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ARTICLE

# Prediction of the Half-metallic Properties of $Co_2MnGa_{1-x}Al_x$ Heusler Alloys

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**Abstract:** The stability, structural, electronic and magnetic properties of the doped Heusler compounds $Co_2MnGa_{1-x}Al_x$ with (x= 0, 0.25, 0.50, 0.75 and 1) were studied theoretically by using first-principles density functional theory within the generalized gradient approximation (GGA) scheme. The magnetic state is found to be energetically more favorable than the non-magnetic one. The calculated results reveal that with increasing *Al* concentration, the lattice parameter slightly decreases. Furthermore, the calculated densities of states for $Co_2MnGa$, $Co_2MnAl$ and $Co_2MnGa_{1-x}Al_x$ *(x = 0.25, 0.50 and 0.75)* show a half-metallic behavior.

**Keywords:** Heusler, Half metallic, Co-based heusler, Magnetic moment.

## 1. Introduction

Half-metallic ferromagnets (HMFs) have been generally considered due to their possible applications in spintronics, such as spin-injection, spin-filters, tunnel junctions, and giant magnetoresistance spin-valves [1, 2].

Heusler alloys have been the subject of a lot of research since their discovery by the German engineer F. Heusler in 1903 [3, 4]. This research, being either experimental or theoretical works, showed that in stoichiometric compositions, the majority of Heusler alloys are ferromagnetic [5, 6]. Heusler compounds have attracted a great deal of interest, because they have been expected to be new candidates for future applications and due to their potential request in many fields, such as spintronic [7] and photovoltaic devices [8]. Based on the first prediction of Groot et al. on the half-Heusler alloys, NiMnSb and PtMnSb [9], many predictions of the half- and full-Heusler alloys have been realized [10, 11].

Theoretically, a half-metallic ferromagnet (HMF) takes action like a metal for one spin direction and an insulator or semiconductor for the other spin orientation [12]. Formally, the description of the spin polarization of the charge carriers in HMF materials is only up to defining the case of zero temperature.

In particular, Co-based Heusler alloys are very promising materials, because some of them are expected to have a very large spin polarization [13, 14] and they show a greater stability in half-metallic properties both in

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experimental and theoretical analyses [15]. They also have advantageous properties, such as a structural compatibility with semiconducting substrates, high magnetization, as well as high Curie temperatures $T_c$ up to 1100 K [16].

The present study can be a reference for future investigations that can be fruitful and helpful for experimental and theoretical studies. The novelty of our work is to show the effect of doping as well as the concentration of the Al atoms on the different physical properties. For this reason, we have followed four important purposes. The first purpose is to determine the phase stability of $Co_2MnGa_{1-x}Al_x$ alloys. The second purpose is to investigate the structural properties of $Co_2MnGa_{1-x}Al_x$alloys for different values of x (x = 0, 0.25, 0.5, 0.75 and 1) and to explain the effect of Al concentration on these properties. The third purpose is to investigate the electronic properties of $Co_2MnGa_{1-x}Al_x$ alloys using band structure and density of states and to study the effect of the direction of spin on the nature of alloys. The fourth purpose of this article is to study the magnetic properties of these alloys and confirm the results obtained by both DOS and band structure.

## 2. Computational Method

The calculations were carried out using the full-potential linearized augmented plane wave (FPLAPW) method based on density functional theory (DFT) [17, 18] as implemented in the Wien2k package [19]. In this method, the space is divided into non-overlapping muffin-tin (MT) spheres separated by an interstitial region. Kohn– Sham wave functions were expanded in terms of spherical harmonic functions inside non-overlapping muffin-tin spheres surrounding the atomic sites and Fourier series in the interstitial region.

The exchange-correlation potential was calculated using the generalized gradient approximation based on Perdew, Burke and Ernzerhof scheme (PBE-GGA) [20]. The maximum value of angular momentum $l_{max}$ is chosen 10 for the wave-function expansion inside the muffin-tin spheres. The magnitude of the largest vector in charge density Fourier expansion $G_{max}$ was 12 $(a.u)^{-1}$. The plane wave cut-off ($K_{max}$) was taken $7.0/R_{MT}$ for the expansion of the wave functions in the interstitial region. Self-consistent calculations are considered to be converged only when the total energy of the crystal is converged to less than $10^{-4}$ Ry. The cut-off energy was chosen as −6.0 Ry; this energy defines the separation of valence and core states.

