1. Introduction

In last few years, Heusler alloys have become the promising material due to major applications in spintronics and memory shape devices [1]. In this system, the full Heusler compounds are characterized by the formula XYZ that crystallize in the L2₁ structure while half Heusler alloys are referred as XYZ which crystallize in the cř₁ structure [2,3]. There are four Wyckoff-positions which is given by P (0, 0, 0), Q (0.25, 0.25, 0.25), R (0.5, 0.5, 0.5) and S (0.75, 0.75, 0.75). Here X and Y elements are positioned in P, Q and R sites while main group element Z takes always place in S sites [4].

The electronic structure of these Heusler alloys are obtained to range from metallic to semiconductor relying on their composition. In fact, full Heusler alloys are popular due to half-metallic nature means these alloys possess 100% spin polarization at the Fermi level. In similar way, the full Heusler alloy shows many attractive magnetic phenomena like localized and itinerant magnetism, helimagnetism, antiferromagnetism, Pauli paramagnetism or heavy fermionic behaviour [5]. Therefore, understanding of electrical, mechanical and magnetic behaviors of these alloys is very important for application point of view. It is well established that mechanical properties are defined in term of bulk modulus of compound. The bulk modulus (B) is a parameter of materials that determines the ability of a solid, within elastic region, to resist compression deformation. In microscopic framework, valence electrons play an important role in the compression process and attractive interaction between atom and valence electrons results from the electronegativity (EN) of atoms which are not only affect mechanical properties but also influence electrical and magnetic properties of materials [6]. Hence, magnetic moments and band gap are also considerably influenced by the delocalization degree of valence electrons. Among the Heusler materials, Cobalt-based Heusler alloys are very popular because of their high Curie temperature that make them favorable for various applications, e.g. tunneling magnetoresistance (TMR). Upto date, many Cobalt-based full Heusler alloys have been investigated as half metallic materials which is advantageous for spintronics devices. In addition, disordered phase like A₂B₂ or DO₃ of Heusler alloys [7–9] also have a great influence on their physical properties. Disorder can be found due to replacement of element in the parent alloys or the presence of defects which lead the structural, mechanical and electrical properties of Heusler alloys.

Keeping it mind, we aimed to study substitution effect of Ga, Ge and Si on mechanical, electrical and magnetic properties of Co₂MnAl₁₋ₓZₓ (where Z = Si, Ge and Ga) Heusler alloy using density functional theory for numerical calculations. We employed density functional theory for numerical calculations. It is found that Co₂MnAl₁₋ₓZₓ with Z = Ga, Ge follow the Vegard’s law while Co₂MnAl₁₋ₓSiₓ does not follow the same trend. Among all composition Co₂MnAl₁₋ₓSiₓ alloy is found to be more compressible. Electronic density distribution depicts the ionic nature of Co₂MnAl₁₋ₓZₓ alloy systems. The Co₂MnAl₁₋ₓZₓ with Z = Si, Ge possess larger magnetic moment and band gap with respect to Co₂MnAl₁₋ₓGaₓ system which results from the EN difference, degree of delocalization of valence electron, atomic size and atomic number, respectively.

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functional theory based method to search the materials of potential application.

2. Calculation method

The numerical investigations were accomplished by using the Density Functional Theory (DFT) based WIEN2k code [10]. The exchange correlation potential was characterized by the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) function [11]. The plane wave basis set with an energy cut-off of 300 eV is used for all cases. The energy threshold between the core and the valence states and k points were set to 6.0 Rydberg (Ry) and 1000, respectively. The primitive cell was taken for Co2MnAl, Co2MnGa, Co2MnGe and Co2MnSi while 1 × 1 × 1 super cells were made for Co2MnAl1−xZx (where Z = Ge, Si, Ga except x = 0) alloy systems. In case of Co2MnGa alloy Co, Mn and Ga take place at wyckoff coordinates Mn (0, 0, 0), Co1 (0.75, 0.75, 0.75), Co2 (0.25, 0.25, 0.25) and Ga (0.5, 0.5, 0.5), respectively, as shown in Fig. 1. All compounds were optimized by using Hellmann-Feynman forces on atoms. We used lattice parameter a = 5.749 Å as we reported previously [12].

3. Results and discussion

In order to evaluate the mechanical properties of Co2MnAl1−xZx (where Z = Si, Ge and Ga and x = 0.0, 0.25, 0.75, and 1.0 compositions) Heusler alloys, the volume optimization was performed by minimizing the total energy for a number of volumes of Ga, Si and Ge substituted alloys as shown in Fig. 2. We found the equilibrium lattice parameters (a0) and the bulk modulus (B) from the Birch Murnaghan equation as given by [13]

\[
E_{\text{Tot}}(V) = E_0 + \frac{VB}{B'(B'-1)} \left[ \left( \frac{V_0}{V} \right)^B - 1 \right] + \left( \frac{V_0}{V} \right)^{-1} \]

(1)

where \(E_0\), B and \(B'\) refer to equilibrium energy, bulk modulus and its first derivative at equilibrium volume \(V_0\), respectively. Generally, the bulk modulus B is defined by the following equation:

\[
B = -V \frac{\partial P}{\partial V} = V \left( \frac{\partial^2 E}{\partial V^2} \right)
\]

(2)

where P and V are the pressure and volume of the system, respectively.

It can be seen from Fig. 3 (a) that with increasing Ge and Ga content, the lattice constant increases linearly. This higher value of the lattice parameter is a result of greater atomic radius of Ge and Ga atoms in compare to Al atom. However, Co2MnAl1−xZx follow the opposite trend that is usual for Heusler alloys.

