Investigation of thermoelectric properties of half-metallic Co$_2$MnGe by using first principles calculations

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Abstract
By combining the electronic structures obtained from first principles calculations with Boltzmann transport theory we have investigated the electronic, magnetic and transport properties of the Co$_2$MnGe Heusler compound. The density of state plots, dispersion curves and the total energy of paramagnetic and ferromagnetic (FM) phases clearly show the half-metallic FM ground state for the compound, with an indirect band gap of about 400 meV in the minority spin channel. It has an integer value of the magnetic moment equal to 5 $\mu_B$. In the FM phase a very large value ($\sim 550 \mu V K^{-1}$) of the Seebeck coefficient ($S$) is obtained for down-spin electrons due to the existence of an almost flat conduction band along X in the $\Gamma$ direction. The two-current model has been used to find the total $S$ and the obtained value is about 10 $\mu V K^{-1}$. The calculated values of the Seebeck coefficient, resistivity and electronic thermal conductivity show nice agreement with the experimental results.

Keywords: electronic structures, half-metallic, Seebeck coefficient, resistivity, electronic thermal conductivity

(Some figures may appear in colour only in the online journal)
The half-metallic compounds show metallic behaviour for one spin channel but semiconducting for the other. The total thermopower is expected to be more in these compounds than that of the metals and less than the semiconductors. Experimental studies also suggest that the half-metallic ferromagnetic materials have a relatively larger value of the Seebeck coefficient [17, 18]. Co$_2$MnX-like Heusler alloys are expected to be good thermoelectric materials in the high temperature range because there exists a band gap in the minority spin state of these alloys [19] and they have a high Curie temperature [20]. Also it is possible to tune their magnetic properties [6] and $E_F$ position [21] by the substitution of atoms that have similar radii and charges.

For many years, it was a very challenging task to calculate accurately the transport properties of materials [22]. Recently, progress has been made by combining the first principles band structure calculations and the Boltzmann transport theory [23–25]. According to this theory electrical conductivity can be calculated from electronic structures [25, 26] and usually electrical conductivity has a large dependence on the density of states [27]. Co$_2$MnGe has a narrow band gap in the minority spin state, so it is expected that the minority spin state will give a larger value of $S$ than of the metals. The Curie temperature of the compound is nearly 905 K [17]. In the present work we study the electrical transport properties of Co$_2$MnGe in both the paramagnetic and FM phases of a high temperature range.

Full-potential linearized augmented-plane wave methods within local spin density approximation (LSDA) have been employed to calculate the electronic band structures, magnetic states and electronic transport properties of Co$_2$MnGe. Study of its electronic and magnetic properties shows that this compound is a half-metallic ferromagnet with a band gap of about 400 meV in the minority spin channel. The temperature-dependent electronic transport coefficients are evaluated for both the paramagnetic (PM) and FM phases of the compound. The negative value of $S$ for both phases indicates the presence of N-type charge carriers. In the FM phase the obtained value of $S$ for down spin electrons is $\sim$550 $\mu$V K$^{-1}$, which is almost 55 times greater than that of the up spin electrons. Total $S$ is computed by using the two-current model which is almost 55 times greater than that of the up spin electrons. The Curie temperature of the compound is nearly 905 K [17]. In the present work we study the electrical transport properties of Co$_2$MnGe in both the paramagnetic and FM phases of a high temperature range.

2. Computational details and crystal structure

Calculations of electronic and magnetic properties were performed by using the full-potential linearized augmented plane-wave (FP-LAPW) method within the density functional theory (DFT) implemented in WIEN2k code [28]. The exchange-correlation function was treated within the local spin density approximation (LSDA) of Perdew and Wang [29]. The muffin-tin radii were set to 2.2 Bohr for Co, Mn and Ge atoms. $R_{MTK_{max}}$, which determines the matrix size for convergence, was set equal to seven, where $R_{MT}$ is the smallest atomic sphere radius and $K_{max}$ is the plane wave cut-off. The maximum $l$ value ($l_{max}$) for partial waves used inside atomic spheres was kept at ten. An experimental lattice parameter of 5.743 Å [30] was used in the calculations. The volume of the unit cell was about 284 Bohr$^3$. The self-consistent loop was repeated until the total energy/cell of the system converged to less than $10^{-4}$ Ry. The 40 x 40 x 40 k-point mesh was used as the accurate calculations of transport properties of metals require dense sampling of the Brillouin zone. The transport properties of the compound have been calculated by using the BolzTrap code [25] under the constant relaxation time approximation for the charge carriers. The Fermi energy obtained in the self-consistent calculations was considered to be the chemical potential for the calculation of transport properties of the compound. The values of chemical potential used in the calculation were 0.7926 eV and 0.8051 eV for PM and FM phases, respectively.