In order to simulate $Co_2MnGa_{1-x}Al_x$ (x = 0.25, 0.50 and 0.75) quaternary alloy, we have used a supercell with 16 atoms. For x = 0.25 we substituted one atom of Ga by Al, for x = 0.50 we substituted 2 atoms of Ga by 2 atoms of Al and for x = 0.75 we substituted 3 atoms of Ga by 3 atoms of Al.

## 3. Results and Discussion

Heusler alloys can be classified into two main groups; namely, half-Heusler XYZ alloys and full-Heusler $X_2YZ$ alloys. X and Y are transition metal elements and Z is an SP element. Full-Heusler $X_2YZ$ alloys usually have two types' structures. The first one is the $Cu_2MnAl$ structure, where X atoms are located at the A (0, 0, 0) and C (0.5, 0.5, 0.5) sites, while Y and Z atoms are situated at the B (0.25, 0.25, 0.25) and D (0.75, 0.75, 0.75) sites. The second one is the $Hg_2CuTi$; in this structure, X atoms are positioned at the A (0, 0, 0) and B (0.25, 0.25, 0.25) sites, whereas Y and Z atoms are located at the C (0.5, 0.5, 0.5) and D (0.75, 0.75, 0.75) positions.

It is established that the favorite place of the X and Y atoms is influenced by the number of their 3d electrons. Those elements with a higher number of 3d electrons prefer to occupy the A and C sites and those with a lower number of 3d electrons tend to reside in the B sites. In the case of $Co_2MnGa$ and $Co_2MnAl$, the nuclear charge of X (Co) is larger than that of Y (Mn); therefore, the $Cu_2MnAl$ structure will be clearly observed. Many works predicted that the $Cu_2MnAl$-type structure is more stable than the $Hg_2CuTi$-type structure for $Co_2$-based full Heusler alloys [14, 21-23].

To determine the ground-state properties of $Co_2MnGa_{1-x}Al_x$, the calculation results of total energy *versus* lattice constant for both non-magnetic (NM) and magnetic cases are plotted in Fig. 1 and fitted to the Murnaghan equation of state [24]:

$$E = E_0(V) + \frac{BV}{B'(B'-1)}\left[B\left(1-\frac{V0}{V}\right)+\left(\frac{V0}{V}\right)^{B'}-1\right]$$

where $E_0$, $V_0$, B and B' are the equilibrium energy, volume, bulk modulus and its first

derivative. Observing the results, they reveal that the FM state is more energetically favorable than the NM state. The calculated equilibrium lattice constant at the ferromagnetic (FM) state equals 5.7135 Å, 5.7106 Å, 5.7062 Å, 5.6997 Å, 5.6960 Å.

Therefore, the following calculations are based on the ferromagnetic (FM) state at the equilibrium lattice constant.

