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ORIGINAL ARTICLE

Robust Half-Metallic Character In KMnGe Half-Heusler Compound

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ABSTRACT – The search for spin injectors and spin sources in spintronic devices is a significant facet of materials research today. Consequently, half-Heusler (HAH) KMnGe alloy has been recommended as one such admissible materials. Herein, a rigorous examination of the structural, magnetic and electronic properties of HAH KMnGe alloy is done using ab initio method within the bolstered up rendition of the functional by Perdew and his group. Our result shows that HAH KmnGe alloy expresses type-1 and type-2 HAH structural ground state at high and low pressures respectively, which may pose a challenge in application. Impressively, HAH KMnGe alloy exhibits half metallic characteristic with an indirect energy gap in the Γ-X symmetry k-point and direct band gap at X-point in the minority electronic spin states for type-1 and type-2 phase respectively. Our findings agree fundamentally with some previous findings in the literature and suggests that the HAH KMnGe alloy is a credible excellent spin source in future spintronic devices.

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INTRODUCTION

The class of compounds termed Half-Heusler (HAH) compounds with formula XYZ, have become very attractive in the literature as future spintronic materials. This category of materials was first identified by de Groot and his collaborators in the year 1903 [1]. These materials have been demonstrated to have potential applications in opto-electronic, thermoelectric and spintronics devices. The atoms occupy the positions 4a (0, 0, 0), 4b (1/2, 1/2 , 1/2) and 4c (1/4 , 1/4 , 1/4) leaving the 4d (3/4 , 3/4 , 3/4) vacant in the half-Heusler compound. Three possible atomic conformations usually categorized to as type-1 sub-structure, type-2 sub-structure and type-3 sub-structure are in 4b, 4c, 4a; 4b, 4a, 4c; 4c, 4b, 4a respective positions [2,3]. The X atom could be S-metal or heavier transition metal; Y is a lanthanide or relatively lighter transition metal while Z is a late main-group element. Half-Heusler compounds present enormous opportunities since their properties differ systematically with their valences as prescribed by the periodic table often called valence electron content (VEC) [4].

Some of the previous results which appear promising includes the first principles research on the electronic and magnetic properties of the HAH CNaCa alloy and SiNaCa alloy by Wei and his collaborators [5] who employed the full-potential local-orbital minimum-basis method. It was divulged from their investigations that both alloys are half metals with 1.00 μ_B as the total magnetic moment per formula unit (pfu). In another research work, Abada et al. [6] determined the electronic structure along with the magnetic properties of HAH MgCaB alloy and characterized the alloy as stable, ductile and robustly half metallic with 1.00 μ_B pfu as the total magnetic moment. Umamaheswari and his collaborators [7] again examined the structural arrangements, electronic structure and magnetic ground state properties of HAH LiCaC and HAH NaCaC alloys adopting the local density approximation. Their result presented these alloys as half-metals with electronic energy gap of 2.27 eV and 2.0 eV in the majority spin of HAH LiCaC and HAH NaCaC alloys respectively, each with magnetic moment of 1.00 μ_B pfu.

The structural, electronic structure along with the magnetic properties of some other non *d* elements HAH alloys were investigated by adopting the first principles method but with different approaches. For example, Zhao et al. [8] investigated HAH LiXGe (X = Ca, Sr and Ba) compounds, Mishra, et al. [9] examined HAH LiNaN, LiKN and LiRbN alloys, Shakil et al. [10] investigated HAH KMnZ (Z=B, Si, Ge, As) . Their results indicate that these compounds exhibit half metallic character with a total magnetic moment of 1.00 μ_B pfu. On the other hand, some HAH alloys involving the d orbitals were studied. These include LiMnZ (Z=N,P,Si) HAHalloy investigated by Damewood, et al. [11] and HAH NaZrP, NaZrAs and NaZrSb studied by Moradi, et al. [12] in which LiMnSi, NaZrP, NaZrAs and NaZrSb exhibited half-metallic character with relatively high Curie temperature. Heusler compounds with 3d and 4d elements have also been studied [13-15].

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Despite the report by Shakil and his group [10], the ground state structural properties of HAH KmnGe alloy is still a controversial issue as different approaches appear to give different results. Moreover there has not been any comparative studies on the phase diagram and electronic properties of the high pressure and low pressure structural phases. In the present study, the structural, magnetic and electronic properties of the half-Heusler KMnGe alloy for the stable structural phases have been examined using the augmented version of the exchange correlation of Perdew-Burke-ernzerhof and the results have been compared with existing published reports.

