

# Magnetic Full-Heusler Compounds for Thermoelectric Applications

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## Abstract

Full-Heusler compounds exhibit a variety of magnetic properties such as non-magnetism, ferromagnetism, ferrimagnetism and anti-ferromagnetism. In recent years, they have attracted significant attention as potential thermoelectric (TE) materials that convert thermal energy directly into electricity. This chapter reviews the theoretical and experimental studies on the TE properties of magnetic full-Heusler compounds. In Section 1, a brief outline of TE power generation is described. Section 2 introduces the crystal structures and magnetic properties of full-Heusler compounds. The TE properties of full-Heusler compounds are presented in Sections 3 and 4. The relationship between magnetism, TE properties and order degree of full-Heusler compounds is elaborated.

**Keywords:** full-Heusler compounds, half-metal, spin-gapless semiconductor, thermoelectric properties, order degree

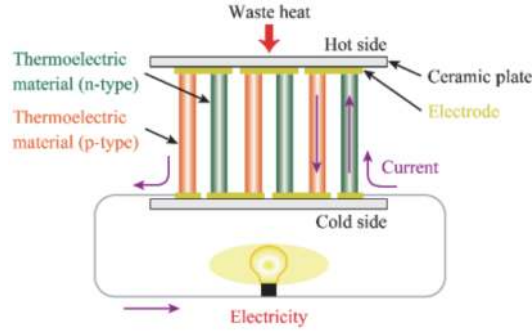
## 1. Introduction

Thermoelectric (TE) power generation using TE devices is one of the key technologies to solve global energy problem, owing to its availability of direct conversion of thermal energy into electricity [1–3]. A schematic figure of a TE device is shown in **Figure 1**. It consists of n- and p-type TE materials connected in series electrically with metal electrodes and arranged thermally in parallel. The TE materials are wedged between ceramic plates. When one side of the device is heated and the other side is cooled, electrons and holes in the n- and p-type TE materials, respectively, diffuse from the hot side to the cold side, thus generating a flow of electric current.

To commercialise TE devices, there is a need to improve their TE efficiency. The maximum TE efficiency,  $\eta_{\max}$ , is an increasing function of the dimensionless figure-of-merit,  $zT$ , expressed as:

$$\eta_{\max} = \frac{T_H - T_C}{T_H} \frac{\sqrt{1 + zT} - 1}{\sqrt{1 + zT} + T_C/T_H}, \quad (1)$$

where  $T_H$  and  $T_C$  are the heating and cooling temperature, respectively. The dimensionless figure-of-merit,  $zT$ , is determined by TE properties ( $S$ : Seebeck



**Figure 1.**  
Schematic figure of a thermoelectric (TE) power generation device.

coefficient,  $\sigma$ : electrical conductivity,  $\kappa$ : thermal conductivity) of the individual TE materials in the device.

$$zT = \frac{S^2 \sigma}{\kappa} T, \quad (2)$$

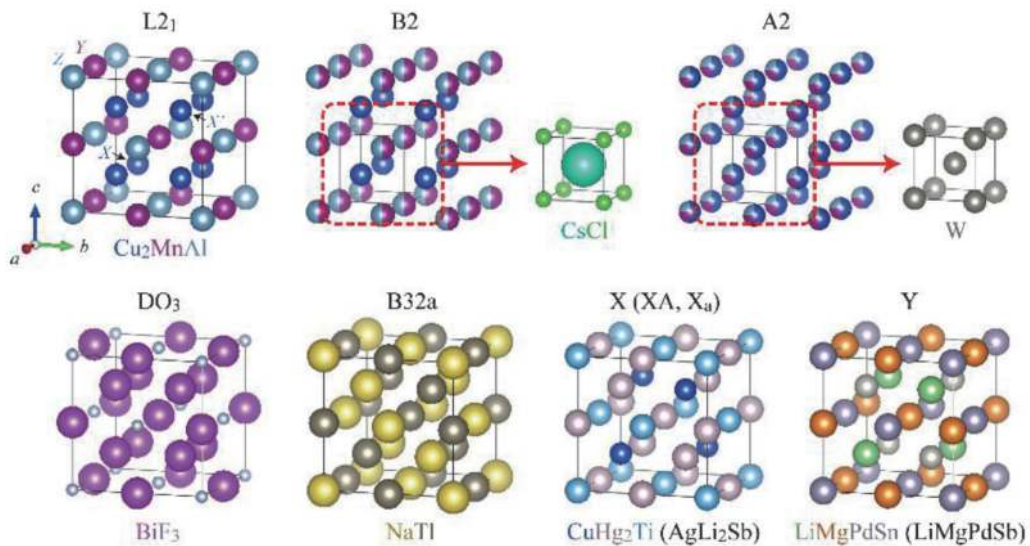
where  $T$  is the absolute temperature. The product  $S^2 \sigma$  is called the power factor (PF), which is a measure of electric power generated using the TE material. To achieve high TE efficiency (standard levels for practical use are  $zT > 1$  and  $PF > 2 \times 10^{-3} \text{ W/K}^2\text{m}$ ), high  $S$ , high  $\sigma$  and low  $\kappa$  are required. To meet these requirements, a variety of TE materials have been explored, such as chalcogenides, skutterudites, clathrates, silicides, Zintl compounds, half-Heusler compounds and oxides [1–3]. Most of these materials are semiconductors because in general they have high  $S$  than metals. However, recent theoretical and experimental studies have revealed that metals, in particular, half-metallic full-Heusler compounds have relatively high  $S$  as well as high  $\sigma$ . In addition, their junction with a metal electrode is robust compared to that of semiconductors, which is also an advantage.

In Section 2, the crystal structures and magnetic properties of full-Heusler compounds are introduced. Sections 3 and 4 demonstrate that magnetic full-Heusler compounds are promising for the TE power generation device.

## 2. Crystal structures and magnetic properties of full-Heusler compounds

The physical properties of full-Heusler compounds depend on their crystal structures. As shown in **Figure 2**, there are several types of crystal structures with different order degrees [4–6]. The full-Heusler compounds have four interpenetrating fcc sublattices, and each sublattice consists of the  $X$ ,  $X'$ ,  $Y$  or  $Z$  atom. The  $X$ ,  $X'$  and  $Y$  atoms are transition metals, whereas  $Z$  is a main group element. In some cases, the  $Y$  atom is a rare earth element or an alkaline earth metal.

When the  $X$  and  $X'$  atoms are of the same element, the chemical composition of the compounds is written as  $X_2YZ$ , which generally crystallises in the  $L2_1$  structure. The prototype of the  $L2_1$  structure is  $\text{Cu}_2\text{MnAl}$  (space group:  $Fm\bar{3}m$ ). The Cu atoms occupy the  $8c$  ( $1/4 \ 1/4 \ 1/4$ ) site, whereas the Mn and Al atoms occupy the  $4b$  ( $1/2 \ 1/2 \ 1/2$ ) and  $4a$  ( $0 \ 0 \ 0$ ) sites, respectively. The  $L2_1$  structure is a highly ordered structure of the full-Heusler compounds. Disorder among the Cu, Mn and/or Al atoms, that is, antisite defects, gives rise to different crystal structures. In a case where the Mn and Al atoms are evenly located at the  $4b$  and  $4a$  sites, the  $\text{Cu}_2\text{MnAl}$  becomes the B2 structure. Its prototype is CsCl (space group:  $Pm\bar{3}m$ ). In a fully



**Figure 2.** Crystal structures of full-Heusler compounds. The Strukturbericht symbol and a prototype structure are written above and below each crystal structure, respectively.

disordered phase, all the atoms are randomly distributed in the  $8c$ ,  $4b$  and  $4a$  sites, thus resulting in the A2 structure. In such a structure, all the sites are equivalent, which are expressed as a bcc lattice (prototype: W, space group:  $Im\bar{3}m$ ). There are other disordered phases, including the DO<sub>3</sub> and B32a structures. The former is caused by the random distribution of the X, X' and Y atoms at the  $8c$  and  $4b$  sites (prototype: BiF<sub>3</sub>, space group:  $Fm\bar{3}m$ ). In the B32a structure, the  $8a$  (0 0 0) and  $8b$  ( $1/2$   $1/2$   $1/2$ ) sites are occupied by the X/Y and X'/Z atoms, respectively. The prototype is NaTl (space group:  $Fd\bar{3}m$ ).

