom has negative magnetic moments indicating that they are anti-parallel to the spin magnetic moments of M atoms.

3.2.2 Charge densities

Here, we compare the chemical bond nature and the appearance of ferromagnetism in all CdMAs_2 ($M = \text{Sc, Ti, V}$) compounds from the charge density contour plots which are shown in Fig. 5 for both spin up and spin down states along the (110) plane. These plots show the charge transfer of valence electrons from As to Cd and As to M ions. Mixtures of ionic and covalent characters are present for Cd-As and M-As atomic bonds in both the spin channels for all the compounds. The electronic charge distribution is spherical around As atom shows that majority of charge is accumulated around As atom resulting in the formation of Cd-As and M-As bonds.

In CdScAs_2 the As ion moves towards Cd due to higher electronegativity difference between them, leads to the strong ionic character for Cd-As bond. Whereas for CdVAs_2 the charge transfer between V and As ions is larger, show that the As ion moves towards V cation due to the strong $p-d$ exchange interaction of V (d) and As (p) states lead to the high degree of covalence nature between As and M. From this, it could be inferred that the HMF in CdVA_2 compound is due to the high degree of covalence nature and its absence in CdScAs_2 due to decrease in covalence. The Cd-As and Ti-As bonds are almost same in CdTiAs_2 shows the presence of mixed ionic/covalent bond in this compound.

4. Conclusion

In summary, the electronic and magnetic properties of CdMAs_2 ($M = \text{Sc, Ti and V}$) compounds in the chalcopyrite structure were calculated from first principles calculations within LSDA and GGA scheme. Ground state properties are calculated from the energy-

volume relation. The structural parameters of CdGeAs_2 are in good agreement with other experimental and theoretical data and for CdMAS_2 compounds no other experimental or theoretically calculated data are available to compare. FM is achieved in CdScAs_2 and CdVAs_2 by the substitution of M atoms at group IV (Ge) position in CdGeAs_2 and it originates mainly from the hybridization of M $-3d$ (t_{2g}) and As $-4p$ like states. Also CdVAs_2 exhibit HMF property with an integer magnetic moment of $1.00 \mu_B$ per formula unit. Formation energies are negative shows that these compounds are energetically preferable when M (Sc and V) occupies the group IV (Ge) position in CdGeAs_2 . Thus the CdScAs_2 and CdVAs_2 semiconducting materials may be useful for the practical applications when they fit into the silicon or other semiconducting lattice.

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Figure Captions

Fig. 1. The unit cell of chalcopyrite crystal structure of $\text{Cd}(\text{Ge}/\text{M})\text{As}_2$

Fig. 2. Total energy (Ry) / f.u. as a function of Volume ($\text{\AA}^3$) plots for nonmagnetic (NM) and ferromagnetic (FM) phases of CdMAs_2 ($\text{M} = \text{Sc}, \text{Ti}$ and V) compounds using GGA - PBE scheme.

Fig. 3. The spin polarized electronic band structure of CdMAs_2 ($\text{M} = \text{Sc}, \text{Ti}$ and V) compounds for majority and minority spin using GGA - PBE scheme.

Fig. 4. Spin dependent total and partial density of states of CdMAs_2 ($\text{M} = \text{Sc}, \text{Ti}$ and V) at its equilibrium lattice constant using GGA - PBE scheme.

Fig. 5. Total valence electron charge density contour plots in the (110) plane for CdMAs_2 ($\text{M} = \text{Sc}, \text{Ti}$ and V) compounds using GGA - PBE scheme.

Figure 1.

Only

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Table captions

Table 1 Calculated equilibrium lattice constants (a), (c) Å, tetragonal ratio (c/a), internal parameter (u), bulk modulus (B_0) GPa for ferromagnetic (FM) phase, total energy difference ($\Delta E = E_{\text{NM}} - E_{\text{FM}}$) in eV, Heat of formation (ΔH) in eV and bond length in Å of CdMAS₂ (M = Sc, Ti and V)

Table 2 Total and local magnetic moments in μ_B , half-metallic gap (E_{HM}) in eV and minority spin gap (E_{gl}) in eV for CdMAS₂ (M = Sc, V) compounds

Compounds			u	a	c	B ₀	ΔE	ΔH	Bond length	
									Cd-As	M-As
CdGeAs ₂	LSDA	Present	0.274	5.94	10.94	66.93		-3.214	2.31	2.33
		others	0.265 ^a	5.91 ^a	11.32 ^a	57.03 ^a				
	GGA	Present	0.275	6.19	11.69			-5.337	2.31	2.36
		others	0.265 ^a	5.94 ^a	11.23 ^a					
CdScAs ₂				5.95 ^b	11.21 ^b	69.71 ^b				
	LSDA		0.252	6.04	12.70	58.37	1.10	-2.874	2.36	2.23
	GGA		0.250	6.24	10.99	48.15	0.91	-3.989	2.21	2.07
CdTiAs ₂	LSDA		0.278	5.76	11.68	71.16		-2.940	2.31	2.26
	GGA		0.277	6.08	11.48	60.22		-4.061	2.23	2.12
	LSDA		0.306	5.75	11.83	86.35	1.64	-2.826	2.67	2.33
CdVAs ₂	GGA		0.305	5.76	11.87	60.03	1.95	-3.948	2.31	2.23

^aRef. [28]; ^bRef. [29]

		Cd	M	As	Int	Total	E _{HM}	E _{gl}
CdScAs ₂	LSDA	0.000	0.0196	0.0007	0.0051	0.312	-	-
	GGA	0.017	0.03510	0.0707	0.4275	0.816		
CdTiAs ₂	LSDA	-0.001	0.004	-0.003	-0.0001	0		
	GGA	-0.003	-0.002	0.005	0.00001	0		
	GGA	0.039	0.0755	0.1458	0.8518	0.884	-	-
CdVAs ₂	LSDA	0.006	0.8958	-0.0458	0.3240	1.00	0.851	0.103
	GGA	0.006	1.1705	-0.1076	0.1576	1.00	1.089	0.501

For Review Only