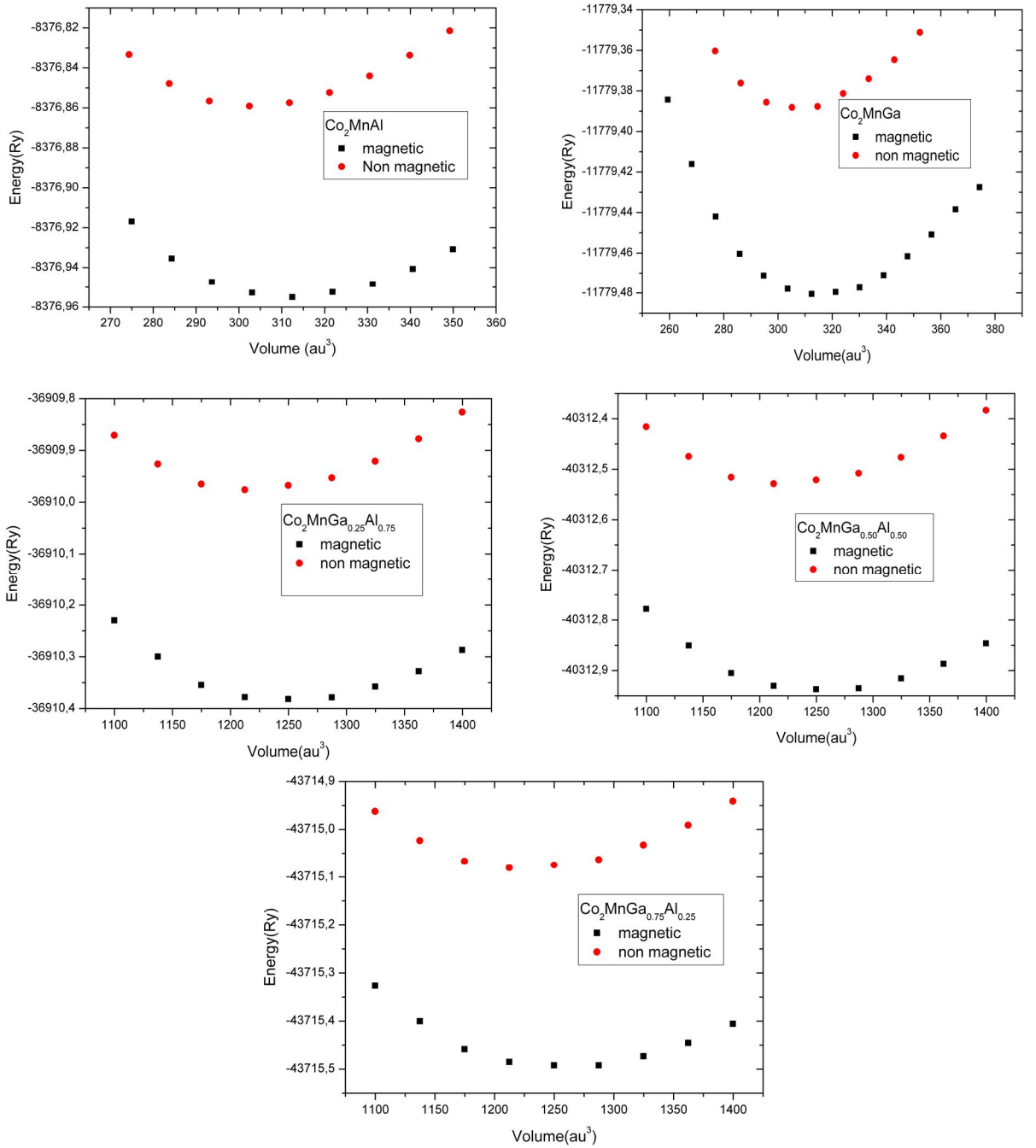


FIG. 1. Variation of the total energy as a function of the unit-cell volume for both magnetic and non-magnetic states.

The substitution of Al by Ga leads to an increase in the number of valence electrons. With increasing Ga concentration, the lattice parameter increases linearly. The increase in lattice constant is due to the larger atomic radius of Ga as compared to Al, which is also in agreement with Vegard's law [25]. The obtained results along with available literature are listed in Table 1.

To the best our knowledge, there are no similar studies for $Co_2MnGa_{1-x}Al_x$ (x = 0.25, 0.50

and 0.75) and hence, we have compared the lattice constants to the Vegard's law given by:

$$Co_2MnGa_{0.75}Al_{0.25} = 5.7135 \times 0.75 + 5.6960 \times 0.25 = 5.70912 \text{ Å}$$

$$Co_2MnGa_{0.50}Al_{0.50} = 5.7135 \times 0.50 + 5.6960 \times 0.50 = 5.70475 \text{ Å}$$

$$Co_2MnGa_{0.25}Al_{0.75} = 5.7135 \times 0.25 + 5.6960 \times 0.75 = 5.7003 \text{ Å}.$$

To check the thermodynamic stability of the phases under consideration, we have calculated the formation energy of the alloys for (x = 0.25, 0.50 and 0.75) using:

$$\Delta E = E_{total} - (1-x)E_{Ga} - xE_{Al}$$

where $E_{total}$, $E_{Ga}$ and $E_{Al}$ denote energies of $Co_2MnGa_{1-x}Al_x$, $Co_2MnGa$ *and* $Co_2MnAl$, respectively. The value of formation energies for all the three x-values is negative, which indicates thermodynamic stability of the alloys.

In this section, the electronic structure and density of states of $Co_2MnGa_{1-x}Al_x$ are presented and discussed in detail. The band structures of $Co_2MnGa_{1-x}Al_x$ for the spin-down and spin-up channels are plotted in Fig. 2.

The gap in half-metallic Heusler alloys takes place in one spin direction, while in the opposite spin state, $E_F$ cuts through the bands. The task of transition metals' 3d-states is extremely significant in the explanation of spin-polarized electronic band structures; the density of states of one spin has a peak at $E_F$, while in another spin state the density of the state is zero around $E_F$.

The metallic nature from majority spin-channels and the semiconducting gaps from minority spin-channels guide to a full spin polarization of these compounds and stable half-metallic behavior at optimized lattice parameters.

From Fig. 2, one can notice that $Co_2MnGa$ *and* $Co_2MnAl$ alloys (with magnetic phase) exhibit a semiconducting behavior with a narrow indirect band gap of about 0.35 eV and 0.62 eV along the Γ–X high-symmetry line. The conduction band is characterized by flat states close to the Fermi level, whereas the states in the valence band have a parabolic shape. This behavior is reflected in the density of states.