When the X' and Y atoms are of the same element, the chemical composition becomes  $XX'_2Z$ , which crystallises in the X (XA or X<sub>a</sub>) structure. This structure is called the inverse Heusler phase. The prototype is CuHg<sub>2</sub>Ti (or AgLi<sub>2</sub>Sb), and the space group is  $F\bar{4}3m$ . In the structure, the X and Z atoms occupy the  $4d$  ( $3/4$   $3/4$   $3/4$ ) and  $4a$  (0 0 0) sites, respectively, and the X' atoms occupy the  $4b$  ( $1/2$   $1/2$   $1/2$ ) and  $4c$  ( $1/4$   $1/4$   $1/4$ ) sites.

In addition to the above ternary full-Heusler compounds, there are quaternary full-Heusler compounds,  $XX'YZ$ , which crystallise in the Y structure (prototype: LiMgPdSn or LiMgPdSb, space group:  $F\bar{4}3m$ ). The X, X', Y and Z atoms are situated at the  $4d$ ,  $4b$ ,  $4c$  and  $4a$  sites, respectively, occupying one of the fcc sublattices. It should be noted that the inverse Heusler and the quaternary full-Heusler phases are ordered phases, and any disorder among the constituent atoms causes a structural change; the structure changes to the B2, A2, DO<sub>3</sub> or B32a structure.

Earlier theoretical studies demonstrated a half-metallic nature in full-Heusler compounds [7, 8]. Since then, many studies have been dedicated to investigate the electronic and magnetic properties of ternary and quaternary full-Heusler compounds. It has been revealed that full-Heusler compounds exhibit a variety of electronic properties; they exhibit the properties of semiconductors [9–18], spin-gapless semiconductors (SGSs) [19–26], semimetals [27–29], metals [30–34] and half-metals (HMs) [32, 35–78]. Considering the magnetic properties, they have been reported to exhibit nonmagnetism [9–11, 14–18], ferromagnetism [12, 19–24, 30–33, 36–46, 48–58, 61–66, 68–78], ferrimagnetism [13, 30, 35, 47, 59, 60, 67] and antiferromagnetism [25, 26, 34]. The full-Heusler, inverse Heusler and quaternary Heusler compounds obey the Slater-Pauling rule [79–81]: the total spin

magnetic moment per unit cell scales with the total number of valence electrons in the unit cell.

### 3. Thermoelectric properties of half-metallic full-Heusler compounds

In this section, we present some of the theoretical and experimental studies on the TE properties of half-metallic full-Heusler compounds. The TE properties can be calculated on the basis of the Boltzmann transport equations [82–84]. Using the electronic energy-wavenumber dispersion curve of the  $i$ -th band  $\varepsilon_i(\mathbf{k})$ , the tensors of the Seebeck coefficient,  $S(T)$ , electrical conductivity,  $\sigma(T)$ , and carrier thermal conductivity,  $\kappa_e(T)$ , can be expressed as:

$$S(T) = -\frac{1}{|e|T} \frac{\int_{-\infty}^{+\infty} \tilde{\sigma}(\varepsilon, T) (\varepsilon - \varepsilon_F) \left( -\frac{\partial f_{\text{FD}}(\varepsilon, T)}{\partial \varepsilon} \right) d\varepsilon}{\sigma(T)}, \quad (3)$$

$$\sigma(T) = \int_{-\infty}^{+\infty} \tilde{\sigma}(\varepsilon, T) \left( -\frac{\partial f_{\text{FD}}(\varepsilon, T)}{\partial \varepsilon} \right) d\varepsilon, \quad (4)$$

$$\kappa_e(T) = -\frac{1}{e^2 T} \int_{-\infty}^{+\infty} \tilde{\sigma}(\varepsilon, T) (\varepsilon - \varepsilon_F)^2 \left( -\frac{\partial f_{\text{FD}}(\varepsilon, T)}{\partial \varepsilon} \right) d\varepsilon - \frac{1}{e^2 T} \frac{\left\{ \int_{-\infty}^{+\infty} \tilde{\sigma}(\varepsilon, T) (\varepsilon - \varepsilon_F) \left( -\frac{\partial f_{\text{FD}}(\varepsilon, T)}{\partial \varepsilon} \right) d\varepsilon \right\}^2}{\sigma(T)}, \quad (5)$$

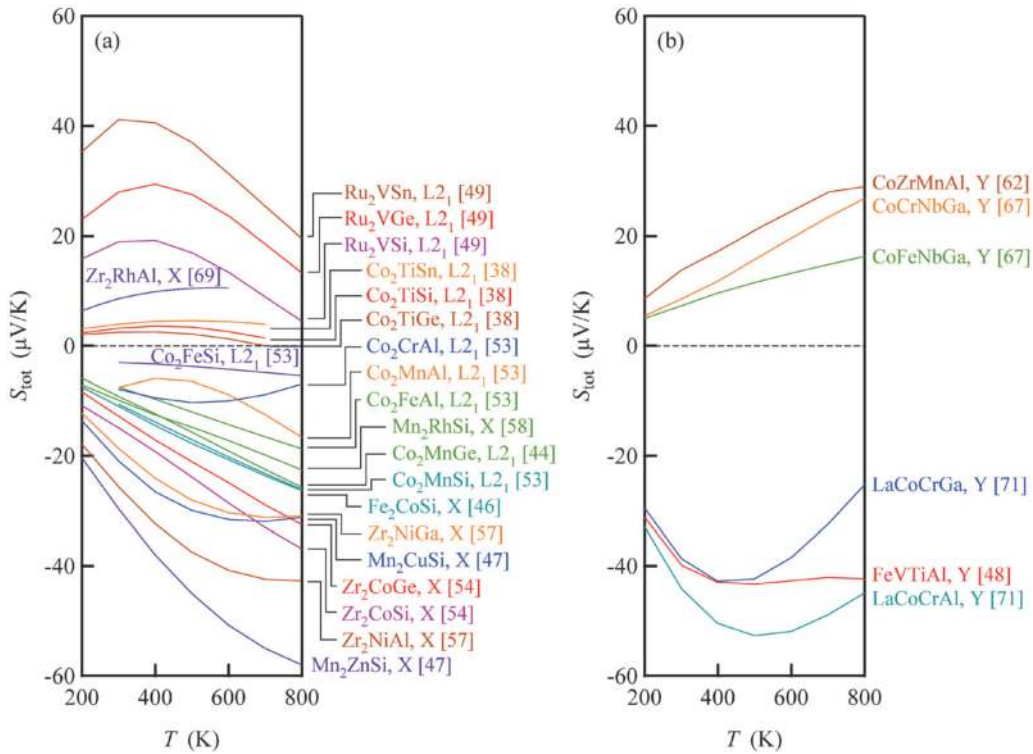
$$\tilde{\sigma}_{\alpha\beta}(\varepsilon, T) \equiv \frac{1}{N_k} \sum_{i,k} \frac{e^2 \tau(k, T)}{\hbar^2} \frac{\partial \varepsilon_i(k)}{\partial k_\alpha} \frac{\partial \varepsilon_i(k)}{\partial k_\beta} \delta(\varepsilon - \varepsilon_i(k)), \quad (\alpha, \beta = x, y, z), \quad (6)$$

