Electronic structure and thermoelectric property of Co$_2$YGe (Y=Mn, Fe) Heusler compounds: a first principle study

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Abstract. The electronic and thermoelectric properties of Co$_2$YGe (Y=Mn, Fe) Heusler compounds have been studied by first principle density functional theory and compared with the known experimental and theoretical results. Results of the density of states (DOS) and band structures shows the half-metallicity of the Heusler alloy Co$_2$MnGe, whereas the Heusler alloy Co$_2$FeGe fails to give half-metallicity when treated with GGA. The ZT value calculated for these materials is much below the benchmark value 1.

1. Introduction
Heusler thermoelectric materials have been attracting extensive research interest since their discovery in 1903 [1]. Heusler compounds are ternary intermetallic compounds consisting usually of two transition metals (X, Y) and one main group element (Z). They can be divided into two groups: Compounds with chemical formula X$_2$YZ having four $fcc$ sublattices, and compounds with formula XYZ, consisting of three $fcc$ sublattices [2].

The full-Heusler compounds commonly appear as metals. However semi-metallic behavior was observed for Co$_2$MnGe, as evidenced by several theoretical calculations [3, 4]. The presence of pseudogap in Co$_2$MnGe is predicted to be due to hybridization effects [3]. The pseudogap formation arises from an indirect band overlap at the Fermi energy ($E_f$) and thus Co$_2$MnGe is characterized as semi-metal. In this report, we intend mainly to study the thermoelectric properties by calculating the figure of merit $ZT$, which is defined as the maximum efficiency of a thermoelectric material and is given by

$$ZT = \frac{S^2 \sigma}{\kappa} T$$  \[5\]

where, $S$ is the Seebeck coefficient, $\sigma$ the electrical conductivity, and $\kappa$ the thermal conductivity. The thermal conductivity $\kappa$ compromises of two parts, $\kappa = \kappa_e + \kappa_p$, where, $\kappa_e$ and $\kappa_p$ are respectively the electronic and phononic contribution to thermal conductivity. Results obtained for Co$_2$FeGe and Co$_2$MnGe excludes the phononic contribution to thermal conductivity.

2. Crystal structure and computational details

2.1. Crystal Structure
The full-Heusler crystal structure consists of four penetrating fcc sublattices with atoms at \(X_1(1/4,1/4,1/4), X_2(3/4,3/4,3/4), Y(1/2,1/2,1/2)\) and \(Z(0,0,0)\) positions which result in the \(L_2\) structure having space group \(Fm\-3m\). The two Co-site fcc sublattices combine to form a simple cubic sublattices as shown in figure 1.

![Figure 1: (a) Unit cell structure of Co\(_2\)FeGe, (b) Unit cell structure of Co\(_2\)MnGe](image)

2.2. Computational Details

The total energy is calculated by using Generalized Gradient Approximation (GGA) [6] and Linearized Augmented Plane Wave method (LAPW) [7], the electronic and thermoelectric properties were calculated using Full Potential Linearized Augmented Plane Wave method (FP-LAPW) [8] as implemented in the code WIEN2k [9]. The convergence of basis set was controlled by a cutoff parameter \(R_{MT} \times K_{\text{max}} = 7\), where \(R_{MT}\) is the smallest of the MT sphere radii and \(K_{\text{max}}\) is the largest reciprocal lattice vector used in the plane wave expansion and made the expansion up to \(l_{\text{max}} = 6\) in the muffin tins, where \(l_{\text{max}}\) is the maximum value of the angular momentum. The magnitude of the largest vector in charge density Fourier expansion (\(G_{\text{max}}\)) was 12 a.u. The cutoff energy which defines the separation of valance and core states was chosen as -6.0 Ry. For k-point sampling, a 31x31x31 k-point mesh in the first Brillouin zone was used resulting in 816 k-points in the irreducible part of the Brillouin zone. The convergence criterion for self-consistence calculations was set up to charge convergence equal to \(10^{-3}\)e\(^-\) and the energy convergence criterion was set to \(10^{-5}\)Ry. The set of valance orbitals in the calculations were selected as \(3s, 3p, 4s, 4p, 3d\) for Co atoms, \(3s, 3p, 4s, 4p, 3d\) for Mn atoms, \(3d, 4s, 4p\) for Ge atoms and \(3s, 3p, 4s, 4p, 3d\) for Fe atoms. All lower states were treated as core states.

A program code called BoltzTraP based on Boltzmann semi-classical transport equation was used to calculate the electron transport properties as implemented in a code BoltzTraP [10]. This code depends on the data provided by WIEN2k code.