For nonstoichiometric alloys, it is evident that the valence bands overlap with the conduction bands in spin-up band structure and the Fermi level passes through the overlapping regions. Thus, the spin-up channel exhibits a metallic character. Different from the spin-down channel, a semiconducting band gap around the Fermi level is clearly observed in the spin-down band structure for all compounds. The values of the band gaps are found to be larger than that of $Co_2MnGa$ with 0.901 eV, 1.339 eV and 1.022 eV for $Co_2MnGa_{1-x}Al_x$ ($x = 0.25, 0.50$ *and* $0.75$) alloys, respectively.

The origin of such gaps has been connected to the hybridization of the Co and Mn d-orbital. Kübler et al. [26] reported for the first time the existence of a band gap for the minority electrons in the $Co_2MnAl$ Heusler compound.

In the following paragraph, we will report on the magnetic properties. For this purpose, we have evaluated the magnetic moments for the herein studied compounds. The total and the local magnetic moments for these compounds are listed in Table 1.

The magnetic moment is represented by the net spin magnetic moment defined by the spin of the majority spin orbitals minus that of the minority spin orbitals. For a half-metallic material, the density of states has an asymmetry between the spin-up states and the spin-down states with an energy gap at the Fermi level, which gives rise to spin polarization. The net magnetic moment results from the difference between the number of spin-up and spin-down electrons. The results in Table 1 show that both compounds $Co_2MnGa$ and $Co_2MnAl$ have a total magnetic moment of 4 $\mu_B$. The main contribution to the magnetic moment is due to the Mn atom with a minor contribution of Ga, Al and interstitial magnetic moment.The integer values of the magnetic moment per formula unit confirm that the compounds are of a half-metallic character.

The total spin magnetic moments of the $Co_2MnZ$ compounds follow the relation $M_t = Z_t - 24$ [27], the well-known Slater-Pauling behavior rule [27]. 24 means that there are 12 occupied spin-down states, as the total moment, which is the number of uncompensated spins, is given by the total number of valence electrons $Z_t$ minus two times the number of minority electrons. $Z_t$ is the number of valence electrons and $M_t$ is the total magnetic moment. For $Co_2Mn$ (Ga, Al), $Z_t = ((9*2) + 7 + 3) = 28$.