where  $e$ ,  $\varepsilon$ ,  $\varepsilon_F$ ,  $f_{\text{FD}}(\varepsilon, T)$ ,  $N_k$ ,  $\tau(k, T)$ , and  $\tilde{\sigma}(\varepsilon, T)$  are the elementary charge, electron energy, Fermi level, Fermi-Dirac distribution function, total number of the  $k$ -points, relaxation time, Dirac constant and conductance spectrum tensor, respectively. It is difficult to calculate the relaxation time; hence, the calculation of TE properties generally gives  $S(T)$ ,  $\sigma(T)/\tau$  and  $\kappa_e(T)/\tau$  [84]. In context to magnetic materials, the electronic states of the majority and minority spin electrons are considered. Assuming that  $\tau$  for the majority and minority spin electrons is the same, the total  $S$  for the magnetic materials,  $S_{\text{tot}}(T)$ , is calculated by

$$S_{\text{tot}}(T) = \frac{S_{\uparrow}(T)\sigma_{\uparrow}(T)/\tau + S_{\downarrow}(T)\sigma_{\downarrow}(T)/\tau}{\sigma_{\uparrow}(T)/\tau + \sigma_{\downarrow}(T)/\tau} = \frac{S_{\uparrow}(T)\sigma_{\uparrow}(T) + S_{\downarrow}(T)\sigma_{\downarrow}(T)}{\sigma_{\uparrow}(T) + \sigma_{\downarrow}(T)}, \quad (7)$$

where  $S$  and  $\sigma$  with the up- and down-arrow subscripts those evaluated from the electronic states of the majority and minority spin electrons, respectively.

**Figure 3(a)** and **(b)** shows the temperature dependence of the calculated  $S_{\text{tot}}$  for ternary and quaternary half-metallic full-Heusler compounds, respectively. To calculate the electronic band, the full-potential linearised augmented plane wave (FLAPW) method was employed, adopting the local spin density approximation (LSDA) or the generalised gradient approximation in the Perdew-Burke-Ernzerhof parametrisation (PBE-GGA) as the local exchange-correlation potential. As seen in the figure, the negative and positive  $S_{\text{tot}}$  are presented, indicating that both n-type and p-type materials can be obtained from half-metallic full-Heusler compounds. The  $S_{\text{tot}}$  is observed to increase with increasing temperature for almost all the compounds, which is the typical behaviour of metal. Furthermore, the  $S_{\text{tot}}$  is observed to attain values as high as several tens of  $\mu\text{V}/\text{K}$ . These values are lower



**Figure 3.** Temperature dependence of the calculated  $S_{tot}$  for half-metallic full-Heusler compounds. Their crystal structures are also shown. The calculation of the electronic structure was performed using the full-potential linearised augmented plane wave (FLAPW) method with local spin density approximation (LSDA) or generalised gradient approximation in the Perdew–Burke–Ernzerhof parametrisation (PBE–GGA).

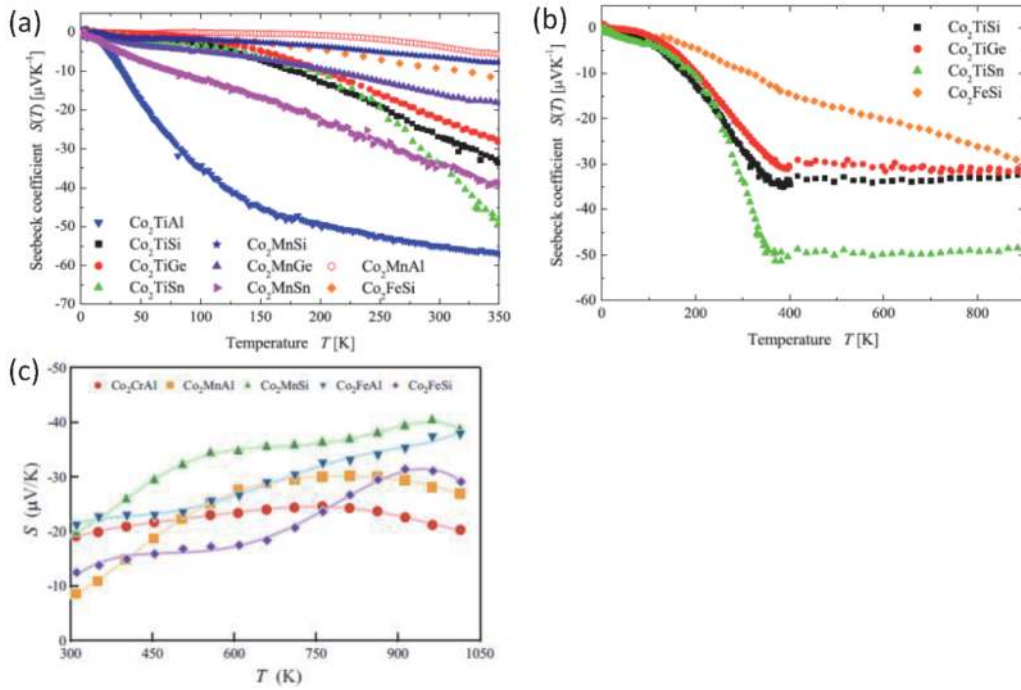
than those of TE semiconductors but higher than those of common metals, demonstrating the potential of half-metallic full-Heusler compounds as high-temperature TE materials.

The temperature dependence of  $S$  for several half-metallic Co-based full-Heusler compounds was determined by Balke et al. [37] and Hayashi et al. [53]. For the measurements, the  $S_{tot}$  values for the compounds were obtained. Hereafter, we use  $S$  to represent  $S_{tot}$ . As shown in **Figure 4(a)–(c)**, the Co-based full-Heusler compounds exhibit negative  $S$  in the order of several tens of  $\mu\text{V/K}$ . For metals, the sign of  $S$  is well explained by Mott’s formula [85]:

