FP-LAPW calculations on electronic and thermoelectric properties of Mn₂CoCr Heusler compound

Vipul Srivastava¹*, Navdeep Kaur¹ and Sajad A Dar²

¹Department of Physics, School of Chemical Engineering and Physical Sciences, Lovely Professional University, Phagwara-144411, Punjab State, India
²Department of Physics, Govt. Motilal Vigyan Mahavidyalaya, Bhopal-462001, Madhya Pradesh State, India
*E-mail: vipsri27@gmail.com

Abstract. Heusler compounds have been remarkable among the materials due to their fascinating properties. These materials are also important in terms of applications in thermoelectric device formation. The Mn₂CoCr is one of the Heusler compounds investigated in reference to its band structure and thermo-electric properties by using density functional theory. Mn₂CoCr crystallizes in Fm-3m (space group 225) phase and ferromagnetically stable under ambient conditions. We have calculated its bulk modulus, first order pressure derivative of bulk modulus, band structure, density of states, Seebeck coefficient and power factor.

1. Introduction
On the discovery of Cu₂MnAl by Fritz Heusler in 1903, that it behaves like a ferromagnetic material nevertheless its constituent elements do not show magnetism. Such class of materials came into existence and Cu₂MnAl was the first family member. Not only Cu₂MnAl but now-a-days many more materials [1-3] show such behaviour and are known as Heusler compounds. Further, Heusler compounds are generally intermetallic compounds. Interestingly, these compounds have various applications in different fields and exhibit ferromagnetism, half-metallicity, large magnetic moment, large Curie temperatures, thermoelectric properties [4-6], etc. As far as experimental synthesis and theoretical analysis on such materials are concerned, number of Heusler compounds is being predicted, day by day. As most of the Heusler compounds come into half-metallic category in which one the spins shows its semiconducting nature and other spin shows metallic nature. The theoretical band profile helps to understand such behaviour of the materials. Mn₂CoCr is a full–Heusler compound and crystallizes in Fm-3m symmetry (SG 225). To the best of our knowledge not much attention has so far been paid in the literature. Therefore, an attempt has been made to understand its band profile and other physical properties under ambient as well as low and high temperature. This paper includes calculation on bulk modulus, density of states (DOS), band profile, Seebeck coefficient and power factor using the theory described briefly in below Section. The motivation behind the study is to identify one more candidate of the Heusler compounds family and its suitability for thermoelectric application.

2. Method of calculation
In this Section we have described computation and method of estimation of electronic structure and DOS. The calculations were done using FP-LAPW method [7] with generalized gradient approximations (GGA) [8] following the DFT [9] as executed in Wien2k code [10]. First of all optimization of structure was done. We had considered two phases Fm-3m (Sodium Chloride-type...
structure) and F-43m (Zinc blende-type structure). Mn$_2$CoCr found to be crystallized in Fm-3m structure. The respective atomic positions in this crystal structure were Mn (0.25, 0.25, 0.25), Co (0,0,0) and Cr (0.5, 0.5, 0.5).

For energy convergence $R_{MT}K_{\text{max}}$ was set to 7, where $R_{MT}$ is the muffin tin radius and $K_{\text{max}}$ is largest wave vector in plane-wave progression. The total energy of the system converges by considering stability of total energy within 0.001 Ry and for charge it was 0.001e/a.u.$^3$ per unit cell. 1200 $K$-points were used in Brillouin zone and the tetrahedral method [11] was employed to estimate density of states. More detail of methodology can be found from ref. [12].

In order to investigate transport properties, thermo-electric properties of Mn$_2$CoCr have been calculated by employing semi-classical Boltmann theory as applied in Boltz-Trap code [13] interface with Wien2k code. By using this code, we have estimated Seebeck coefficient and power factor of Mn$_2$CoCr under different temperature range. The details of formulism of calculation of Seebeck coefficient and power factor can be found elsewhere [12]. However, number of theoretical and experimental methods are avialavle to solve problems on materials for further applications [14-18].