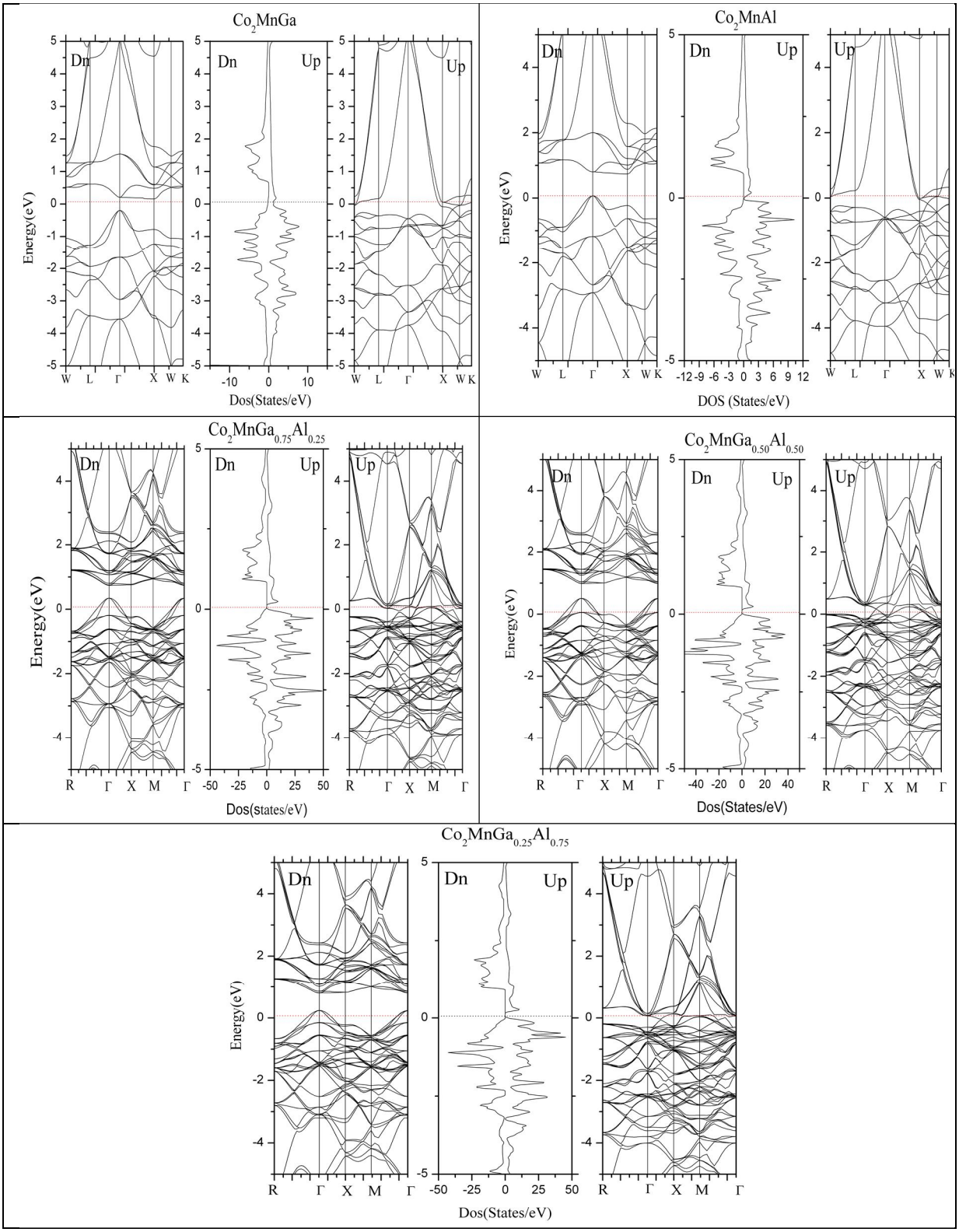


FIG. 2. The spin-polarized density of state and band structure of $Co_2MnGa_{1-x}Al_x$ (x = 0, 0.25, 0.50, 0.75 and 1).

For $Co_2MnGa_{1-x}Al_x$ *(x = 0.25, 0.50 and 0.75)* alloys, the obtained total spin and atomic magnetic moments are listed in Table 1. The results show that all the present investigated compounds have a total magnetic moment nearly equal or equal to 16.00 $\mu_B$ (15.98 for $Co_2MnGa_{0.75}Al_{0.25}$, 15.97 for $Co_2MnGa_{0.50}Al_{0.50}$ and 16.00 $\mu_B$ for $Co_2MnGa_{0.25}Al_{0.75}$).

Table 1: Calculated bulk parameters, total and local magnetic moments of the $Co_2MnGa_{1-x}Al_x$ (x = 0, 0.25, 0.50, 0.75 and 1).

| Compounds | a(Å) | B(GPa) | B' | M total | M($Co_1$) | M($Co_2$) | M(Mn) | M(Ga) | M(Al) | M(inter) | Eg(eV) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $Co_2MnGa$ | 5.7135<br>5.65<br>[21]<br>5.6259<br>[27]<br>5.724<br>[28]<br>5.70<br>[29] | 197.1395 | 4.896 | 4.00<br>4.00 [21] | 0.747 | 0.746 | 2.70 | -0.05 | - | -0.087 | 0.35 |
| $Co_2MnGa_{0.75}Al_{0.25}$ | 5.7106 | 197.1648 | 4.621 | 15.98 (with unit cell of 16 atoms) | | | | | | | 0.901 |
| $CoMnGa_{0.50}Al_{0.50}$ | 5.7062 | 196.5709 | 4.544 | 15.97 (with unit cell of 16 atoms) | | | | | | | 1.339 |
| $Co_2M_nGa_{0.25}Al_{0.75}$ | 5.6997 | 197.4881 | 4.877 | 16.00 (with unit cell of 16 atoms) | | | | | | | 1.022 |
| $Co_2MnAl$ | 5.6960<br>5.69<br>[29]<br>5.707<br>[28]<br>5.65<br>[21] | 192.3338 | 5.595 | 4.00<br>4.00 [21] | 0.808 | 0.808 | 2.603 | - | -0.062 | -0.155 | 0.62 |

## 4. Conclusion

Theoretical prediction of electronic and magnetic properties of the $Co_2MnGa_{1-x}Al_x$ full-Heusler alloy has been reported. The electronic band structure and magnetic properties were analyzed with the self-consistent FP-LAPW basis scheme based on density functional theory with the GGA.

The calculated results reveal that the lattice parameter slightly decreases with increasing *Al* concentration.

The calculations show that the magnetic state is found to be energetically more favorable than the non-magnetic one. The spin-polarized calculations showed that $Co_2Mn$ (Ga, Al) Heusler compound is half-metallic with a magnetic moment of 4 $\mu_B$.

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