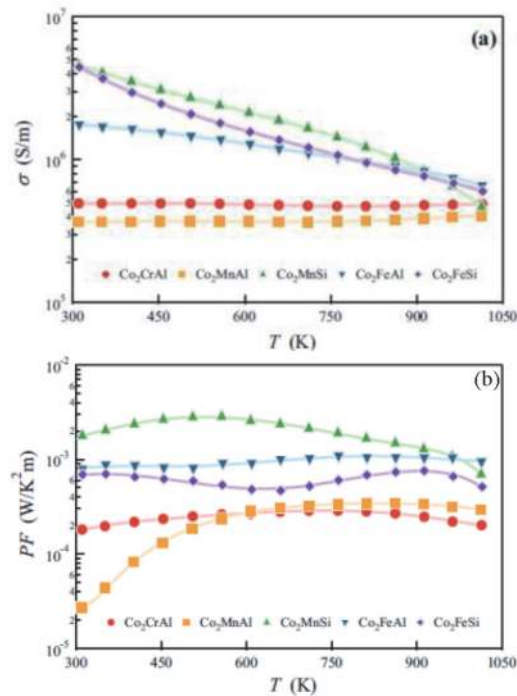
$$S \propto - \left. \frac{1}{\text{DOS}(\epsilon_F)} \frac{d \text{DOS}(\epsilon)}{d\epsilon} \right|_{\epsilon=\epsilon_F}, \quad (8)$$

where DOS is the electronic density of states. Adopting Eq. (8) for the partial DOS of the  $sp$ -electrons and  $d$ -electrons of Co<sub>2</sub>MnSi, it was obtained that in half-metallic full-Heusler compounds, the itinerant  $sp$ -electrons contribute more to  $S$  than the localised  $d$ -electrons [53]. In **Figure 4**, Co<sub>2</sub>TiAl is shown to exhibit the highest  $|S|$  of  $|-56| \mu\text{V/K}$  at 350 K among other compounds. It is observed that Co<sub>2</sub>TiSi, Co<sub>2</sub>TiGe and Co<sub>2</sub>TiSn exhibit a characteristic temperature dependence of  $|S|$ ; the value of  $|S|$  increases with increasing temperature and becomes constant at temperatures above 350 K. This characteristic behaviour is further discussed later in this section.

The half-metallic full-Heusler compounds are predicted to have high electrical conductivity  $\sigma$  owing to their metallic properties; hence, they are considered to be superior to the semiconductors. **Figure 5(a)** shows the temperature dependence of



**Figure 4.** Temperature dependence of the measured  $S$  of several Co-based full-Heusler compounds. ((a) and (b) Reprinted from [37]. Copyright 2010, with permission from Elsevier. (c) Reprinted from [53]. Copyright 2017, with permission from Springer).



**Figure 5.** (a) Measured  $\sigma$  and (b)  $PF$  of several Co-based full-Heusler compounds as a function of temperature. (Reprinted from [53]. Copyright 2017, with permission from Springer).

the measured  $\sigma$  for several Co-based full-Heusler compounds [53]. The  $\sigma$  values of the compounds are observed to be high, ranging from  $10^5$  to  $10^7$  S/m. Among all the compounds,  $\text{Co}_2\text{MnSi}$  exhibits the highest  $\sigma$  in the whole temperature range. The  $\sigma$

value of  $\text{Co}_2\text{MnSi}$  decreases from  $4.6 \times 10^6 \text{ S/m}$  at 300 K to  $4.7 \times 10^5 \text{ S/m}$  at 1000 K. This is a typical electrical conductivity-temperature relation in metals. From the  $S$  and  $\sigma$  values (shown in **Figures 4(c)** and **5(a)**, respectively), the PF was calculated and plotted in **Figure 5(b)** [53]. Owing to the high  $S$  and high  $\sigma$ ,  $\text{Co}_2\text{MnSi}$  exhibits the highest PF ( $2.9 \times 10^{-3} \text{ W/K}^2\text{m}$  at 500 K) among other compounds, which is comparable to that of a  $\text{Bi}_2\text{Te}_3$ -based material [86]. Since  $\text{Co}_2\text{MnSi}$  exhibits a negative  $S$ , it could be a potential n-type TE material. Thus, to develop a TE device using full-Heusler compounds, a p-type counterpart to  $\text{Co}_2\text{MnSi}$  is needed. For this purpose, Li et al. [60, 78] prepared a half-metallic  $\text{Mn}_2\text{VAl}$  compound and measured its TE properties. Although  $\text{Mn}_2\text{VAl}$  is a p-type material showing positive  $S$ , its highest PF ( $2.84 \times 10^{-4} \text{ W/K}^2\text{m}$  at 767 K [78]) is lower than that of  $\text{Co}_2\text{MnSi}$ . Thus, there is a need to explore more p-type half-metallic full-Heusler compounds with high PF.

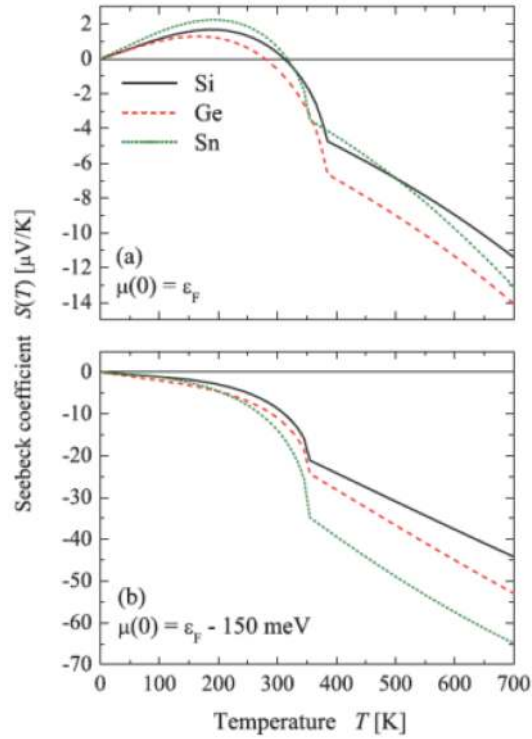
Here, the temperature dependence of  $S$  for the various full-Heusler compounds is discussed. Comparing the calculated  $S$  values for  $\text{Co}_2\text{TiSi}$ ,  $\text{Co}_2\text{TiGe}$  and  $\text{Co}_2\text{TiSn}$  (**Figure 3(a)**) with the measured values (**Figure 5(b)**), it is obtained that not only the temperature dependence but also the sign of the  $S$  values are different. As mentioned earlier, the measured  $S$  value is almost constant at temperatures above 350 K; however, the calculated values do not display such relation. To explain this difference, Barth et al. [38] considered the difference in the electronic structure of the ferromagnetic (FM) state and nonmagnetic (NM) states. They obtained that the FM-NM phase transition occurs around 350 K for  $\text{Co}_2\text{TiSi}$ ,  $\text{Co}_2\text{TiGe}$  and  $\text{Co}_2\text{TiSn}$  [38]. Using the temperature dependence of  $S$  for the FM and NM states,  $S_{\text{FM}}(T)$  and  $S_{\text{NM}}(T)$ , and that of the normalised magnetisation calculated by using the molecular field theory,  $M(T)$ , a modified  $S$  value,  $S_{\text{FM} + \text{NM}}$ , can be calculated according to the formula [38]:

$$S_{\text{FM}+\text{NM}}(T) = \frac{S_{\text{FM}}(T)\sigma_{\text{FM}}(T)M(T) + S_{\text{NM}}(T)\sigma_{\text{NM}}(T)\{1 - M(T)\}}{\sigma_{\text{FM}+\text{NM}}(T)}, \quad (9)$$

where  $\sigma_{\text{FM} + \text{NM}}$  is the modified electrical conductivity of a mixture of FM and NM states weighted by using  $M(T)$ . Although the above consideration is plausible, the calculated  $S_{\text{FM} + \text{NM}}$  values for  $\text{Co}_2\text{TiSi}$ ,  $\text{Co}_2\text{TiGe}$  and  $\text{Co}_2\text{TiSn}$  (**Figure 6**) do not coincide with the measured values. The inconsistency between the  $S_{\text{FM} + \text{NM}}$  values and the measured ones is also observed in the case of  $\text{Co}_2\text{CrAl}$ ,  $\text{Co}_2\text{MnAl}$ ,  $\text{Co}_2\text{MnSi}$ ,  $\text{Co}_2\text{FeAl}$  and  $\text{Co}_2\text{FeSi}$  [53].

