First-Principles study of thermoelectric properties of Half-Metallic Non-Magnetic Half-Heusler alloy Mn$_2$Ge

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Abstract. Research about Heusler alloys have been massively conducted through experimental and theoretical studies due to their fascinating properties. Most of Heusler alloy compounds exhibit half-metallic behavior, in which one of the spin channels of such a material behaves as a metal and the other behaves as an insulator because there is an open energy gap at the Fermi level. On the other hand, the thermoelectric properties of the materials usually work well in the insulator or semiconductor phase rather than in the metal phase. Motivated by such interesting phenomena, we conduct first-principles study to explore the thermoelectric properties of Mn$_2$Ge, one of Heusler compounds that exhibit half-metallic behavior. Our calculation results show that Mn$_2$Ge of the spin-down channel has a high Seebeck coefficient and ZT value (electron part) at room temperature around 892 μV/K and 0.97, respectively. The positive sign of the Seebeck coefficient on spin-up and spin down indicate that the majority charge carrier in Mn$_2$Ge are positive charges (holes).

1. Introduction

The discovery of Heusler alloys in the 20$^{th}$ century gave rise to extensive researches because of their fascinating properties [1]. Heusler alloys are well known by their magnetic properties that can be utilized such as for spintronic technology, shape-memory materials, superconductors, and thermoelectric devices [2]. The magnetic moment of these materials in many cases can be predicted by a simple calculation known as the Slater-Pauling rule (SP-rule) [3]. For the specific case of half-Heusler alloys, many of which are believed to have potential for thermoelectric (TE) applications [4], its magnetic moment ($m$) can be predicted by using the formula

$$ m = N_{\text{VEC}} - 18, $$

where $N_{\text{VEC}}$ is the number of valance electrons per formula unit. Equation (1) suggests that one can tune the magnetic moment of this class of materials by changing its constituent elements. This triggers many researches to deal with these materials [5–7]. In general, the family of Heusler alloys is very interesting because it offers extensive tunability through chemical substitutions and structural motifs [8]. All Heusler alloy compounds known today are found to be half-metals, meaning that one spin direction behaves as a metal, and the other spin direction behaves as an insulator with an open energy gap around the Fermi level. This half-metallic behavior with a typical small energy gap for one spin makes the materials promising for thermoelectric applications. In this research, we are interested in...
Mn$_2$Ge, one of the half-Heusler materials which has a unique behavior since it has been theoretically predicted to have zero net magnetic moment [9], hence, unlike most other half-metallic materials which are ferro- or ferrimagnetic, Mn$_2$Ge is not magnetic. This fact motivates us to investigate its thermoelectric properties.

Thermoelectric effect is a phenomenon occurring in a material where one can directly convert the temperature difference across the material to electric voltage and vice versa through a thermocouple mechanism [10]. Theoretically, the half-metallicity in Heusler alloys allows one to separate the thermoelectric properties of the material according to the spin-up and spin-down channel at the Fermi level. This idea is expected to lead to fascinating properties promising for technological applications. Here, we conduct first-principles Density-Functional Theory (DFT) calculations using Quantum-Espresso package [11] followed by BoltzTraP package [12], to investigate the thermoelectric properties of half-Heusler Mn$_2$Ge. In order to study the effect of the half-metallicity on the thermoelectric properties we conduct the calculations for two different magnetic phases, that is the paramagnetic phase and the antiferromagnetic phase.

2. Method
We conduct the DFT calculations by running Quantum-Espresso (QE) package to obtain the band structure, density of states (DOS), and the magnetic moment of Mn$_2$Ge [11]. To reduce the computing time, we perform parallel computation using the Message Passing Interface (MPI) [13]. To investigate the effect of half-metallicity, we perform the calculations for two magnetic phases of Mn$_2$Ge, that is, the paramagnetic (PM) phase and anti-ferromagnetic (AFM) phase. In the PM case, we restrict the DFT calculation such that the electron density or wave functions corresponding to both spin components are always the same. While, for the AFM case, we initialize the DFT calculation by letting the magnetic moment of the electrons around one Mn atom to be opposite to that of the other Mn atom in a unit cell, and allow the electron density of different spin components to evolve independently. For further technical details of the DFT calculations, we use the Perdew-Zunger (LDA) exchange-correlation pseudopotential of the Psilibrary [14]. Mn$_2$Ge has the crystal structure of C1b with lattice constant of 3.862 Å and with Wyckoff positions of Mn (1), Mn (2), and Ge located at (0,0,0), (0.25,0.25,0.25), and (0.75,0.75,0.75), respectively, as shown in figure 1 (a) [15].

![Figure 1](image)

Figure 1. (a) Conventional unit cell of Mn$_2$Ge, (b) Primitive unit cell of Mn$_2$Ge.

3. Result and Discussion
3.1 Density of states (DOS) and Band Structure
For both the PM phase and AFM phase, we use 12 × 12 × 12 k-points grid mesh in self-consistency calculation (SCF), and 24 × 24 × 24 k-points grid mesh in non-self-consistent calculation (NSCF). We dense the k-points grid in NSCF calculation in order to obtain a good quality DOS and accurate chemical potential value. The chemical potential value of the PM phase system is 12.458 eV and lies down both in spin-up and in spin-down bands, indicating that both spin-up and spin-down states are metallic.
The identical DOS of spin-up and spin-down of PM phase shown in figure 2 (a), of course, gives the zero net magnetic moment value.

