First principles band structure investigation of cubic spinel CuMn$_2$Te$_4$ compound for thermoelectric applications

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Abstract. Spinel CuMn$_2$Te$_4$ material is investigated for its nonmagnetic and ferromagnetic phases by first principles calculation using the FP-LAPW method. Exchange and correlation are treated with GGA. Total energy calculations reveal that CuMn$_2$Te$_4$ compound tend to stabilise at ferromagnetic phase. Non vanishing bands at the Fermi Energy level illustrates the metallic nature of CuMn$_2$Te$_4$ at both of its nonmagnetic and ferromagnetic phases. Transport properties are studied using the BoltzTraP code at 325K. Thermo power of -26.22µv/k is estimated for nonmagnetic CuMn$_2$Te$_4$. At ferromagnetic phase, these values are predicted as 84.85µv/k and 53.39µv/k respectively for spin-up and spin-down states. Computed power factor values are 2.29 ×10$^{14}$Wm$^{-1}$s$^{-1}$K$^{-2}$ for NM phase and 2.33×10$^{17}$Wm$^{-1}$s$^{-1}$K$^{-2}$/1.001×10$^{10}$Wm$^{-1}$s$^{-1}$K$^{-2}$ respectively for FM up-spin/down-spin phases. A total magnetic moment of 7.11003 µB/F.U. is obtained for the energetically favourable ferromagnetic phase of CuMn$_2$Te$_4$ compound. High pressure investigations reveal the possibility of electronic topological transition that may lead to changes in the Fermi Surface topology and hence changes in the physical properties of nonmagnetic CuMn$_2$Te$_4$.

Keywords: Lotgering model, Thermoelectric, Seebeck coefficient, power factor, compression, ferromagnetic, cubic spinel, Lifshitz transition

1. Introduction

In the present scenario, demand for the global energy and depletion of fossil fuels are increasingly alarming. Henceforth search of alternative energy resources are very much essential and in this regard thermoelectric materials stand as potential candidates due to their possession to convert heat energy directly into electrical energy through the so called Seebeck effect and contribute to the growing demands of energy. Efficiency of the given thermoelectric material is determined by its (ZT) figure of merit given by, $ZT = \frac{S^2\sigma}{K}T$, where $\sigma$ is the electrical conductivity, $S$ is the Seebeck coefficient, $K = (K_e + K_l)$, where $K_e$ is the total thermal conductivity, $K_e$ is the electronic thermal conductivity, $K_l$ is the lattice thermal conductivity and $T$ is the absolute temperature. The term $S^2\sigma$ is often called as the power factor. Potential thermoelectric (TE) material requires simultaneous attainment of high Seebeck coefficient, high electrical conductivity and low thermal conductivity. Generally, high effective mass of ions of the given TE material contributes to higher thermo power or higher Seebeck coefficient whilst the same obstructs the mobility of ions and hence it’s
electrical conductivity. Therefore, this sort of intricate interdependency among these parameters namely S, σ and K often makes the synthesis of TE material to be a challenging [1] one to realise materials with simultaneous high S, high σ and low K. Thermoelectric based power generation is well known since the discovery of Seebeck effect in 1800. However, a very slow progress had been observed in improving the figure of merit but significant developments occurred quite during 1990s [2-5] and noteworthy efforts have been made to identify the materials with higher TE efficiency. Copper based chalcogenides inspired researches for their interesting structural characteristics, higher thermoelectric performance, less toxic nature, low-cost, environment friendly and grabs the attention owing to the presence of abundance of copper in the earth’s crust [6-8]. Spinel structured copper based compounds [9] play a vital role in solid state materials. CuMn$_2$Te$_4$ is a normal spinel with the general chemical formula of AM$_2$X$_4$ mineral and the parent spinel is the MgAl$_2$O$_4$[10].Similar such cubic spinel namely CuTi$_2$S$_4$ with the space group of 227 Fd-3m has been reported by Michail [11] et al., where CuTi$_2$S$_4$ has a low symmetry spinel modification with the spacegroup of rhombohedral R3m and irreversible transformation is possible into cubic spinel at the temperature 450°C. Origin of the present band structure investigation on the compound namely ‘cubic spinel CuMn$_2$Te$_4’ is considered during our investigation on ‘rhombohedral Cu$_4$Mn$_4$Te$_4’ that has been simulated based on the Lotgering Model [12-14]. Ab-initio study on rhombohedral Cu$_4$Mn$_4$Te$_4$ by the authors is reported elsewhere. In this paper, we report here for the first time, the systematic ground state band structure investigation of the cubic spinel CuMn$_2$Te$_4$ at its nonmagnetic and ferromagnetic phases. Transport properties are reported at room temperature. Besides, electronic structure investigation of cubic spinel CuMn$_2$Te$_4$ under hydrostatic compression has been performed for nonmagnetic phase of CuMn$_2$Te$_4$ and it shows a possibility of Lifshitz type of transition.