It is suggested that the constant  $S$  value in the NM state for  $\text{Co}_2\text{TiSi}$ ,  $\text{Co}_2\text{TiGe}$  and  $\text{Co}_2\text{TiSn}$  (**Figure 4(b)**) is governed by the relaxation time rather than by the electronic structure [38]. The  $S$  value is calculated by using Eq. (1), where both the numerator and denominator of the fraction are functions of relaxation time  $\tau(k, T)$ ;  $\tau$  is included in both numerator and denominator of the fraction through  $\tilde{\sigma}(\epsilon, T)$  described in Eq. (6). However, in the calculation, the  $\tau$  in the numerator and denominator cancels each other. In addition, the total  $S$  is calculated assuming that  $\tau$  for the majority and minority spin electrons is the same (Eq. (7)). The neglected  $\tau$  in Eqs. (1) and (7) could be a reason for the difference in the temperature dependence of the calculated and measured  $S$ . Another possible reason for this discrepancy is the method employed in calculating the electronic structure. The calculation results shown in **Figures 3** and **6** are based on the LSDA or PBE-GGA. The use of the onsite Hubbard interaction in combination with PBE-GGA, namely, PBE + U or GGA + U [51, 55, 70, 73], and the Tran-Blaha modified Becke-Johnson (TB-MBJ) [64, 73] gives electronic structures different from that obtained using the LSDA or PBE-GGA, which may lead to a temperature dependence of  $S$  well-fitted to the measured one.

Also, defect and/or disorder in full-Heusler compounds affect the temperature dependence, as well as the sign of  $S$ , which could be another reason for the



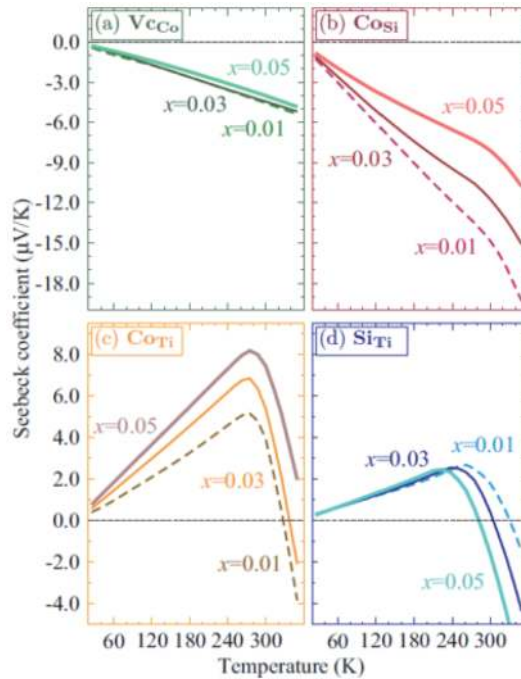
**Figure 6.**

Temperature dependence of the calculated  $S$  of  $\text{Co}_2\text{TiZ}$  ( $Z = \text{Si}, \text{Ge}, \text{Sn}$ ) considering the FM-NM phase transition. In the calculation, the chemical potential at  $T = 0$ ,  $\mu(0)$ , was set to (a)  $\epsilon_F$  and (b)  $150 \text{ meV}$  below  $\epsilon_F$ . (Reprinted from [38]. Copyright 2010, with permission from American Physical Society).

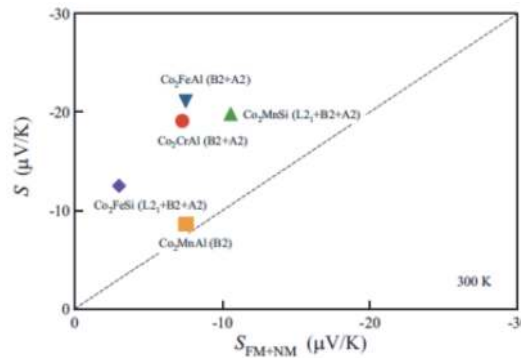
discrepancy in the temperature dependence of  $S$ . The structure model used for the calculation in **Figures 3** and **6** is the  $L2_1$ , X or Y structure, which is highly ordered phases, devoid of any defect, for the ternary and quaternary full-Heusler compounds. Popescu et al. [52] investigated the effect of several defects on the temperature dependence of  $S$  for  $\text{Co}_2\text{TiZ}$  ( $Z = \text{Si}, \text{Ge}, \text{Sn}$ ) in the FM state. As shown in **Figure 7**, off-stoichiometric defects, such as Co vacancy and the substitution of excess atoms at a particular site, change the sign of  $S$ .

The effect of structural disorder on  $S$  for  $\text{Co}_2\text{CrAl}$ ,  $\text{Co}_2\text{MnAl}$ ,  $\text{Co}_2\text{MnSi}$ ,  $\text{Co}_2\text{FeAl}$  and  $\text{Co}_2\text{FeSi}$  has been obtained, as shown in **Figure 8** [53]. The figure compares the calculated  $S_{\text{FM} + \text{NM}}$  with the measured  $S$ . It is observed that the measured values of  $S$  are individually higher than the calculated value ( $S_{\text{FM} + \text{NM}}$ ). Considering the crystal structure,  $\text{Co}_2\text{CrAl}$ ,  $\text{Co}_2\text{MnAl}$ ,  $\text{Co}_2\text{MnSi}$ ,  $\text{Co}_2\text{FeAl}$  and  $\text{Co}_2\text{FeSi}$  are not in the fully ordered  $L2_1$  structure; most of them crystallise in the disordered B2 and/or A2 structures. This result implies that the B2 and/or A2 structures exhibit higher  $S$  than the  $L2_1$  structure. Recently, Li et al. [78] investigated the effect of structural disorder on the value of  $S$  for half-metallic  $\text{Mn}_2\text{VAl}$  compounds by varying the B2 order degree. **Figure 9(a)** shows the measured  $S$  values for  $\text{Mn}_2\text{VAl}$  with the B2 order degree of 27 and 66%. The  $S$  values for the structure having 66% B2 order degree are observed to be higher than those for 27% B2 order degree in the entire measurement temperature range. In addition, it is observed that the  $S$  value increases with increasing the B2 order degree (**Figure 9(b)**). The increase in the B2 order degree means an increase in the disorder between the V and Al atoms, that is, a decrease in the  $L2_1$  order degree. To understand the reason for the difference in  $S$  between the  $L2_1$  and B2 structures, the DOS of  $\text{Mn}_2\text{VAl}$  with the  $L2_1$  and B2 structures was calculated by using the Korringa-Kohn-Rostoker method. It was obtained that the B2 structure exhibits a steeper DOS of the majority-spin  $sp$ -electrons than the  $L2_1$