THEORETICAL METHODS

Hohenberg and Kohn Density functional theory of 1964 [16] was adopted in a spin polarized calculations in this work. The augmented version of the exchange correlation of Perdew-Burke-ernzerhof (PBEsol) [17] was employed. The Kohn-Sham equation (Eqn.(1)) [18],

$$[-\frac{1}{2}\nabla^2+V_{ext}+V_H(r)+V_{xc}(r)]\phi_i(r)=\epsilon_i\phi_i(r) \quad (1)$$

was solved using the variational principle. In the Kohn-Sham equation, $-\frac{1}{2}\nabla^2$ is the quantum kinetic energy of the electrons, V_{ext} connotes the external potential created by the ions, $V_H(r)$ is the Hartree potential given by

$$V_H(r)=\int d^3r'\frac{\rho(r')}{|r-r'|}. \quad (2)$$

$V_{xc}(r)$ connotes the exchange-correlation potential expressed as

$$V_{xc}(r)=\frac{\delta E_{xc}[\rho(r)]}{\delta\rho(r)}, \quad (3)$$

where,

$$E_{xc}^{GGA}[\rho(r)]=\int d^3rf[\rho(r),\nabla\rho(r)]=E_x^{GGA}[\rho(r)]+E_c^{GGA}[\rho(r)] \quad (4)$$

ϵ_i is the energy eigenvalue and ϕ_i is the Kohn-Sham orbital.

The Quantum-Espresso program package [19] with plane wave basis sets was used in the calculations. Kinetic energy as well as augmented charge density cutoff of 60 Ry and 600 Ry respectively were used. At this kinetic energy cutoff, the total energy of the HAH system was converged to about 1 mRy/atom. K 3s, ,4s, 3p; Mn 3s, 4s, 3p, 3d; Ge 4s, 4p, 4d were engaged as valence orbitals. Scalar relativistic ultrasoft pseudopotentials [20] were selected for the description of the interaction of the ions with valence electrons. Sampling of k-points in the Brillouin zone was done with 12 x 12 x 12 grid with Monkhorst-Pack scheme [21]. Total energy convergence of 0.0001 Ry and Hellmann-Feynman forces 0.001Ry/au was used in the geometry optimization. . Total energy calculations was used to determine the structural ground phase of the HAH KMnGe alloy. Using the optimized geometric structure, the magnetic properties as well as the electronic properties of HAH KMnGe alloy was examined using the primitive unit cell containing one K, one Mn and one Ge atoms (see Figure 1) in both type-1 and type-2 phases.

RESULT AND DISCUSSION

Structural Properties

Crystal structures of type-1 and type-2 phases of KmnGe are shown in Figure 1. Total energy calculations were done and compared for the three possible structural phases as presented in Figure 2. The result shows that type-1 has the lowest energy (stable phase) at high pressure while type-2 has the lowest energy (stable phase)at low pressure. Type-3-phase is unstable with respect to the other two phases since it has highest energy both at high and low pressures. The lattice constants of the type-1 and type-2 phases are presented in Table 1. It is observed that the lattice constant of type-1 phase is lower than type-2 phase indicating that type-1 is the high pressure phase while type-2 is the low pressure phase. Our findings propose that this alloy possibly dangles easily between the high pressure and low pressure phase with variations in experimental conditions.