![DOS of Mn2Ge: (a) Paramagnetic phase and (b) Anti-ferromagnetic phase.](image)

In the AFM phase calculation, we give initial magnetic moments of \(0.5 \mu_B\) for \(\text{Mn}_1\) atom and \(-0.5 \mu_B\) for \(\text{Mn}_2\) atom in the unit cell. We obtain that both the SCF and NSCF calculations converge to AFM phase, yielding zero net magnetic moment in the system. However, the DOS and the band structure are different for different spin components. The spin-down channel forms a gap around which the chemical potential lies, while the spin-up channel forms no gap, hence we obtain that \(\text{Mn}_2\text{Ge}\) is half-metallic with AFM phase. The half-metallicity in Heusler alloys is governed by the correlation effects among the electrons in the d-states atoms [16]. Within DFT, these effects are incorporated in the exchange-correlation energy functional, which, to some degree, manifests both the on-site Coulomb repulsions and the spin-dependent magnetic exchange interactions. These effects are prevented to appear when we do the calculation with spin-up and spin-down wave functions being forced to be equal, as it is confirmed by comparing between the DOS of PM and AFM phases.

![AFM phase band structure of Mn2Ge: (a) spin-up and (b) spin-down](image)

3.2 Electrical Conductivity and Electron Thermal Conductivity

Figure 4 shows the temperature-dependent electrical conductivity per \(\tau\) of \(\text{Mn}_2\text{Ge}\) for spin-up and spin-down. In this scenario, \(\tau\) is assumed to be a constant, and its value is typically of \(10^{-14} \sim 10^{-15}\) seconds. In figure 4 (a), the spin-up channel electrical conductivity of \(\text{Mn}_2\text{Ge}\) displays a metallic behavior, which gives the same result as in the PM phase (figure not shown). On the other hand, the spin-down channel acts as an insulator with no spectrum under 300 K.

As we see in figure 4, the value of \(\sigma\) increases as the temperature is increased, and the trend of \(\sigma\) typically shows that the material act as a good metal. The information about electron transport is in...
agreement with the electron thermal conductivity (ETC) data of Mn$_2$Ge as shown in figure 5 which indicates that ETC increases as the temperature of the system is increased.

From the electron thermal conductivity data as shown in figures 5 (a) and (b), the ETC of the spin-up channel follows the natural trend of a metal that still has values at low temperatures. This situation is very different from the PM phase in which both of the spin-up and spin-down channels act as a metal. Conversely, the ETC of the spin-down channel shows the natural trend of insulator or semiconductor, which has no values in the low temperature range. From the information above, it is clear that the behavior of spin-up and spin-down channels are very different around the Fermi level where the spin-up channel acts as a metal while the spin-down channel acts as an insulator or a semiconductor. Note that the thermal conductivity has two contributions, one from electrons (κ$_e$) and the other from phonons (κ$_{ph}$), i.e. κ = κ$_e$ + κ$_{ph}$. In this study, however, we ignore the phonon contribution for the moment, since the calculation for κ$_{ph}$ requires a rather expensive calculation.

3.3. Seebeck Coefficient
The Seebeck coefficient of Mn$_2$Ge in PM phase (figure not shown) shows the metallic behavior with positive majority charge carrier (holes). The Seebeck coefficient values are very low and only achieve around 20 $\mu$V/K at 900 K. This situation makes this material in the PM phase not good for TE application.

Figures 6 (a) and (b) show the Seebeck coefficient of Mn$_2$Ge in AFM phase for spin-up channel and spin-down channel, respectively. In the spin-up channel, the Seebeck coefficient increases as the temperature is increased and its trend is quite similar to that of the PM phase with low Seebeck coefficient values. In the spin-down channel, the Seebeck coefficient decreases as the temperature is increased and shows a good trend of the p-type thermoelectric material even for high temperature regime in the order of $10^2$ $\mu$V/K.
3.4. Figure of Merit

$ZT$ is the figure of merit that measures the relative utility of the material to be used for thermoelectric application. The $ZT$ values of the PM phase only achieve the highest value around 0.01 at 900 K and give low values at room temperature (figure not shown).

The low $ZT$ in PM phase is caused by the low Seebeck coefficient due to the metallic behavior of the system that gives high ETC which in turn reduces the $ZT$ values. Figures 7 (a) and (b) show the $ZT$ of Mn$_2$Ge from the electron contribution for spin-up and spin-down channel, respectively. The $ZT$ values of the spin-up channel are very low and the highest value is only around 0.08 at 900 K. The low $ZT$ value at spin-up channel is caused by the metallic behavior similar to that of the PM phase which gives low Seebeck coefficient but high ETC. On the other hand, the $ZT$ value of the spin-down channel is quite high around 0.99 at 150 K and stays at high value of 0.97 at the room temperature. The $ZT$ value of the spin-down channel then decreases as the temperature is increased because the electron thermal conductivity increases very fast as the temperature is increased. However, the $ZT$ value at 900 K is still quite high around 0.83.

4. Conclusion

We have performed first-principles density functional theory calculation to study the thermoelectric behavior of half-Heusler Mn$_2$Ge. Our results show that, in the paramagnetic phase, Mn$_2$Ge behaves as a metal, while in anti-ferromagnetic phase, Mn$_2$Ge shows the half-metallic behavior where the spin-up channel acts as a metal, and the spin-down channel acts as an insulator or a semiconductor. We also obtain the Seebeck coefficient and figure of merit (electron part) of the spin-down electrons at room temperature around 892 $\mu$V/K and 0.97, respectively. In 900 K, the spin-down channel still gives high Seebeck coefficient and figure of merit (electron part) around 401 $\mu$V/K and 0.83, respectively. As we
still neglect the contribution from phonons to the calculation of figure of merit \((ZT)\) of \(\text{Mn}_2\text{Ge}\), we realize that our results may not yet give a fully realistic prediction for the real material. In order to improve our calculation results so as to give a more realistic prediction of the \(ZT\) values, we acknowledge that the phonon contribution to the thermal conductivity needs to be taken into account.

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