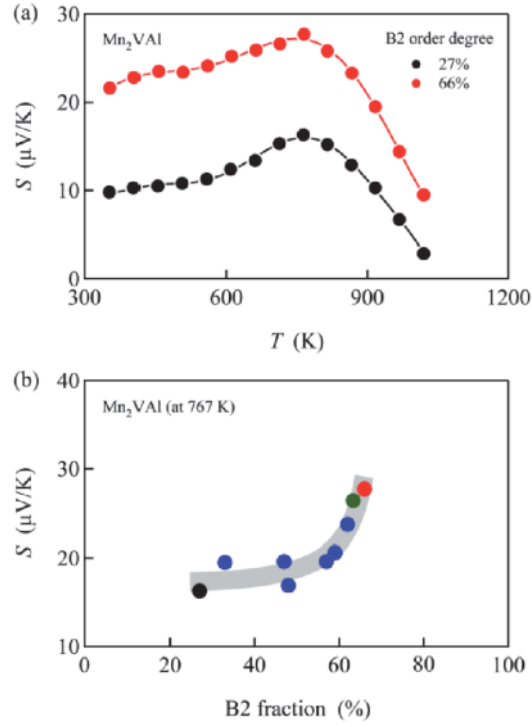
**Figure 7.** Change in calculated  $S$  for  $\text{Co}_2\text{TiSi}$  with several off-stoichiometric defects such as (a) Co vacancy ( $V_{\text{Co}}$ ), (b) excess Co atoms at the Si site ( $\text{Co}_{\text{Si}}$ ), (c) excess Co atoms at the Ti site ( $\text{Co}_{\text{Ti}}$ ) and (d) excess Si atoms at the Ti site ( $\text{Si}_{\text{Ti}}$ ). (Reprinted from [52]. Copyright 2017, with permission from American Physical Society).



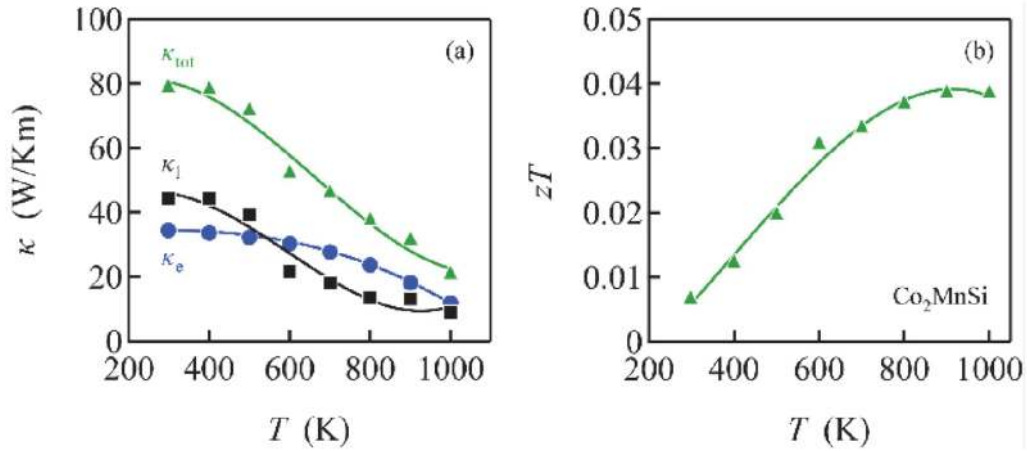
**Figure 8.** Comparison between the calculated  $S_{\text{FM} + \text{NM}}$  and the measured  $S$  at 300 K for several Co-based full-Heusler compounds. (Reprinted from [53]. Copyright 2017, with permission from Springer).

structure, which is considered as the main reason for the higher  $S$  of the B2 structure than that of the  $L2_1$  structure. Further increase in the B2 order degree is expected to yield a higher  $S$  for  $\text{Mn}_2\text{VAI}$ . The modulation of the order degree can be a key strategy to enhance the  $S$  value of the half-metallic full-Heusler compounds; the disorder in  $\text{Co}_2\text{CrAl}$ ,  $\text{Co}_2\text{MnAl}$ ,  $\text{Co}_2\text{MnSi}$ ,  $\text{Co}_2\text{FeAl}$ ,  $\text{Co}_2\text{FeSi}$  and  $\text{Mn}_2\text{VAI}$  gives rise to the higher  $S$ . To establish this strategy, the effects of the order degree, not only on  $S$  but also on  $\sigma$ , should be investigated for several half-metallic full-Heusler compounds.

Considering the TE performance of the half-metallic full-Heusler compounds, not only PF but also  $zT$  are important. To evaluate the  $zT$  of  $\text{Co}_2\text{MnSi}$ , we obtained the temperature dependence of the total thermal conductivity,  $\kappa_{\text{tot}}$  (**Figure 10(a)**). Similar to the case of common metals, a high  $\kappa_{\text{tot}}$  was obtained. It decreases with increasing temperature from 79 W/Km at 300 K to 21 W/Km at 1000 K.


**Figure 9.**

(a) Temperature dependence of the measured  $S$  of  $\text{Mn}_2\text{VAl}$  with the B2 order degree of 27 and 66%.  
 (b) Measured  $S$  values of  $\text{Mn}_2\text{VAl}$  at 767 K plotted against the B2 order degree. (Reprinted from [78].  
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**Figure 10.**

Temperature dependence of (a) measured  $\kappa_{\text{tot}}$ ,  $\kappa_e$  and  $\kappa_l$  and (b) evaluated  $zT$  of  $\text{Co}_2\text{MnSi}$ .

**Figure 10(b)** shows the temperature dependence of  $zT$  for  $\text{Co}_2\text{MnSi}$  calculated using the PF value (**Figure 5(b)**) and the  $\kappa_{\text{tot}}$  value (**Figure 10(a)**). Due to the high  $\kappa_{\text{tot}}$ , the maximum  $zT$  value,  $zT_{\text{max}}$ , of  $\text{Co}_2\text{MnSi}$  is 0.039, which is obtained at temperatures above 900 K. Although this  $zT_{\text{max}}$  value is far below the standard level of  $zT = 1$ , it is higher than that of  $\text{Co}_2\text{TiSn}$  (0.033 at 370–400 K) [38] and those of semi-metallic full-Heusler compounds (0.0052 at 300 K for  $\text{Ru}_2\text{NbAl}$  [28] and 0.0027 at 300 K for  $\text{Ru}_2\text{VAl}_{0.25}\text{Ga}_{0.75}$  [29]).

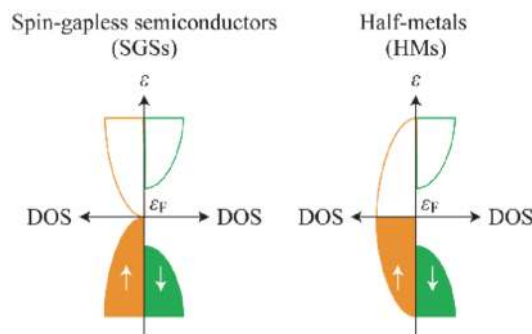
It should be noted that the  $\kappa_{\text{tot}}$  of  $\text{Co}_2\text{MnSi}$  is not equal to the carrier thermal conductivity,  $\kappa_e$ . The  $\kappa_e$  value can be calculated by using the Wiedemann-Frantz

law,  $\kappa_e = L\sigma T$ , where  $L$  is the Lorentz number. Evaluating the  $L$  value on the basis of the single parabolic band model [87] and using the measured  $\sigma$  value (**Figure 5(a)**), the  $\kappa_e$  value of  $\text{Co}_2\text{MnSi}$  was calculated and plotted in **Figure 10(a)**. It can be observed from the figure that  $\kappa_e$  is only half as high as  $\kappa_{\text{tot}}$ . The rest is attributed to the lattice thermal conductivity,  $\kappa_1 (= \kappa_{\text{tot}} - \kappa_e)$ , as shown in **Figure 10(a)**, which amounts to a half of the  $\kappa_{\text{tot}}$ . This is contrary to the case of common metals where the  $\kappa_{\text{tot}}$  is mainly dominated by  $\kappa_e$  [88]. The non-negligible  $\kappa_1$  suggests that, for the theoretical evaluation of  $zT$  of the half-metallic full-Heusler compounds, the contribution of  $\kappa_1$  should not be ignored. Experimentally, the high contribution of  $\kappa_1$  to  $\kappa_{\text{tot}}$  indicates that the  $\kappa_{\text{tot}}$  of half-metallic full-Heusler compounds could be reduced by decreasing the  $\kappa_1$ .