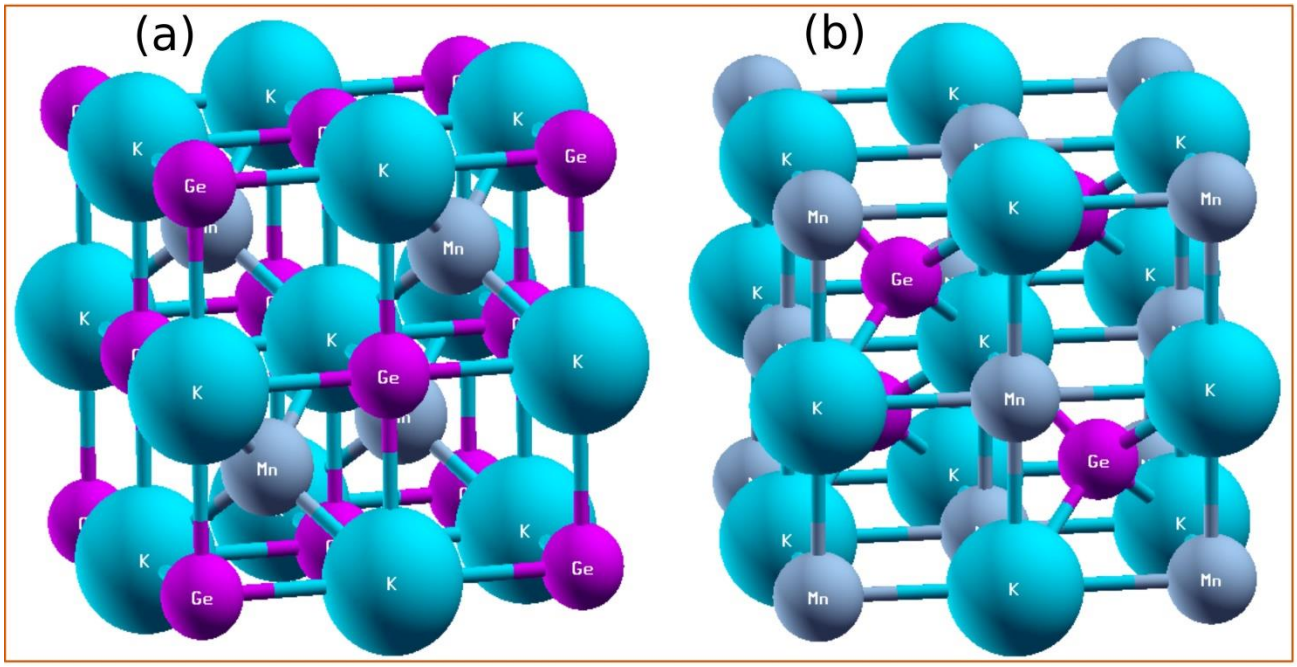

Figure 1: Crystal structure of HAH KMnGe in the (a) type-1 structural phase and (b) type-2 structural phase. The turquoise colour denote the K atoms, grey colour denote the Mn atoms while the violet colour denote the Ge atoms.

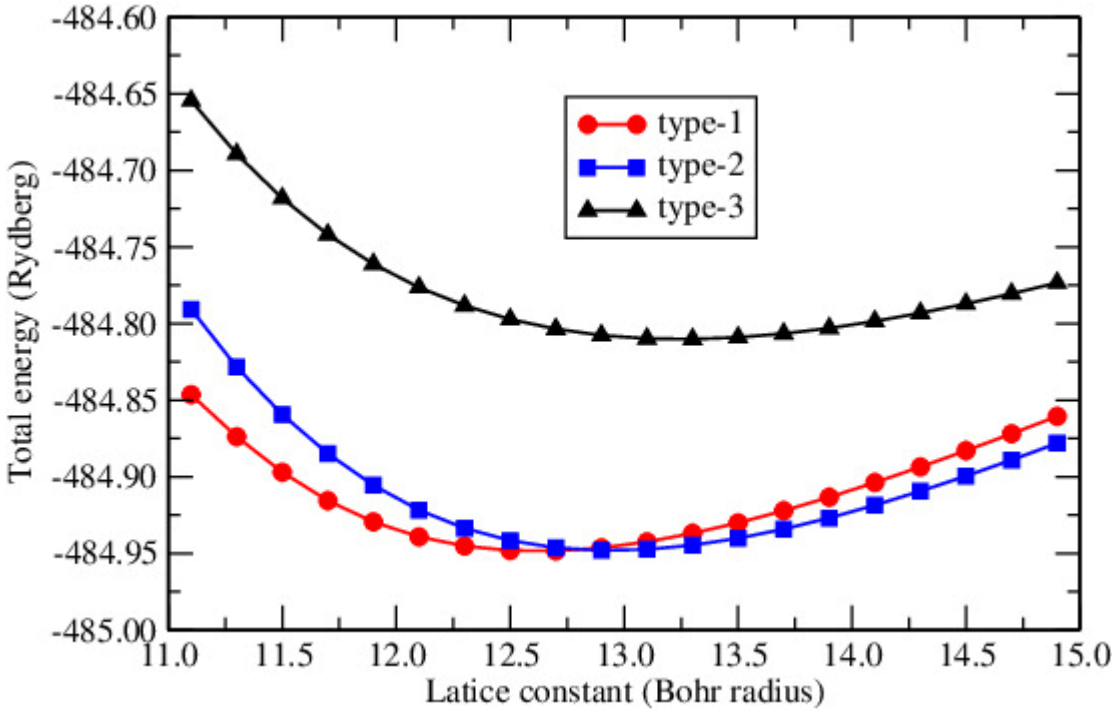

Figure 2: Dependence of total energy on the lattice constant for type-1, type-2 and type-3 structural phases of the HAH KMnGe alloy.

Magnetic Properties

The magnetic properties of the HAH KMnGe alloy are presented in Table 1. The result shows that the significant part of the total magnetic moment is contributed by the Mn atoms while contributions from K and Ge are marginal. Our result also indicate that the K atoms are coupled ferromagnetically to the Mn atoms while the Ge atoms on the other hand are coupled antiferromagnetically to the Mn atoms. The ferromagnetism in the HAH KMnGe alloy comes largely from this ferromagnetic coupling between the Mn atoms through the conduction electrons originating from the K and Ge atoms. The total magnetic moment of 3.9591 μ_B for HAH KMnGe alloy is in agreement with the prediction of the Slater-Pauling rule given as M_{tot}=VEC-8 for HAH compounds with combination of d^0 and 3*d* elements, where VEC is the valence electron content of the HAH compound. The total magnetic moment obtained from our calculations is also in agreement with the value of 4.0078 μ_B reported by Shakil et al. [10].