3. Results and discussion

3.1 Ground state and electronic band structure

Mn$_2$CoCr is full Heusler compound and has been investigated in reference to its band structure and thermo-electric properties using the methodology explained in Section 2. Optimization of structure can be understood by considering energy-volume (E-V) diagram of Mn$_2$CoCr (Figure 1) in Fm-3m and F-43m phases. Figure 1 depicts, in Fm-3m structure, the minimum of total energy value of -9523.319928 Ryd. calculated to be at equilibrium cell volume of 317.3373 a.u.$^3$. On the other hand, in F-43m structure, the minimum of total energy value of -9523.287901 Ryd. calculated to be at equilibrium cell volume of 305.301 a.u.$^3$. Overall Figure 1 shows stability of the structure in Fm-3m phase. In cubic NaCl-type structure equilibrium cell parameter is found as 5.7296 Å, which is in accordance to the ref. [19]. Further, we have estimated bulk modulus and its first order pressure derivative values as 171 GPa and 5.91, respectively.
Secondly, total energy calculations are also performed for paramagnetic, ferromagnetic and antiferromagnetic phases. It is found that magnetically, ferromagnetic (FM) state is optimized state in NaCl-type structure. Therefore, further calculations are performed in FM state only. In the preliminary work, we have used generalized gradient approximation (GGA).
As far as electronic structure of Mn$_2$CoCr is concerned, we have plotted various electronic states in E-
K diagram in Figure 3 and 4.. The Fermi level is set to zero and it is shown by horizontal line at the
centre of E-K graph. Figure 3 shows band structure of Mn$_2$CoCr for spin up case, while Figure 4
shows band structure for spin down case. From Figure 3, one can notice various electronic states are
present near the Fermi level, $E_f$. These states are mainly due to p-states of Mn, Co and Cr, which is
characterising material to be metallic (spin up case). Similar, behaviour can be understood for spin
down case, nevertheless material seems semiconducting in '┌' direction. Overall band profile of
Mn$_2$CoCr suggests metallic nature in spin down too. In order to understand these electronic states, we
have calculated and plotted DOS in both the spins. Fermi level is set to zero and states crossing this
level in both the Figures 5 and 6, showing its metallic nature. In Figure 5, Mn-$d$ states are found in the
region of -5 to -2 eV, Co-$d$ states can be seen near -2eV and Cr-$d$ states is seen by sharp peak at 2eV.

The inspection of BS and DOS in both the spins are not identical under ambient conditions,
nevertheless showing metallic nature in both spins, may indicate that spin dependent behaviour of
material under pressure and temperature.

3.2 Thermo-electric properties

Initially, Bismuth compound, Bi$_2$Te$_3$ and Silicon-Germanium compounds were found to be the
potential candidates for thermo-electric applications [20]. Bismuth compounds were appropriate for
below room temperature, while Silicon-Germanium compounds were appropriate for elevated
temperature applications. Heusler compounds are being designed and analyzed day by day using
theory because of these compounds are mechanically stable and thermally strong [21]. These materials
are of importance because of possible applications in high temperature thermoelectric power generator
owing to power factor, figure of merit, thermal conductivity, Seebeck coefficient. Dealing with the
Heusler compounds, they show a weakness of providing high thermal conductivity. For this reason
number of solid solutions are made [22] and thermal conductivity is reduced to some extent. On the
other hand, it is always the requirement of materials to fall in such category. Recently, YNiBi [23]
half-Heusler material has been prepared with excellent power factor and less thermal conductivity
value.

Secondly, Seebeck coefficient, also termed as thermo-electric sensitivity, is related with Seebeck
effect and is the measure of induced thermoelectric voltage when material is subjected to temperature
difference. In this regard an effort has been made to calculate Seebeck co-efficient and power factor
under temperature range 100-1000 K of Mn$_2$CoCr Heusler compound. In Figures 7 we show
temperature dependent behaviour of Seebeck coefficient, while similar is done for power factor of Mn$_2$CoCr heusler compound in Figure 8. The value of Seebeck coefficient is estimated to be -17.16 micro volt per Kelvin. Negative sign indicates that charge carriers are predominantly electrons, as band structure (BS) diagram indicates the metallic nature of the material.

![Figure 7. Variation of Seebeck Coefficient under different temperatures for Mn$_2$CoCr.](image1)

![Figure 8. Variation of Power factor under different temperatures for Mn$_2$CoCr.](image2)

To calculate power factor of the material, we have also estimated electrical conductivity for Mn$_2$CoCr. In Figure 8 we have shown the temperature dependent behaviour of power. It is noticed that this power factor increases as temperature increases and it shows maximum value at ~600 K. At room temperature (300K) this value is found to be 6.05 x10$^{10}$ WK$^{-2}$ m$^{-1}$. Gao et. al. have discussed the criteria for increasing power factor upto 30%. [24]. Our present work on thermoelectric properties on Mn$_2$CoCr is purely prediction and open scope for the researchers and technocrats.