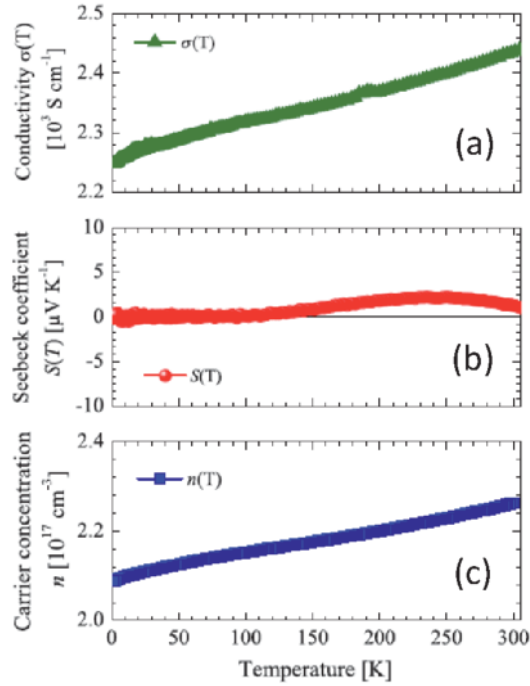
#### 4. Future prospects of magnetic full-Heusler compounds as potential thermoelectric materials

In this section, we introduce other full-Heusler compounds to demonstrate the potentials of magnetic full-Heusler compounds in TE applications. First, we consider the full-Heusler SGSs as an example. Schematic illustrations of the DOS of SGSs and HMs are shown in **Figure 11**. The DOS of SGSs has an open band gap in one spin electron and a closed gap in the other. Since the Fermi level  $\varepsilon_F$  is located just at the closed gap, the electron or hole concentration in SGSs is expected to be less than that in HMs. One of the investigated SGSs is the full-Heusler  $\text{Mn}_2\text{CoAl}$ , which crystallises in the X structure (the inverse Heusler phase). The variation of its  $\sigma$ ,  $S$  and carrier concentration,  $n$ , with temperature is shown in **Figure 12**, as determined by Ouardi et al. [19]. It can be observed that the  $\sigma$  and  $n$  vary slightly with the temperature, which is attributed to the typical behaviour of gapless semiconductors [89]. In addition, the  $S$  value is nearly equal to 0  $\mu\text{V/K}$ . The reduced Seebeck effect indicates the occurrence of electron and hole compensation, which is the evidence that  $\varepsilon_F$  is at the top of the valence states and at the bottom of the conduction states.

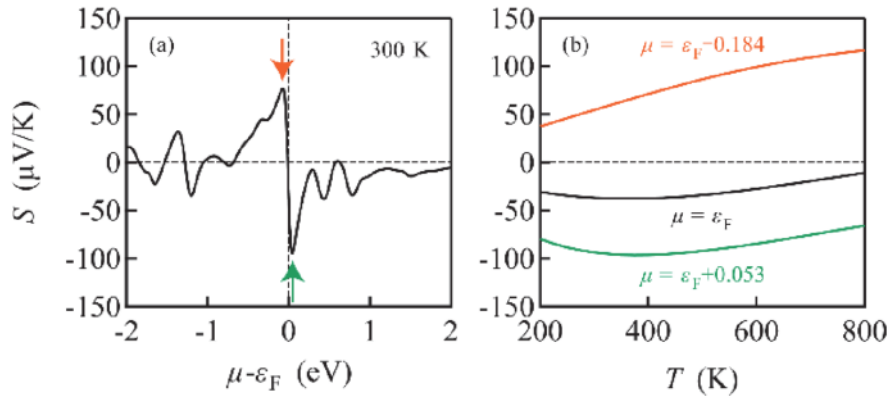
Owing to the nearly zero  $S$  values,  $\text{Mn}_2\text{CoAl}$  cannot be used as a TE material; however, there is a possibility of achieving high  $|S|$  in  $\text{Mn}_2\text{CoAl}$  by tuning the position of  $\varepsilon_F$ . The position of  $\varepsilon_F$  can be varied via partial substitution, which increases the hole or electron carrier concentration in  $\text{Mn}_2\text{CoAl}$ . We calculated the  $S$  value for the partially substituted  $\text{Mn}_2\text{CoAl}$ , as shown in **Figure 13(a)**. The calculation was based on a rigid band model; thus, the electronic structure of the partially substituted  $\text{Mn}_2\text{CoAl}$  is assumed to be the same as that of  $\text{Mn}_2\text{CoAl}$ . In the figure, the horizontal axis is  $\mu - \varepsilon_F$ , where  $\mu$  and  $\varepsilon_F$  are the chemical potential (i.e., the Fermi



**Figure 11.** Schematic illustration of DOS for spin-gapless semiconductors (SGSs) and half-metals (HMs).


**Figure 12.**

Temperature dependence of the measured (a)  $\sigma$ , (b)  $S$  and (c)  $n$  of  $Mn_2CoAl$ . (Reprinted from [19]. Copyright 2020, with permission from American Physical Society).


**Figure 13.**

(a) Calculated  $S$  value at 300 K for the partially substituted  $Mn_2CoAl$  plotted as a function of  $\mu - \epsilon_F$ , where  $\mu$  and  $\epsilon_F$  are the Fermi levels of partially substituted  $Mn_2CoAl$  and that of  $Mn_2CoAl$ , respectively. The highest  $|S|$  values are obtained at  $\mu = \epsilon_F - 0.184$  and at  $\mu = \epsilon_F + 0.053$ , as denoted by orange and green arrows, respectively. (b) Temperature dependence of  $S$  at  $\mu = \epsilon_F$ ,  $\mu = \epsilon_F - 0.184$  and  $\mu = \epsilon_F + 0.053$ .