Table 1: The lattice constant, magnetic moments and minority band gap of of HAH KMnGe alloy. The bulk modulus (*B*), local atomic magnetic moment of the K atom (M_K), local atomic magnetic moment of the Mn atom (M_{Mn}), local atomic magnetic moment of the Ge atom (M_{Ge}), total magnetic moment (M_{tot}) and energy gap in the minority spin (E_g) in the alloy are denoted accordingly.

	a (Å)	M_K (μ_B)	M_{Mn} (μ_B)	M_{Ge} (μ_B)	M_{tot} (μ_B)	*B* (GPa)	E_g (eV)	Reference
Type-1	6.68	0.0502	4.3895	-0.4806	3.9591	27.9	0.9	Present study
	6.82	-0.0183	4.2972	-0.3399	4.0078	27.2	1.0	Shakil (2021)
Type-2	6.87	0.0306	4.5671	-0.6522	3.9455	27.1	0.9	Present study
	6.98					26.4		Shakil (2021)

Electronic Properties

The electronic structure of HAH KMnGe alloy has been calculated and presented, adopting the spin polarized electronic band structure and electronic density of states. The results, recorded in Table 1 and Figures 3-8 show that the minority spin states of HAH KMnGe alloy is a semiconductor while the majority spin states is a conductor. The electronic band structures (see Figures 4) show that the minority spin band gap is indirect at the Γ-X symmetry point for the type-1 phase since the energy maximum of the valence band and the energy minimum of the conduction band occured at the Γ symmetry k-point and X symmetry k-point respectively. The type-2 phase has a direct energy band gap at the X symmetry k-point in the minority spin states (see Figure 7) The size of the indirect energy band gap is 0.9 eV. Our band gap is comparable with the result of Shakil et al. [10] obtained using ordinary functional of Perdew et al. [21] . It is also observed that the top (with maximum energy) of the valence band is three fold degenerate while the bottom of the conduction band (with minimum energy) is a singlet states for type-1 phase. In order to gain deeper insight into which states dominates around the Fermi level, the atomic density of states projected on the orbital of the constituent atoms (PDOS) was calculated (see Figures 5 and 8). We observe from the PDOS that the top of the valence band in the minority spin states is dominated by the Ge-4p states with little presence of the Mn-3d states with the Fermi level on top of the occupied band (valence band) in both type-1 and type-2 phase. The lowest energy part of the unoccupied band (conduction band) is dominated by the Mn-3d states. It is obvious from our result that the electronic structure for both type-1 and type-2 structural ground states are similar in the sense that they both show half metallic ferromagnetic property in the minority spin orbitals with 0.9 eV electronic energy band gap.