In any system bulk modulus (B) represents the hardness of compounds. Thus, bulk modulus variation for Co2MnAl1−xZx (where Z = Si, Ge and Ga) alloys have been shown in Fig. 3 (b). It is clear that all Ge, Si and Ga substituted composition upshot bigger modulus relative to parent Co2MnAl alloy except only Co2MnAl0.25Si0.75 composition. Interestingly, all Co2MnAl1−xZx (where Z = Si, Ge and Ga) alloys follow the same trend. Initially on addition of 25% of Ge, Si or Ga in place of Al site (for example Co2MnAl0.25Si0.75 composition), bulk modulus increases. However, bulk modulus decreases for 75% substitution of Ge, Si or Ga and again increases for pure Co2MnSi, Co2MnGa and Co2MnGe alloys. Such kind of variation occurs according to the following order: Co2MnAl1−xZx > Co2MnAl1−xGa > Co2MnAl1−xGe. Above variation in bulk modulus after the addition of 25% Si, Ge and Ga substitution might be the result of valence electrons difference (excluding core electrons), taking part in the compression process or EN difference Al (1.61 eV1/2), Ga (1.81 eV1/2), Si (1.90 eV1/2) and Ge (2.01 eV1/2) which controls the attractive and repulsive interaction between atom and valence electrons [14,15].

Since EN value of Ga, Ge and Si are larger than that of Al atom, the average binding force of chemical bonds in the alloys increases when alloying Co2MnAl with Ga, Si and Ge, respectively. It is noteworthy that bulk modulus of alloys is expected to increase with increasing of these p-element content in Co2MnAl alloy according to simple chemical bonding formulation based on tight-binding model. In contrast, substitution of 75% Ge, Si or Ga in Co2MnAl alloy, B decreases that might be the result of increasing number of p-p and p-d bonds, which make them more rigid than 25% substitution of Ge, Si or Ga in parent alloys [16]. Among all

![Fig. 1. Crystal structure of Co2MnGa Heusler alloy.](image1)

![Fig. 2. Calculated total energy as the function of volume of Co2MnGa/Al Heusler alloy.](image2)
compositions, Co$_2$MnAl$_{25}$Si$_{75}$ is found to be more compressible. There may be two reasons: either sharp changes in B upon doping of Si might be related to local Al magnetic moment contribution (Fig. 4 a) or significant contraction of the lattice occurs on Si doping due to less variation in atomic number of Si and Al elements.

Another important parameter is electron density distribution. Basically, electronic charge density is useful for studying the nature of bond character in any materials. Moreover, it provides information on the charge transfer, bonding nature (e.g., the ionic, metallic and covalent bonding) in alloys. As we predicted earlier that atomic number, EN etc. plays an important role in above mentioned properties. For this purpose, we studied the electronic charge density distribution curve. Here only curve for Co$_2$MnAl and Co$_2$MnGe/Al bonds has a similar character with the ionic bond. This contribution can be outcome of the same number of valence electron in Al and Ga shells. Secondly, at 25% doping of Ga could not be enough for formation of number of p-d bonds that tends to reduce the Co, Mn moment. In contrast 75% substitution of Ga increases Co and Mn moment offer the large expansion of the lattice caused by the p-p or p-d bonds. It is found that the local moments of Si and Ge are negligibly small as in Fig. 4 (a, b), but Ga substituent possess some partial moment. The moments of Al are the negative and small values, while the Co and Mn moments are the positive values and most of the moment come from Mn. This abnormal local moment of Mn arises from a small d-d wave function overlapping and hence larger exchange interaction due to the decreasing Mn–Mn distances. Fig. 4(c) depicts the band gap for each composition. The band gap is also influenced by the EN term. Additionally, it depends on the distribution of valence electrons i.e. degree of delocalization of valence electrons. In all substituents EN is in order Ge > Si > Ga.
Thus Ge then Si is more electronegative than Ga so that it interacts with the host atoms more strongly which offers large enough bonding-anti-bonding splitting than Ga substitution. Therefore, band gap is found to be maximum for Co$_2$MnAl$_{25}$Ge$_{25}$ and minimum Co$_2$MnAl$_{25}$Ga$_{25}$ composition [15]. It is available in literature (Z = Si, Ge) and We get the same trend. The Co$_2$MnAl$_{0.25}$Si$_{0.75}$ full Heusler alloy, Mater. Lett. 225 (2018) 134–137, 2018 1850121.

4. Conclusion

In brief, we performed the comparative study of mechanical, electrical and magnetic properties of Co$_2$MnAl$_{1-x}Z_x$ Heusler alloys (Z = Si, Ge and Ga and x = 0, 0.25, 0.75 and 1) using the EN model and WEIN2K code for numerical calculations. The electronic density distribution depicts the ionic nature of Co$_2$MnAl$_{1-x}Z_x$ alloy systems. The alloys with Z = Ga, Ge follow the Vegard’s law while Co$_2$MnAl$_{1-x}Si_x$ does not follow the same trend. The Co$_2$MnAl$_{25}$Si$_{75}$ alloy is found to be more compressible than others. For the magnetic moment and the band gap, however, a similar behaviour is found for the alloys with Z = Si and Ge. They possess larger magnetic moment and band gap with respect to Co$_2$MnAl$_{1-x}Si_x$ system. This finding is attributed to the EN difference, degree of delocalization of valence electron, atomic size and atomic number, respectively. They play an important role for making good spintronics devices.

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