A full Heusler compound Co$_2$MnGe crystallizes in a $L_2_1$ crystal structure with space group $Fm\overline{3}m$. Co atoms are placed on the Wyckoff position 8c (1/4, 1/4, 1/4). Mn and Ge atoms are located at the Wyckoff position 4a (0, 0, 0) and 4b (1/2, 1/2, 1/2), respectively [20]. The cubic $L_2_1$ structure consists of four interpenetrating fcc sub-lattices, two of which are equally occupied by Co atoms. The two Co-site fcc sub-lattices, combine to form a simple cubic sub-lattice. Alternatively, the Mn and Ge atoms occupy the centre of the simple cubic sub-lattice, resulting in a CsCl-type superstructure [19].

3. Results and discussions

3.1. Paramagnetic Phase

The total density of states (TDOS) and partial density of states (PDOS) plots for the PM phase are shown in figure 1. The $E_F$ is represented by a dashed line. In figure 1(a) the total DOS at $E_F$ is $\sim$7 states/eV/f.u. (f.u. $\equiv$ formula unit) for both the spin channels, which is very large. Such a large value of TDOS at the $E_F$ may be considered to be an indication of the FM ground state, as per the Stoner theory [31]. It is also clear from the figure that the antibonding bands are extended up to about 0.6 eV below $E_F$. Based on Stoner’s theory one can easily guess that the total energy of the system will be minimized if there is a shift in the spin-up and spin-down bands by about 0.6 eV below and above the $E_F$, respectively. This gives rise to a half-metallic FM ground state for the compound. This is also evident from the total energy calculations, where the total energy of the FM phase is about 1.1 eV less than the PM phase. From the PDOS of the Co atom in figure 1(b), it is clear that the contribution of the $t_{2g}$ and $e_g$ states at the $E_F$ is $\sim$0.4 states/eV/atom and $\sim$1.3 states/eV/atom, respectively, in both the spin channels. It is also evident from figure 1(c) that the Mn $t_{2g}$ and $e_g$ PDOS at $E_F$ is $\sim$1 and 2 states/eV/atom, respectively. The PDOS of the Ge atom (figure 1(d)) shows that occupancy at $E_F$ for the p-orbital is $\sim$0.5 states/eV/atom, with a very small contribution of s and d-orbitals. From these figures it is clear that both $t_{2g}$ and $e_g$ orbitals mainly contribute to the total DOS at the $E_F$. These orbitals are considered responsible for the FM ground state.
The dispersion curves along the high symmetry directions of the first Brillouin zone are presented in figure 2(a). It is evident from the figure that bands labelled 1, 2 and 3 are lie just above the $E_F$, whereas bands 6, 7 and 8 are just below it. Bands 4 and 5 cross the $E_F$ at eight different $k$-points. Bands 2–7 are concentrated around the W-point in the energy range, about −0.2 to 0.2 eV. Shifting of these bands can minimize the total energy of the system and may lead to the FM ground state for this compound.

In figures 2(b)–(e) temperature-induced carrier concentration per unit cell, calculated Seebeck coefficient ($S$), electrical conductivity ($\sigma/\tau$) and electronic thermal conductivity ($\kappa_e/\tau$), where $\tau$ is the relaxation time, are displayed for temperatures ranging from 900 K to 1200 K. It is evident from figure 2(b) that the temperature-induced charge carriers show linear variation with temperature and the absolute value of $N$ decreases from $\sim 0.36$ e/unit cell at 900 K to $\sim 0.007$ e/unit cell at 1200 K. Figure 2(c) shows the linear temperature dependence of the $S$. The value of $S$ is negative for the entire temperature range, which indicates N-type of charge carriers in the PM phase of the compound. The value of $S$ increases from $\sim 0.52 \times 10^6$ (W m$^{-1}$K$^{-1}$s$^{-1}$) at 900 K to $\sim 0.72 \times 10^6$ (W m$^{-1}$K$^{-1}$s$^{-1}$) at 1200 K.