2. Structural and Computational Details

CuMn$_2$Te$_4$ adopts the normal spinel chemical formula of AM$_2$X$_4$ and lattice parameter of a =11.94 ± 0.02Å with the space group of 227 Fd-3m [10, 14]. In the structure of spinel CuMn$_2$Te$_4$, Cu, Mn and Te occupy 8b tetrahedral vacancy, 16c octahedral vacancy and 32e anion vacancy respectively, where the position of anion varies due to the parameter u, the choice for the ccp u 3m = 0.25[10, 15]. In the present study, first principles investigations on nonmagnetic (NM) and ferromagnetic (FM) phases of CuMn$_2$Te$_4$ have been performed by using the FP-LAPW [16] method based on Density Functional Theory as implemented in the wien2k code [17]. The exchange and correlation potentials are treated approximately by generalized gradient approximation (GGA) [18]. The optimized RMT values of the compound CuMn$_2$Te$_4$ are Cu = 1.7, Mn = 2.0, Te= 2.1. The k-point optimization has been carried out and the calculations are proceeded with 1000 k-points where the Rmt $K_{max}$ Value was set to 7. Energy and charge convergence were acquired with an accuracy of 0.0001 Ry and 0.001e respectively. The energy that separates the core and the valence electron state (E$_{val}$) are set to -6.0 Ry. There are two formula units in the given unit cell. Total energies are calculated by reducing the unit cell volume similar to our previous studies [19, 20] and it has been performed both for the NM and FM phases of the compound CuMn$_2$Te$_4$. Volume optimization curves are drawn where V$_0$ represents the equilibrium unit cell volume, V represents the reduced cell volume and E represents the total energy of the compound at ambient condition. Total energy is fitted into the Birch-Murnaghan equation of states [21] and volume optimisation curves are drawn for nonmagnetic and ferromagnetic phases of CuMn$_2$Te$_4$ as shown in Fig 1(a) and 1(b) respectively. By comparing these curves, one could state that at ambient condition, total energy minima occur for the ferromagnetic phase and hence the compound CuMn$_2$Te$_4$ prefers to be stable in the ferromagnetic phase at ambient condition. Minimum energy difference per formula unit between ferromagnetic and nonmagnetic phases of the compound CuMn$_2$Te$_4$ is observed to be -0.16985 Rydberg. The structural parameters are shown in Table1. Density of states histogram and band structure of cubic CuMn$_2$Te$_4$ is plotted and is discussed in the next section.
Table 1. Structural parameters of cubic nonmagnetic and ferromagnetic phases of the Compound CuMn$_2$Te$_4$.