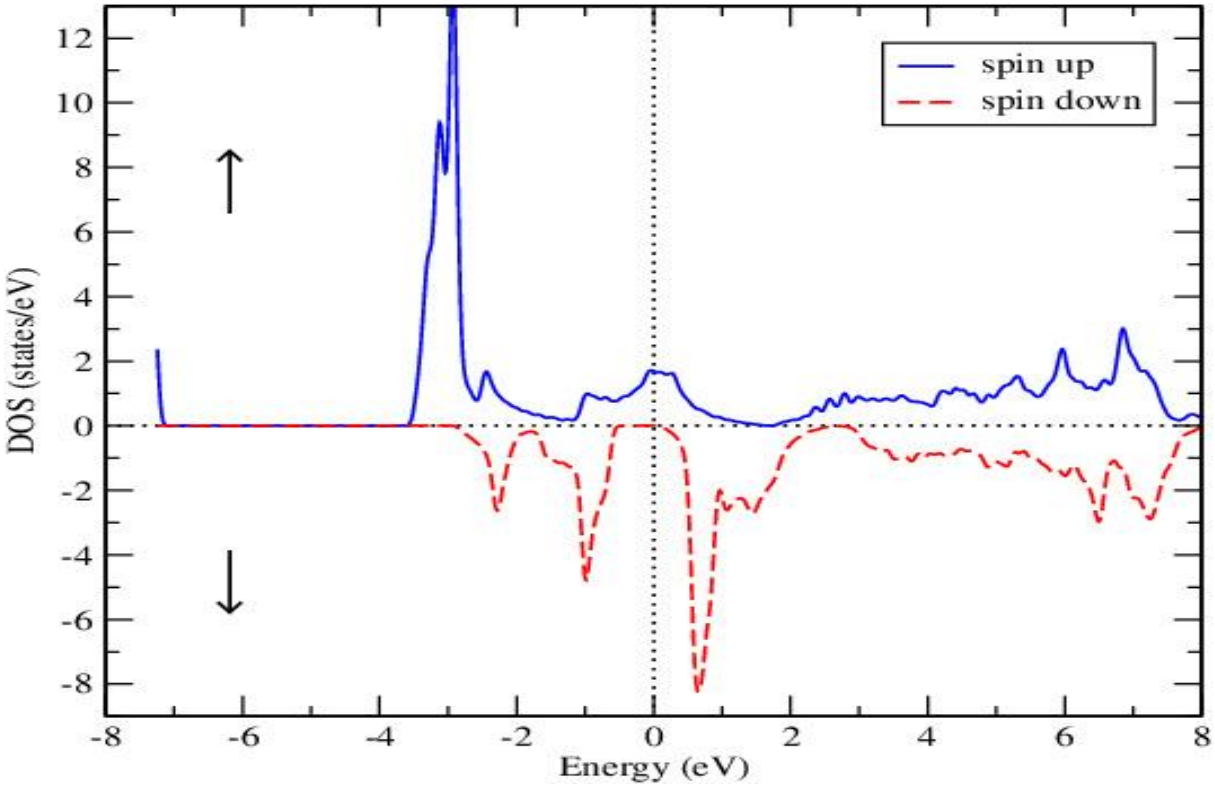

Figure 3: density of states (DOS) of HAH KMnGe alloy for type-1 structural phase. The blue line denotes the majority spin (spin up) DOS while the red (discontinuous) line denote the minority spin (spin down). The spotted vertical line at zero of the energy axis connote the Fermi level.

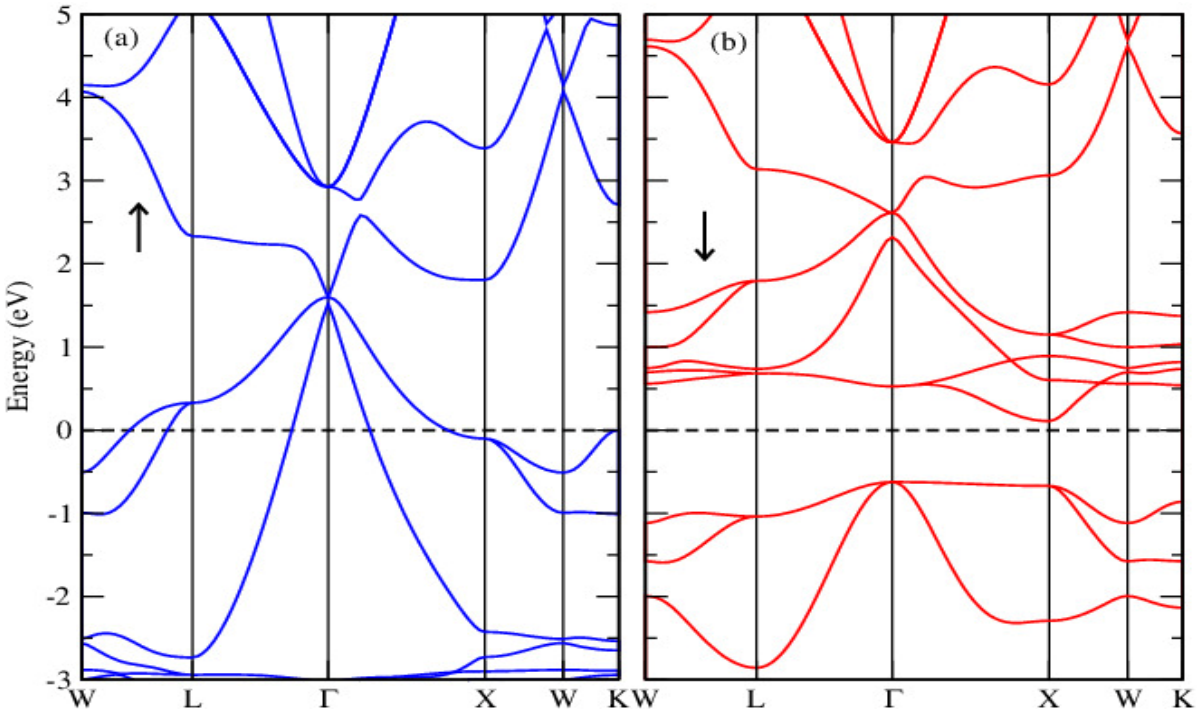

Figure 4: Electronic band structure of HAH KMnGe alloy for type-1 structural phase. (a) majority spin states (spin up) (b) Minority spin states (spin down). The spotted horizontal line at zero of the energy axis connote the Fermi level.