### 3.2. Ferromagnetic Phase

The TDOS and PDOS for the FM solution are shown in figure 3. From the TDOS plots (figure 3(a)), it is clear that the majority of spin states occur at $E_F$, with occupancy of 1.09 states/eV/f.u, and minority spin states are empty. Thus, for the spin-up channel this compound is metallic, while for the spin-down channel it shows semiconducting behaviour. On comparing figures 1(a) and 3(a), one can find that in the spin-up channel TDOS shift towards a lower energy, whereas, in the spin-down channel TDOS shift towards a higher energy, as conjectured above. Because of this shifting the almost empty region of the spin-down channel, at about 0.6 eV below the $E_F$ for the PM phase, lies exactly on the $E_F$, in the FM phase. Therefore, there is creation of a band gap in the minority spin channel. This rigid band shift appears to be responsible for the FM ground state in this compound. Figures 3(b)–(d) shows the PDOS plots for the Co, Mn and Ge atoms. In figure 3(b) the PDOS plots for Co 4s, $t_{2g}$ and $e_g$ orbitals are shown. It is clear from the figure that, in the case of the spin-up channel, the Co $t_{2g}$ and $e_g$ orbitals are occupied, and for the spin-down channel these states are unoccupied. The occupancy at $E_F$ for $t_{2g}$ and $e_g$ orbitals are

$$2.41 \times 10^{20} (\Omega^{-1} m^{-1} s^{-1})$$ at 1200 K. The value of $\kappa_e/\tau$ increases from $\sim 0.52 \times 10^6$ (W m$^{-1}$K$^{-1}$s$^{-1}$) at 900 K to $\sim 0.72 \times 10^6$ (W m$^{-1}$K$^{-1}$s$^{-1}$) at 1200 K.

![Figure 1. Total and partial density of states plots for Co$_2$MnGe in the paramagnetic phase. Shown are (a) the TDOS plot, (b) PDOS of Co atom, (c) PDOS of Mn atom and (d) PDOS of Ge atom.](image-url)
$e_g$ states are 0.2 states/eV/atom and 0.07 states/eV/atom, respectively. One can also see the negligible contribution of the other states. The PDOS plot of 4s, $t_{2g}$ and $e_g$ bands of Mn atom is presented in figure 3(c). The $t_{2g}$ states mainly contribute ($\sim$ 0.4 states/eV/atom) at the $E_F$ with negligibly small contribution from other states. This result is quite different from the PM phase where both $t_{2g}$ and $e_g$ orbitals contribute to the $E_F$. In figure 3(d) the density of states for 4s, 4p and 3d-orbitals of Ge atoms are presented, and shows a negligibly small contribution of these states at the $E_F$ in comparison to the $t_{2g}$ state of the Co and Mn atoms. This result clearly suggests that the $t_{2g}$ electrons of Mn and Co atoms are responsible for the transport behaviour of the compound.

The dispersion curves are presented in figure 4, along the high symmetry directions of the first Brillouin zone. These dispersion curves also show the half-metallic ground state of this compound. For the spin-up channel in figure 4(a), it is clear that bands 1, 2 and 3 cross the $E_F$ at five k-points and are responsible for the transport properties of this compound. The bands which do not cross the $E_F$ make a negligibly small contribution to the transport properties. The electrons lying in these bands have energy of more than $\sim$1 eV, which corresponds to a temperature of $\sim$12000 K, and are not going to influence the transport properties of the compound in the temperature range studied here. Also, the shift in chemical potential is about 1 meV, which is negligible when compared to the 1 eV mentioned above. Therefore, bands crossing the $E_F$ will mainly contribute to the transport properties of the compound. Bands 4 to 8 have shifted deep into the valence band (VB). The bands which do not cross the $E_F$ make a negligibly small contribution to the transport properties. The electrons lying in these bands have energy of more than $\sim$1 eV, which corresponds to a temperature of $\sim$12000 K, and are not going to influence the transport properties of the compound in the temperature range studied here. Also, the shift in chemical potential is about 1 meV, which is negligible when compared to the 1 eV mentioned above. Therefore, bands crossing the $E_F$ will mainly contribute to the transport properties of the compound. Bands 4 to 8 have shifted deep into the valence band (VB). For spin-down channel bands 1 to 7 have shifted far away from $E_F$ into the conduction band (CB) and there is a clear cut gap between bands 7 and 8, as indicated in figure 4(b). This shifting appears to be mainly responsible for the FM ground state for this compound, as stated earlier. The VB maximum is at $\Gamma$-point and the CB minimum at X-point. Therefore, there exists an indirect band gap in the spin-down channel. The computed energy gap with the LSDA exchange correlation functional is about 0.40 eV, which is smaller than the 0.54 eV [9] energy gap obtained by using a GGA exchange correlation functional. However, Galanakis et al [32] observed no real gap in this full-Heusler alloy when using the full-potential screened Korringa–Kohn–Rostoker (FSKKR) Greens function method, in conjunction with the local spin density approximation. There are three degenerate bands at $\Gamma$-point. Along the $\Gamma$ to L and $\Gamma$ to X directions the degeneracy is partially lifted. The effective mass of the VB is expected to have a much smaller value, in comparison to the CB, as there is an almost flat band in the CB along X in the $\Gamma$-K direction. This flat band is responsible for the negative Seebeck coefficient in the spin-down channel.
S Sharma and S K Pandey