4. Conclusion

Full Heusler compound, Mn$_2$CoCr, has been investigated successfully in reference to its band profile, and thermo-electric properties for the first time. Electronic properties were calculated using FPLAPW method implemented in Wien2k code, while thermoelectric properties were estimated by using Boltz-Trap method. Mn$_2$CoCr found stable in ferromagnetic phase in NaCl-type structure. Band profile for both the spins notifies metallic character, which is confirmed by calculating Seebeck co-efficient.

5. References

[1]. Muthui Z, Pathak R, Musembi R, Mwabora J, Skomski R and Kashyap A, Ibrahim A and Smain M 2017 *AIP Advances* 7 055705.
[2]. Belkharroubi F, Mohammed A, Djillali B, Moulay N 2018 *Journal of Magnetism and Magnetic Materials* 448 208.
[3]. Wang P, Xia Jian-Bai, Wu Hai-Bin 2019 *Journal of Magnetism and Magnetic Materials* 490 165490.
[4]. Felser C and Atsufumi H 2016 *Heusler Alloys: Properties, Growth and Applications*, *Springer, Cham, Switzerland* pp-03.
[5]. Lue C S, Huang J W, Tsai D S, Sivakumar K M, Kuo Y K 2008 *J. Phys. Condens. Matter* 20 255233.
[6]. Reshak A H 2014 *R. Soc. Chem. Adv.* 4 39565.
[7]. Blaha P, Schwarz K, Sorantin P, Tricky 1990 *Comput. Phys. Commun.* 59 399.
[8]. Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* 77 3865.
[9]. Schwarz K, Blaha P and Madsen G K H 2002 *Comput. Phys. Commun.* 147 71; Hohenberg P, Kohn W 1964 *Phys. Rev. B* 136 864.
[10]. Blaha P, Schwarz K, Madsen G K H, Kuasnicke D and Luitz J 2001 *Vienna university of technology, Vienna, Austria.*

[11]. Blochl P E, Jepsen O and Andersen O K 1994 *Phys. Rev. B:Condens. Matter Mater. Phys.* 49(23) 16223.

[12]. Dar S A, Sharma R, Srivastava V and Sakalle U K 2019 *R. Soc. Chem. Adv.* 9 9522.

[13]. Madsen G K H and Sing D J 2006 *Comput. Phys. Commun.* 175 67.

[14]. AgnibhaDas M A, Pavras, Munjal N 2019 *Bulletin of Pure & Applied Sciences-Physics* 38d (1) 01-05.

[15]. Salasin J R, Schwerzler S EA, Mukherjee R, Keffer D J, Sickafus K E, Rawn C J 2019 *Materials* 12(1) 84.

[16]. Kaur T, Kumar S, Bhat B H, Srivastava A K 2015 *Journal of materials Research* 30 (18), 2753-2762

[17]. Sarwan B, Chander I S,  Acharya A D, 2019 *AIP Conference Proceedings* 2100(1): 020001

[18]. Gupta M, Kaur D, Shan M, and Diwaker, 2018 *AIP Conference Proceedings* 2006, 030028

[19]. Sanvito S, Oses C, Xue J, Tiwari A, Zic M, Archer T, Tozman P, Venkatesan M, Coey M and Curtarolo S 2017 *Scientific Advances* 3 e1602241.

[20]. Xia Y, Bhattacharya S, Ponnambalam V, Pope A L, Poon S J and Tritt T M 2000 *J. Appl. Phys.* 88 1952.

[21]. Sharma S and Kumar P 2018 *Materials Research Express* 5 46528.

[22]. Hohl H, Ramirez A P, Goldmann C, Ernst G, Wolbing B and Bucher E 1999 *J. Phys.: Condens. Matter* 11 1697.

[23]. Li S, Zhao H, Li D, Jin S and Gu L 2015 *J. Appl. Phys.* 117 205101.

[24]. Gao Yan-Hua, Chen H, Liu N, Zhang Rui-Zhi 2018 *Results in Physics* 11 915.