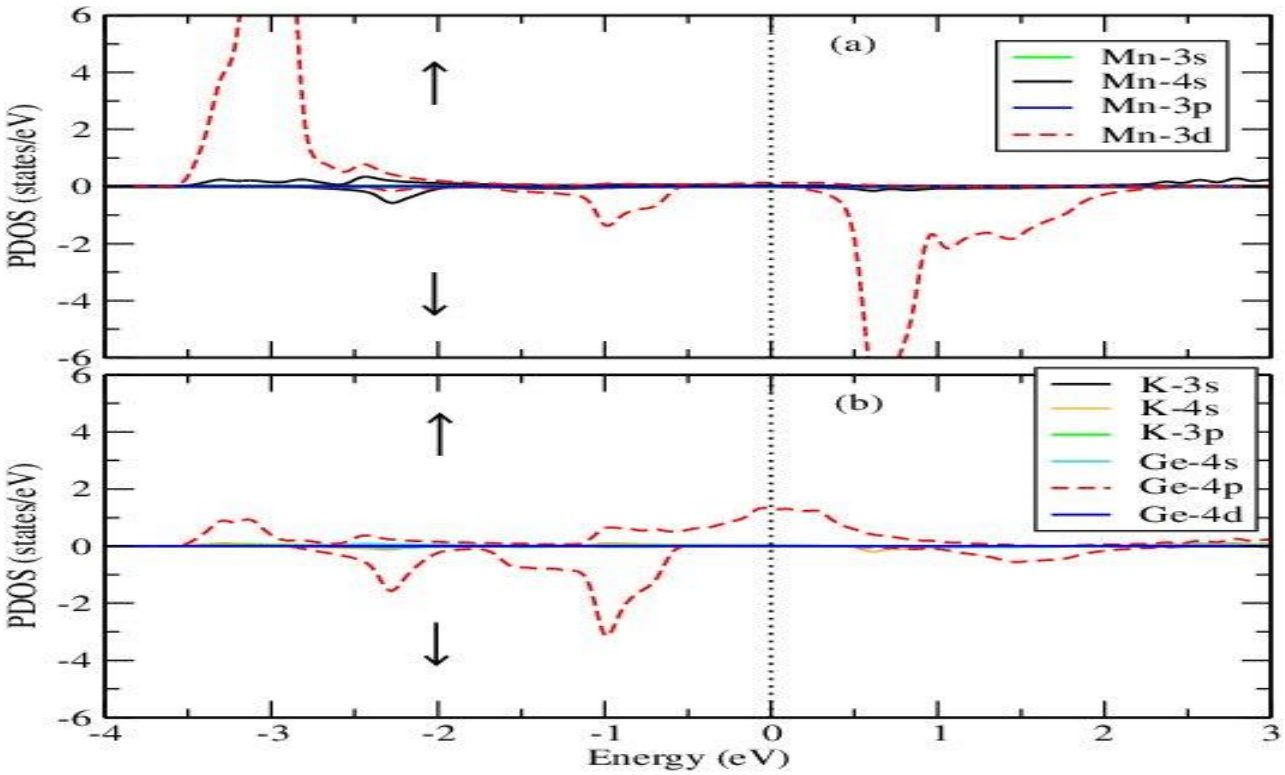

Figure 5: Density of states projected on the atomic orbitals (PDOS) of half-Heusler KMnGe alloy for type-1 phase