The large effective mass for the CB is expected to give a very high negative value of thermopower in the minority spin channel.

The total magnetic moment per formula unit for this compound is 5.0 $\mu_B$, with the contribution from Co, Mn, Ge and interstitial region is 1.06, 2.84, −0.02 and 0.05 $\mu_B$.

Figure 3. Total and partial density of states plots for Co$_2$MnGe in the ferromagnetic phase. Shown are (a) the TDOS plot, (b) PDOS of Co atom, (c) PDOS of Mn atom and (d) PDOS of Ge atom.

Figure 4. Electronic band structures of ferromagnetic Co$_2$MnGe (a) spin-up channel and (b) spin-down channel.
respectively. The total magnetic moment is in agreement with the experimental value [33]. The Mn atom carries the largest magnetic moment and is ferromagnetically coupled with the Co atom. Although the magnetic moment of Ge is small it is coupled antiferromagnetically with Co and Mn atoms. The integer value of the total magnetic moment confirms its half-metallic character.

The transport coefficients are normally found to be very much sensitive to the k-point sampling of the Brillouin zone. In order to check the k-point's dependence on the transport coefficients we have calculated the Seebeck coefficient (S), electrical conductivity (σ/τ) and electronic thermal conductivity (κ_e/τ) at different k-points for the spin-up channel. These coefficients correspond to 64000, 125000 and 175616 k-points in the full Brillouin zone, as shown in figure 5. It is evident from the figure that at low temperatures S and σ/τ are very much sensitive to the k-points considered in the calculations, whereas κ_e/τ does not show any significant k-point dependence. The values of S and σ/τ above 150 K and 200 K are found to be almost the same for all k-points. Thus, the transport coefficients data below 150 K may not be very reliable. In order to evaluate the low temperature transport behaviour of the compound careful study is required.

The temperature-induced carrier concentration per unit cell, Seebeck coefficient, electrical conductivity and electronic thermal conductivity versus temperature plots, corresponding to both the spin channels, are presented in figure 6. It is clear from figure 6(a) that the value of N increases from ~0.001 e/unit cell at 150 K to ~0.01 e/unit cell at 900 K for the spin-up channel. Figure 6(b) shows that for the spin-down channel the value of N increases from about 10^{-6} e/unit cell at 150 K to about 0.03 e/unit cell at 900 K. From figures 6(c) and (d), it is clear that the obtained value of the Seebeck coefficient is negative for the entire temperature range, which suggests the presence of N-type charge carriers. The absolute value of S increases from ~4 µV K^{-1} at 150 k to ~26 µV K^{-1} at 900 K for the spin-up channel and decreases from ~900 µV K^{-1} at 150 K to ~274 µV K^{-1} at 900 K for the down-spin electrons. At room temperature the obtained values of S are nearly 10 µV K^{-1} and 550 µV K^{-1}, for spin-up and spin-down channels, respectively. Such a large value of S for spin-down electrons is essentially due to the presence of the almost flat CB along X in the Γ direction, as seen in figure 4(b). The electrical conductivity of the spin-up channel is shown in figure 6(e). It is clear from the figure that conductivity first increases from ~4.73 × 10^{20}(Ω^{-1} m^{-1} s^{-1}) at 150 K to ~4.75 × 10^{20}(Ω^{-1} m^{-1} s^{-1}) at 300 K and then decreases slowly with temperature to the value ~4.70 × 10^{20}(Ω^{-1} m^{-1} s^{-1}) at 900 K. At room temperature the value of σ/τ is about 4.75 × 10^{20}(Ω^{-1} m^{-1} s^{-1}). The electrical conductivity of the spin-down channel is shown in figure 6(f). The conductivity increases with increased temperature from ~2 × 10^{15}(Ω^{-1} m^{-1} s^{-1}) at 150 K to ~0.05 × 10^{20}(Ω^{-1} m^{-1} s^{-1}) at 900 K and this compound exhibits semiconductor-like behaviour for down-spin electrons. At room temperature the value of σ/τ is nearly 0.001 × 10^{20}(Ω^{-1} m^{-1} s^{-1}) and is very low in comparison to the up-spin electrons. The electronic thermal conductivities for both spin channels are shown in figures 6(g) and (h). For spin-up electrons the thermal conductivity increases linearly from ~0.17 × 10^{16}(W m^{-1} K^{-1} s^{-1}) at 150 K to ~1 × 10^{16}(W m^{-1} K^{-1} s^{-1}) at 900 K. In the case of down-spin electrons the thermal conductivity shows non-linear variation and increases from ~2 × 10^{15}(W m^{-1} K^{-1} s^{-1}) at 150 K to ~0.04 × 10^{16}(W m^{-1} K^{-1} s^{-1}) at 900 K. The room temperature values of κ_e/τ are about 0.34 × 10^{16}(W m^{-1} K^{-1} s^{-1}) and 0.001 × 10^{16}(W m^{-1} K^{-1} s^{-1}) for spin-up and spin-down electrons, respectively. For both the spins κ_e/τ increases with increases in temperature.