| Structural parameters | Nonmagnetic CuMn$_2$Te$_4$ | Ferromagnetic CuMn$_2$Te$_4$ |
|-----------------------|-----------------------------|-----------------------------|
| Lattice constant      | $a_{\text{reported}}=11.96\text{Å}^{\circ}(22.60113\text{\,a.u})$ | $a_{\text{reported}}=11.96\text{Å}^{\circ}(22.60113\text{\,a.u})$ |
|                       | $a_{\text{present/opt}}=10.818895\text{Å}^{\circ}(20.4448\text{\,a.u})$ | $a_{\text{present/opt}}=11.2601\text{Å}^{\circ}(21.2785\text{\,a.u})$ |
| Space group           | 227 (Fd-3m)                 | 227 (Fd-3m)                 |
| Position              | Cu (0.375,0.375,0.375)      | Cu (0.375,0.375,0.375)      |
|                       | Mn (0.000,0.000,0.000)      | Mn (0.000,0.000,0.000)      |
|                       | Te (0.250,0.250,0.250)      | Te (0.250,0.250,0.250)      |
| Fermi Energy (Ryd.)   | 0.55074                     | 0.46087                     |
| Total Energy (Ry /2FU)| -124639.57341               | -124639.91311               |
| Magnetic moment       | ------------               | 14.22007 $\mu_B$ (2FU)     |

Figure 1. Volume optimization curves of nonmagnetic and ferromagnetic phases of the compound CuMn$_2$Te$_4$.
3. Results and Discussion

3.1. Density of states histograms of the compound CuMn$_2$Te$_4$

To analyse the electronic properties of cubic spinel CuMn$_2$Te$_4$, the Density of States (DoS) histograms are plotted for its NM and FM phases and are shown in Fig.2 and Fig.3 respectively. From Fig.2, one can state that, at and vicinity of the Fermi energy ($E_F$) level, the contribution towards total DoS arises mainly because of manganese and is found to be less from tellurium and least from copper.

However, from section 2, it is understood that the compound CuMn$_2$Te$_4$ prefers the ferromagnetic phase at its ambient condition. Hence analysis of Figs 3(a) and 3(b) that are drawn respectively for majority and minority spin configuration of FM phase of CuMn$_2$Te$_4$ is analysed and it shows that near and at the Fermi energy level, the contribution from manganese atom is found to be more than that from copper/tellurium. Hence of the three atoms namely copper, manganese and tellurium, manganese atom plays a major role. Further, one can observe hybridisation between (i) Cu-d and Mn-d from Fig3(a) and (ii) between Mn-d and Te-p from Fig 3(b) at their respective bonding states. To analyse the manganese atom’s total DoS contribution, partial density of states of s, p and d-orbitals of manganese are drawn for up and down spin configuration of CuMn$_2$Te$_4$ and are shown in Fig 3(c) and 3(d) respectively. From Fig 3(c) that is drawn for majority spin configuration, one could observe that below $E_F$, there is more contribution of Mn-d states towards the total DoS than Mn-s/Mn-p states. Similarly, from Fig 3(d) that is drawn for the minority spin configuration, it is observed that just above the $E_F$, the contribution from Mn-d is dominated than that of Mn-s and Mn-p states. A total magnetic moment of 7.11003 $\mu_B$ is obtained for one F.U. of ferromagnetic phase of CuMn$_2$Te$_4$.

![Figure 2. Density of states histograms of nonmagnetic CuMn$_2$Te$_4$](image-url)
3.2 Band Structure of the compound CuMn$_2$Te$_4$

Electronic band structure plot of nonmagnetic CuMn$_2$Te$_4$ is shown in the Fig.4 where one could observe nearly flat bands around the $E_F$ and are due to Mn-d states. Band structures of ferromagnetic CuMn$_2$Te$_4$ for spin-up and spin-down configurations are shown in the Fig 5(a) and 5(b). In Fig 5(a), the bands that lie around the Fermi Energy level are due to Te-p and Cu-d/Mn-d electrons at its majority state and are due to Mn-d and Te-p at their minority state(Fig.5(b)). Low lying bands are due to s-orbitals. Non-vanishing bands that crosses the Fermi Energy level suggests the metallic nature of ferromagnetic and nonmagnetic phase of CuMn$_2$Te$_4$. An analogous behaviour is reported for the compound CuCr$_2$Te$_4$[22].
Parabolic like bands seen around the Fermi energy level in the up-spin state of ferromagnetic CuMn$_2$Te$_4$ are due to Te-p states.