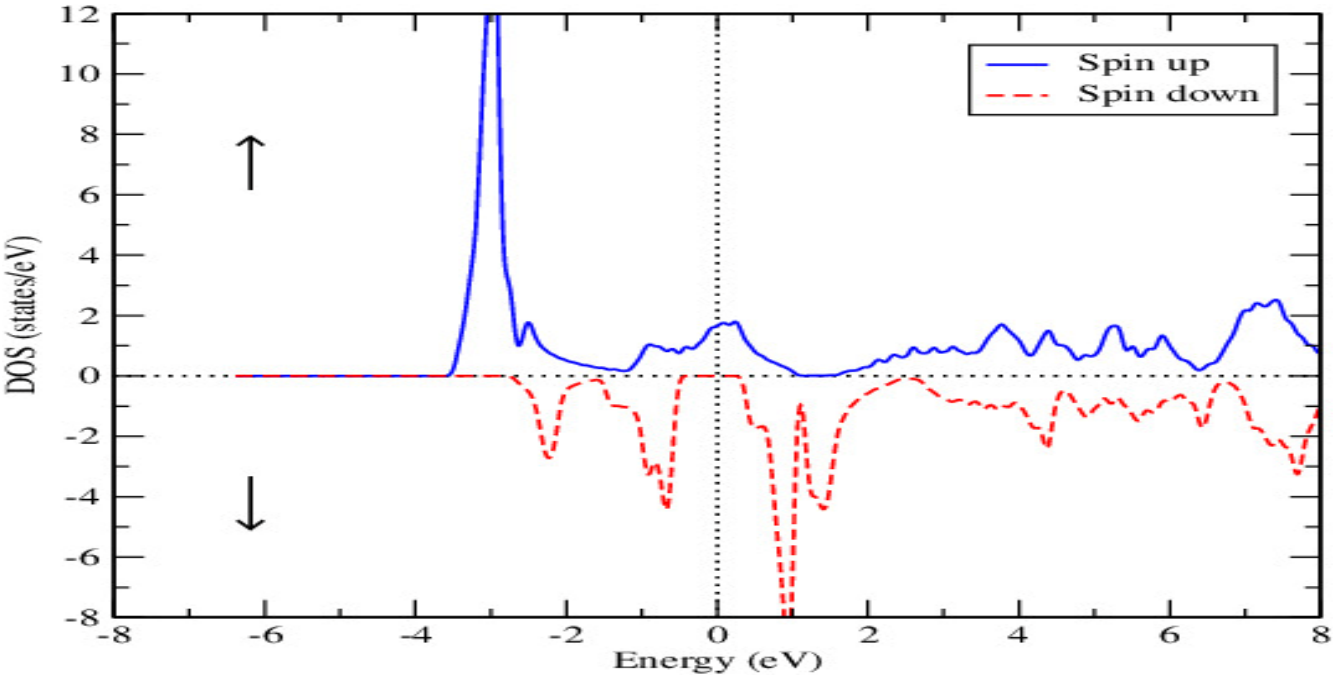

FIGURE 6: Density of states (dos) of hah kmnge alloy for type-2 structural phase. the blue line denotes the majority spin (spin up) dos while the red (discontinuous) line denote the minority spin (spin down). the spotted vertical line at zero of the energy axis connote the Fermi level.

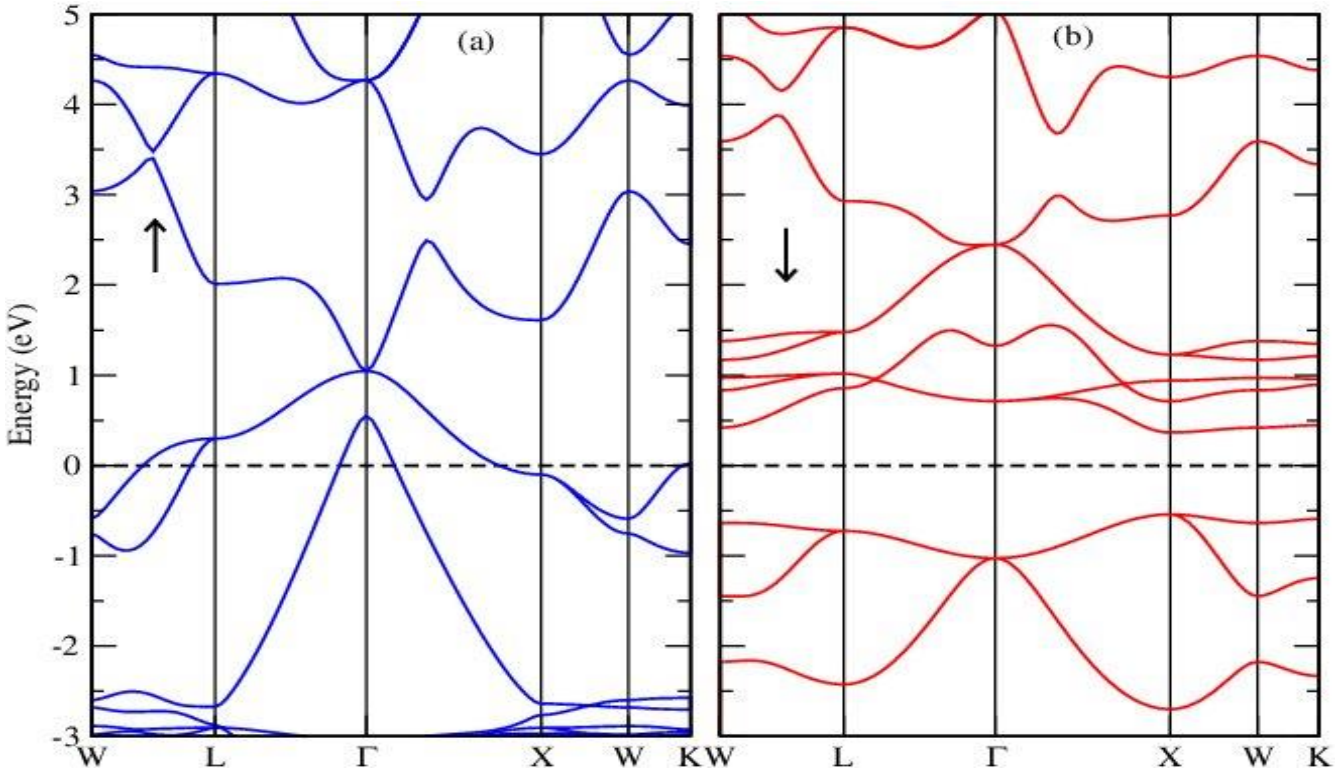

Figure 7: Electronic band structure of HAH KMnGe alloy for type-2 structural phase. (a) majority spin states (spin up direction) (b) Minority spin states (spin down direction). The spotted horizontal line at zero of the energy axis connote the Fermi level.