3. Results

The volume optimization was performed using the lattice constants taken from the experimental results. The calculated total energies with GGA as a function of the volume were used for determination of theoretical lattice constant and Bulk modulus. The Bulk modulus was calculated using the Murnaghan’s equation of state [11]. The calculated value of lattice constant and bulk modulus are presented in Table 1 and the volume optimization curve is shown in figure 2. For Co\(_2\)MnGe, the calculated Bulk modulus is 216.6253 GPa, its pressure derivative is 9.3865 the optimized lattice constant is 5.6748 Å and the change in the lattice constant with that of experimental one is 0.0729. Similarly, for Co\(_2\)FeGe the calculated Bulk modulus is 188.8626 GPa, its pressure derivative is 5.1122, the optimized lattice constant is 5.7469 and the change in the lattice constant with that of experimental one are 0.0039. The change in the lattice parameters is given by \(\Delta (a_0)\).
Table 1. Experimental and theoretical lattice constants

| Compound   | Experimental lattice constant | Calculated lattice constant | $\Delta (a_o)$ | Bulk Modulus B (GPa) | Equilibrium Energy (Ry) |
|------------|-------------------------------|-----------------------------|----------------|----------------------|------------------------|
| Co$_2$MnGe | 5.7477 [12]                   | 5.6748                      | 0.0729         | 216.62               | -12317.717             |
| Co$_2$FeGe | 5.7430 [12]                   | 5.7469                      | 0.0039         | 188.86               | -12089.325             |

3.1. Density of States (DOS)

The total and partial DOS plots of Co$_2$MnGe are shown in figures 3 and 4 respectively.

Figure 3. DOS plots of Co$_2$MnGe. (a) Total DOS plot of Co$_2$MnGe (b) partial DOS plot of Mn (c) partial DOS plot of Co and (d) partial DOS plot of Ge.
It shows that the maximum contribution in total DOS is due to the Co atom in both spin up and spins down the channel (~ 4.9 eV in spin up and ~ 8.2 eV in spin down). The second largest contribution is due to the Mn atom (~ 3.7 eV in spin up and ~ 4.3 eV in spin down), whereas the Ge atom has the least contribution for the total DOS (<1 eV for both spins). The peaks are mostly due to the $d$-state electrons in semi-core and valance region, below $E_F$ for both spin up and down channel. The contribution in Mn DOS is mainly due to Mn-$d$ electrons in the valance region with sharp peaks at -2.35 eV and -2.8 eV. In the conduction region, the sharp peaks are observed at 2.1 eV and 0.9 eV respectively, which are mainly due to the $d$-$e_g$ and $d$-$t_{2g}$ states of Co and Mn atoms in the spin down channel (figure 4 (a) and (b)). In the spin up the region of Co$_2$MnGe (figure 3(a)), DOS intersects $E_f$, giving metallic nature, whereas, in the spin, down channel, DOS intersection to $E_f$ is absent giving semi-metal nature.

The following figures 5 and 6 gives the total and partial DOS of Co$_2$FeGe respectively. DOS plot of Co$_2$FeGe shows that the maximum contribution in total DOS is due to the Co atom (~7.95 eV). The second largest contribution is due to the Fe atom (~5.8 eV), whereas the Ge atom has the least contribution for the total DOS (< 0.6 eV). For Co$_2$FeGe, the peaks are mostly due to the $d$-state electrons in semi-core and valance region, at $E_f$ (figure 6). The contribution in Fe DOS is mainly due to Fe-$d$ electrons in the valance region with sharp peaks at ~3.7 eV, ~2.2 eV and ~2.1 eV and that in Co DOS is mainly due to Co-$d$ electrons in the valance region with sharp peaks at ~2.2 eV and ~2 eV. In the conduction region, the sharp peaks are observed at 1.6 eV and 1.5 eV respectively, which are mainly due to the $d$-$e_g$ and $d$-$t_{2g}$ states of Co and Fe atoms.

In both Co$_2$MnGe and Co$_2$FeGe, the $d$-electrons of Co forms a strong hybridization with Mn-$d$ and Fe-$d$ electrons.
Figure. 6: DOS plots of Co$_2$MnGe (a), Co total, s, p, and d states (b) Co total, d, d-$eg$ and d-$t_{2g}$ states, (c) Fe total, d, d-$eg$ and d-$t_{2g}$ states and (d) Fe total, s, p, and d states.

3.2. Band structures

Figures 7(a), (b) and (c) gives the band structures of Co$_2$MnGe for spin up, spin down channels and for Co$_2$FeGe respectively. The valance region of the spin up and spin down channel of Co$_2$MnGe has more number of bands due to the 3$d$ states of Mn atoms. In the conduction region (spin down), dense bands are observed which is also due to the 3$d$ electrons of Mn atom. In comparison with DOS results, it can be seen that in the valance region, the bands below -3eV consists mainly of the s and p electrons of the Ge atom for both Co$_2$MnGe and Co$_2$FeGe.