![Band structure plot of nonmagnetic CuMn$_2$Te$_4$](image1)

**Figure 4.** Band structure plot of CuMn$_2$Te$_4$ at Nonmagnetic phase

![Band structure plot of CuMn$_2$Te$_4$ at Ferromagnetic Phase](image2)

**Fig.5.** Band structure plot of CuMn$_2$Te$_4$ at Ferromagnetic Phase

3.3. Transport properties of the compound CuMn$_2$Te$_4$

Presence of nearly flat bands around the Fermi Energy level motivates us to compute the transport properties of the compound CuMn$_2$Te$_4$ in order to look for the thermoelectric performance of the material. The same is studied by using the Boltztrap code [23] and the obtained values are listed in Table 2. From this table, it is observed that at 325 K, the Seebeck coefficient ($\mu v/k$) value is given by -26.22µv/k for nonmagnetic CuMn$_2$Te$_4$ and for ferromagnetic phase of CuMn$_2$Te$_4$ these values are computed as 84.85↑ and 53.39↓ respectively for up-spin and down-spin configuration. The negative Seebeck coefficient values of nonmagnetic CuMn$_2$Te$_4$ compound exhibits the n-type nature of the material and the positive Seebeck
coefficient values of ferromagnetic CuMn$_2$Te$_4$ shows the p-type nature of the material in both the up and down spin configuration of the compound. Hence it paves the way for the possibility of synthesis of both n-type and p-type material from the same parent cubic spinel CuMn$_2$Te$_4$. Positive and the negative values of thermo power ‘$S$’ indicates that the majority of charge carriers are holes and electrons respectively. The power factor ($\text{Wm}^{-1}\text{s}^{-1}\text{K}^{-2}$) values are scaled with relaxation time and through the computations power factor values of $2.33 \times 10^{17}$ and $1.001 \times 10^{10}$ are estimated for the majority and minority states of ferromagnetic phase of CuMn$_2$Te$_4$ respectively while the same for nonmagnetic phase of CuMn$_2$Te$_4$ is estimated as $2.29 \times 10^{14}$. Generally, ‘flat’ bands are considered to be ‘heavy’ bands as they arise due to high effective mass of the ions involved and they contribute to higher thermo power ($S$) as it is proportional to the effective mass of the ions; while the more ‘dispersive’ bands are considered to be ‘lighter’ bands as they are associated with less effective mass and hence higher mobility of ions involved [24]. Hence it is understood that attaining higher thermo electric power should be possible if one looks for the combination of both heavy and lighter bands around the Fermi Energy level. In our present study, one could observe, comparatively more number of such combination of ‘flat and dispersive bands’ around the Fermi Energy level (Fig 5(a)) at the ‘Γ’ point in the band structure of ‘majority spin’ configuration of the ferromagnetic CuMn$_2$Te$_4$ than the other down-spin configuration (Fig 5(b)). This may be attributed to the high thermo power offered by the energetically favoured ferromagnetic phase of the compound CuMn$_2$Te$_4$ at its ambient condition during its up-spin configuration.

### Table 2. Transport properties of Non-magnetic CuMn$_2$Te$_4$ and Ferromagnetic CuMn$_2$Te$_4$.

| Parameters | Nonmagnetic CuMn$_2$Te$_4$ | Ferromagnetic CuMn$_2$Te$_4$ |
|-----------|-----------------------------|------------------------------|
| $\sigma/\tau$ ($\Omega^{-1}\text{m}^{-1}\text{s}^{-1}$) | $0.33349 \times 10^{20}$ | $0.32491 \times 10^{26}$ $\uparrow$ $3.51027 \times 10^{19}$ $\downarrow$ |
| $K_{\text{electron}}$ ($\text{Wm}^{-1}\text{K}^{-1}\text{S}$) | $0.28204 \times 10^{15}$ | $0.26024 \times 10^{21}$ $\uparrow$ $3.03373 \times 10^{14}$ $\downarrow$ |
| $S$ ($\mu\text{V/K}$) | -26.22 | 84.85 $\uparrow$ 53.39 $\downarrow$ |
| $S^2\sigma/\tau$ ($\text{Wm}^{-1}\text{s}^{-1}\text{K}^{-2}$) | $2.29 \times 10^{14}$ | $2.33 \times 10^{17}$ $\uparrow$ $1.001 \times 10^{10}$ $\downarrow$ |