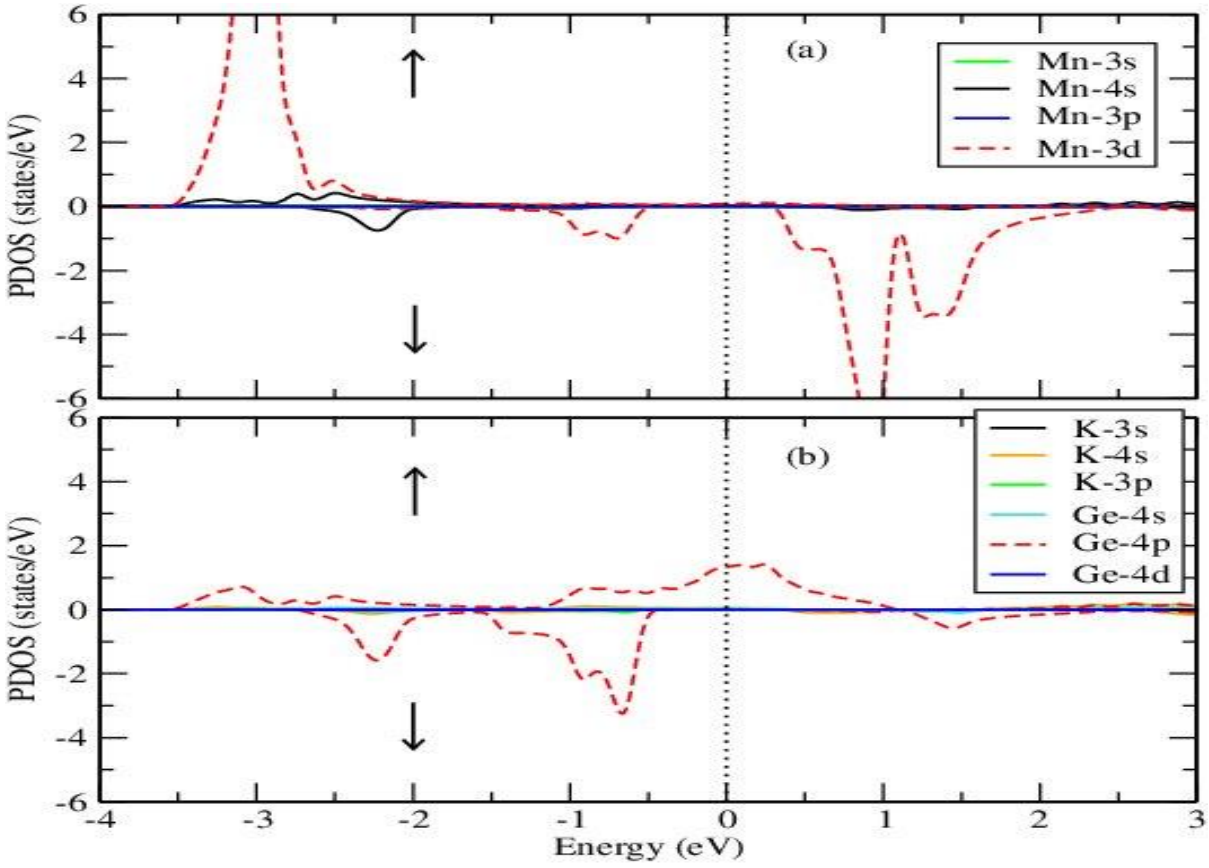

Figure 8: Density of states projected on the atomic orbitals (PDOS) of half-Heusler KMnGe alloy for type-2 phase. The spotted vertical line at the zero of the energy axis connotes the Fermi energy.

CONCLUSION

The structural, magnetic and electronic properties of HAH KMnGe alloy have been studied in this work. Our result shows that the HAH KMnGe alloy has type-1 and type-2 structural ground state at high and low pressure respectively. HAH KMnGe alloy exhibits half metallic ferromagnetism with indirect energy band gap in the Γ-X symmetry k-point in the minority spin states in the type-1 high pressure stable phase. This half-metallic character is retained even in the type-2 low pressure stable phase. The electronic structure of HAH KMnGe alloy in type-1 and type-2 phases are similar in the sense that they both show half metallic ferromagnetism with 0.9 eV band gap in the minority spin states . These results are in consonance with previous published reports and suggests that the HAH KMnGe alloy is promising as excellent material for spintronic applications since the half-metallic property is retained even when there is structural phase transition in the alloy.

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