In the energy gap between -3.0 eV to 2 eV, the bands are mainly due to the d electrons of Co and Mn atoms for Co$_2$MnGe and d electrons of Co and Fe atoms for Co$_2$FeGe. For Co$_2$MnGe, from band structure and DOS calculations, it is seen that the band gap originates due to strong hybridization between the d states of the higher valent and the lower valent transition metal ions.

Rai et al. described that the interaction of Mn with the Z-$p$ states splits the Mn-3$d$ states into a low-lying triplet of $t_{2g}$ states and a higher-lying doublet of $e_g$ states [6]. The band gap in $E_F$ is formed when the Mn-3$d$ states in the majority band is shifted to lower energies, while the Mn 3$d$ states in the minority band are shifted to higher energies and remain unoccupied. The absence of sharp peaks in the DOS is accounted by a low number of bands in the conduction region of spin-up channel. An indirect band gap of 0.61 eV between symmetry point $\Gamma$ and $X$ was obtained. This value is in close agreement with that obtained by Kandpal et al. which was 0.581 eV [13].

Figure 7 (c) gives the energy bands for Co$_2$FeGe. From the figure we see that Co$_2$FeGe has no band gap and thus acts as a metal when treated with GGA. However, when treated with GGA+U, Co$_2$FeGe also acts as a half-metal, giving metallic nature for spin-up channel and semi-metal characteristics for a spin down channel [14].
3.3. Thermoelectric properties

The value of $S$ calculated with the proposed method at the room temperature for Co$_2$MnGe is $16.7\times10^{-6}$ V/K (Figure 8(a)). We find from our study that this value is in agreement with that obtained by Ouardi which was $-16\times10^{-6}$ V/K [12]. The negative sign in $S$ indicates $n$–type carriers. However, the value of $S$ calculated for Co$_2$FeGe is very small. This is because of the absence of band gap in the band structure of Co$_2$FeGe.

The variation of the relaxation time $\tau$ dependent electrical conductivity with temperature is shown in Fig. 8 (b). The electrical conductivity and the power factor have an impact of $\tau$, unless an accurate numerical value of $\tau$ is known, the accurate resistivity and power factor ($\sigma_\tau s^2$) cannot be calculated. The electrical conductivity has high values for lower temperatures and for temperatures above 500K, it almost remains constant. This is because of the low density of states at $E_F$. The value of $\sigma / \tau$ obtained for room temperature was $2.92 \times 10^{22}$ (\Omega ms)$^{-1}$ and $3.37 \times 10^{22}$ (\Omega ms)$^{-1}$ respectively for Co$_2$MnGe and Co$_2$FeGe.

The variation of temperature dependent electronic thermal conductivity ($\kappa_e$) is shown in Fig. 8(c). The thermal conductivity increases linearly with the rise in temperature above 40 K for both Co$_2$MnGe and Co$_2$FeGe. This is in agreement with the results obtained by Ouardi [16]. For lower temperatures, thermal conductivity decreases with the increase in temperature, whereas according to Ouardi, for lower temperatures it increased according to $T^3$ law. Fig. 8 (d) gives the variation of the figure of merit (maximum performance) with temperature. The $ZT$ value calculated at room temperatures are 0.008 and 0.00022 for Co$_2$MnGe and Co$_2$FeGe respectively. The value will further reduce if the phononic contribution to thermal conductivity is included in the calculation.

Figure 7. Energy bands of (a) Co$_2$MnGe Spin up (b) Co$_2$MnGe Spin down and (c) Co$_2$FeGe

However, when treated with GGA+U, Co$_2$FeGe also acts as a half-metal, giving metallic nature for spin-up channel and semi-metal characteristics for a spin down channel [14].
Figure 8. (a) Temperature dependence of Seebeck coefficient ($S$), (b) electrical conductivity over relaxation time ($\sigma/\tau$), (c) electron thermal conductivity ($k_e$) and (d) figure of merit (ZT).

4. Conclusions
We have performed a detailed investigation of the electronic and thermoelectric properties of Co$_2$MnGe and Co$_2$FeGe Heusler compounds. The theoretically calculated transport properties are in agreement with the experimental results except for low-temperature regions around 50K. Although the obtained ZT value is much less than the benchmark value for thermoelectric applications, it may be enhanced by doping, nanostructuring etc which attributes to the reduction of thermal conductivity and enhancement of Seebeck coefficient. Both these compounds exist in a half-metallic state indicating that half-metal compounds are poor candidates for thermoelectric applications under normal conditions.

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