In order to calculate total S one can rewrite the equation (2) as,

\[ S = S(↑) \left\{ \frac{1 + [S(↓)/S(↑)]/[σ(↓)/σ(↑)]} {1 + [σ(↓)/σ(↑)]} \right\} \]  

(3)

Using the room temperature values of S and σ in this equation, we find that the ratio of S(↑) to S(↑) is about 55, whereas the ratio of σ(↑) to σ(↑) is about 0.0001. Due to the extremely small value of S(↑)/σ(↑), in comparison to S(↑)/S(↑) total S is essentially dominated by the value of S(↑) only. The total S obtained by using equation (3) is presented in figure 7. It is evident from the figure that total S is negative and varies linearly with temperature. The value of S increases from ~4 µV K^{-1} at 150 K to ~29 µV K^{-1} at 900 K. The calculated value of
S at room temperature is nearly 10 $\mu$V K$^{-1}$ and is closer to experimental values [17, 34]. At low temperature $\sigma/\tau$ and $\kappa_e/\tau$ are mainly contributed by the spin-up channel, as evidenced in figures 6(c)–(f). We evaluated $\rho$ and $\kappa_e$ at room temperature for the spin-up channel by using the value of $\tau = 0.5 \times 10^{-14}$, because the room temperature value of $\tau$ is typically $10^{-14}$ to $10^{-15}$ seconds [35]. The calculated values of $\rho$ and $\kappa_e$ are 0.42 $\mu\Omega$ m and 17.5 W m$^{-1}$ K$^{-1}$, respectively, which is in good agreement with the experimental values [34].

4. Conclusions

The electronic, magnetic and transport properties of Co$_2$MnGe have been investigated by combining the electronic structures calculated using first principle methods with the Boltzmann transport theory. The paramagnetic and ferromagnetic density of states’ plots, electronic band structures and total energy calculations clearly suggest a half-metallic ferromagnetic ground state for the compound. The indirect band gap from $\Gamma$ to X points is found to be $\sim$400 meV in the spin-down channel. The total magnetic moment obtained from the calculations is 5 $\mu_B$ per formula unit. The integral value of the magnetic moment is in accordance with the half-metallic ground state. For the spin-down channel the value of $S$ is about 55 times greater than that of the spin-up channel and conductivity is

Figure 6. Variation of the transport properties in ferromagnetic phase with temperature for spin-up and spin-down channels. Shown are (a and b) temperature induced carrier concentration per unit cell, (c and d) Seebeck coefficient, (e and f) electrical conductivity and (g and h) electronic thermal conductivity.

Figure 7. Variation of total Seebeck coefficient ($S$) with temperature.

$S$ at room temperature is nearly 10 $\mu$V K$^{-1}$ and is closer to experimental values [17, 34]. At low temperature $\sigma/\tau$ and $\kappa_e/\tau$ are mainly contributed by the spin-up channel, as evidenced
about 0.0001 times smaller. The large value of the Seebeck coefficient in the spin-down channel is attributed to the presence of an almost flat CB along $\Gamma$ in the X direction. By using the two-current model the value of the total Seebeck coefficient comes out to be $\sim 10 \mu V K^{-1}$; only the spin-up channel is found to be responsible for this transport behaviour of the compound. The values of the Seebeck coefficient, resistivity and electronic thermal conductivity show fairly good agreement with the experimental values.

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