3.4. High pressure band structure study of the compound CuMn$_2$Te$_4$

Electronic structure investigation of NM-CuMn$_2$Te$_4$ are performed for various hydrostatic compressions namely $V/V_0 = -30$, -10, 0, 5, 10. Obtained density of states at Fermi energy level N(E$_F$), electronic specific heat coefficient, pressure, and total energy are given in Table 3. A graph is plotted (Fig .6) between density of states at E$_F$(N(E$_F$)) with compression($V/V_0$) and one can note that N(E$_F$) started decreasing from $V/V_0 = -30$ and after that one can note a sharp increase at $V/V_0 = 0$ and attains the maximum at $V/V_0 = 5$ then falls at $V/V_0 = 10$. i.e., the graph shows a type of non-monotonic variation of N(E$_F$) with compression. This is an indication that the material CuMn$_2$Te$_4$ may exhibit Electronic Topological Transition or Lifshitz type of transition i.e., by applying pressure there may be changes in the Fermi surface.
topology [25-27] and hence changes in the physical properties of the nonmagnetic phase of the Cubic CuMn$_2$Te$_4$ compound.

![Figure 6. Density of states under compression of cubic CuMn$_2$Te$_4$ nonmagnetic phase.](image)

**Table 3.** Density of states at Fermi Energy level, Electronic specific heat coefficient, pressure and total energy of nonmagnetic CuMn$_2$Te$_4$ under compression.

| V/V$_0$ | N(E$_F$) Ryd/2(F.U) | Electronic specific heat coefficient mJ/mol K$^{-2}$/ (F.U)/Ryd | Volume (a.u.)$^3$ | Pressure (GPa) | Energy (Ry)/2.F.U |
|---------|------------------|-------------------------------------------------|-----------------|----------------|-------------------|
| -30     | 571.50           | 49.30                                           | 2020.3595       | 5.153          | -124639.5539     |
| -10     | 421.74           | 36.44                                           | 2597.6052       | -9.772         | -124639.3876     |
| 0       | 512.07           | 44.30                                           | 2886.2280       | -11.663        | -124638.1742     |
| 5       | 2106.76          | 182.20                                          | 3030.5394       | -12.056        | -124639.0576     |
| 10      | 1765.36          | 151.60                                          | 3174.8508       | -12.219        | -124639.9383     |

**4. Conclusion**

In Summary, we state that at ambient condition, the compound cubic spinel CuMn$_2$Te$_4$ prefers the ferromagnetic phase as there is a minimum total energy difference of -0.16985 Rydberg/F.U. is detected with this FM phase when compared to its non-magnetic phase. Good agreement between the optimised lattice parameter with the already reported one and the percentage of error in calculating the lattice parameters for FM-CuMn$_2$Te$_4$ is 0.059. Manganese atom (Mn-d) is observed to play a significant role in deciding the properties of the material as it contributes more to the total density of states in the vicinity of the Fermi energy level. The same is justified from the band structure studies of ferromagnetic phase of the compound CuMn$_2$Te$_4$ and the compound CuMn$_2$Te$_4$ exhibits metallic nature as the bands cross the Fermi Energy level. Transport properties of CuMn$_2$Te$_4$ reveals that there is an enhancement power factor by the order of $10^3$ for the energetically favored FM (↑) phase than the corresponding FM (↓) and NM phases of the compound CuMn$_2$Te$_4$ and is supported with the occurrence of flat and dispersive bands in the respective
band structure plot. High pressure investigation reveals that non-monotonic variation of $N(E_F)$ with compression. This suggests ETT or Lifshitz transition and hence Fermi surface / physical property changes is possible for $\text{CuMn}_2\text{Te}_4$ compound.

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