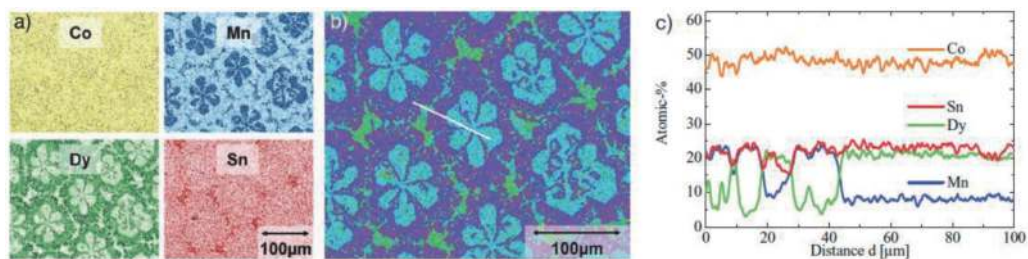
level) of the partially substituted  $Mn_2CoAl$  and the Fermi level of  $Mn_2CoAl$ , respectively. A negative/positive  $\mu - \epsilon_F$  value means an increase in the hole/electron carrier concentration. Although the value of  $S$  at  $\mu = \epsilon_F$ , corresponding to the case of  $Mn_2CoAl$ , is small, it is large at  $\mu = \epsilon_F - 0.184$  and at  $\mu = \epsilon_F + 0.053$  (pointed by orange and green arrows, respectively). The temperature dependences of  $S$  at  $\mu = \epsilon_F$ ,  $\mu = \epsilon_F - 0.184$  and  $\mu = \epsilon_F + 0.053$  are shown in **Figure 13(b)**, which again demonstrates that high  $|S|$  values can be achieved for both p-type and n-type regions. These calculation results prove the full-Heusler SGSs as potential materials for TE applications.

To achieve high  $|S|$  values for  $\text{Mn}_2\text{CoAl}$ , it is important to retain its SGS characteristic. Galanakis et al. [90] theoretically investigated the effects of structural disorder on the electronic structure of  $\text{Mn}_2\text{CoAl}$ . It was obtained that the SGS characteristic is not conserved in the presence of Mn-Co, Mn-Al and Co-Al antisite defects. Instead of the closed gap, low DOS intensity emerges in the electronic structure of the majority spin electrons around  $\varepsilon_F$ , indicating that the disorder induces half-metallic characteristics in  $\text{Mn}_2\text{CoAl}$ . Also, Xu et al. [91] reported that an as-prepared  $\text{Mn}_2\text{CoAl}$  compound is non-stoichiometric and contains the Mn-Co antisite defect. In a case where  $\text{Mn}_2\text{CoAl}$  is not an SGS, the  $|S|$  cannot be increased via partial substitutions.

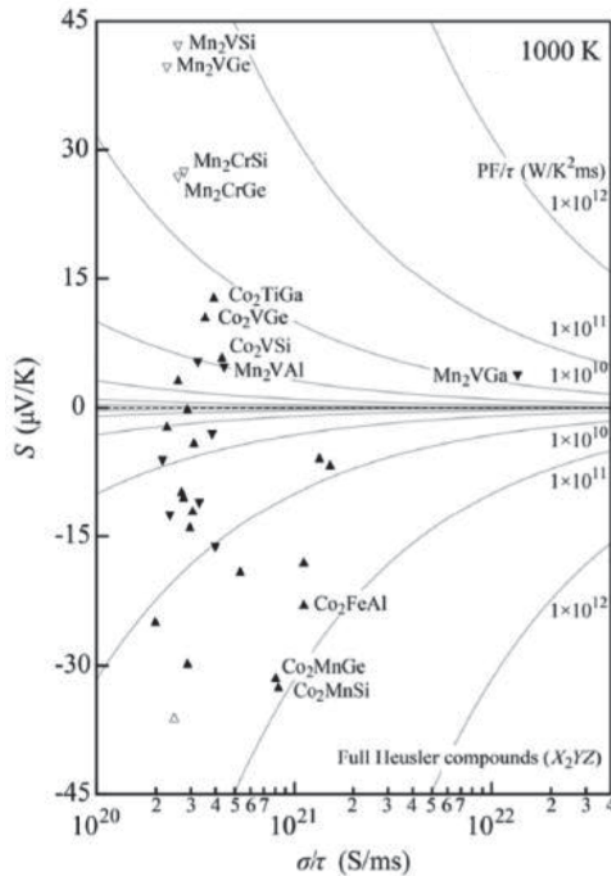
Other examples considered here are the full-Heusler compounds having low values of  $\kappa_1$ . **Figure 14** shows a flower-like microstructure of  $\text{Co}_2\text{Dy}_{0.5}\text{Mn}_{0.5}\text{Sn}$  observed by Schwall et al. [43]. Although the chemical composition of  $\text{Co}_2\text{Dy}_{0.5}\text{Mn}_{0.5}\text{Sn}$  coincides with that of the full-Heusler phase,  $\text{Co}_2\text{Dy}_{0.5}\text{Mn}_{0.5}\text{Sn}$  is not in a single phase. It consists of two major phases: half-metallic  $\text{Co}_2\text{MnSn}$  and ferromagnetic  $\text{Co}_8\text{Dy}_3\text{Sn}_4$  phases. This phase separation is induced by rapid cooling from the liquid phase. Consequently, the  $\kappa_1$  value of  $\text{Co}_2\text{Dy}_{0.5}\text{Mn}_{0.5}\text{Sn}$  is lower than those of  $\text{Co}_2\text{MnSn}$  and  $\text{Co}_8\text{Dy}_3\text{Sn}_4$ .

He et al. [9] theoretically discovered a new class of stable nonmagnetic full-Heusler semiconductors with high PF and ultralow  $\kappa_1$ , attributed to atomic rattling. The compounds contain alkaline earth elements (Ba, Sr or Ca) in the X sublattice and noble metals (Au or Hg) and main group elements (Sn, Pb, As or Sb) in the Y and Z sublattices, respectively. The  $\kappa_1$  value of  $\text{Ba}_2\text{AuBi}$  and  $\text{Ba}_2\text{HgPb}$  was obtained to be lower than 0.5 W/Km at 300 K. At higher temperatures, it was close to the theoretical minimum, that is, the amorphous limit of 0.27 W/Km [92]. Park et al. [16] further examined the TE properties of  $\text{Ba}_2\text{BiAu}$ . They predicted that considerably high  $zT$  of  $\sim 5$  can be achieved at 800 K.

Finally, there are many ternary and quaternary full-Heusler compounds yet to be explored. Among the full-Heusler compounds, nonmagnetic  $\text{Fe}_2\text{VAl}$ -based compounds have been intensively investigated as one of the potential TE semiconductors [93]. Despite the long historical investigation, Hinterleitner et al. [94] discovered quite recently that a metastable  $\text{Fe}_2\text{V}_{0.8}\text{W}_{0.2}\text{Al}$  thin film exhibits extremely high  $zT$  of  $\sim 6$  at 350 K as a result of its high  $S$ . The crystal structure of the thin film is reported to be the disordered A2 structure, which could be the reason for its high  $S$ , as in the cases of several half-metallic Co-based and Mn-based full-Heusler compounds [53, 78]. If the disorder in structure contributes to the high  $S$ , then the strategy of enhancing  $zT$  by controlling structural disorder would be applicable to the other full-Heusler compounds. Herewith, more conventional and novel findings on the full-Heusler compounds can be achieved.



**Figure 14.** Flower-like microstructure of  $\text{Co}_2\text{Dy}_{0.5}\text{Mn}_{0.5}\text{Sn}$ . (a) Elemental mappings, (b) combined image of elemental mappings shown in (a). (c) Line scan along the line indicated in (b). (Reprinted from [43]. Copyright 2012, with permission from WILEY-VCH).



**Figure 15.**

Calculated  $S$  versus  $\sigma/\tau$  at 1000 K for several Co-based and Mn-based full-Heusler compounds. The grey curves indicate  $PF/\tau$ . (Reprinted from [60]. Copyright 2018, with permission from Elsevier).

To explore the potentials of the full-Heusler compounds, theoretical studies are vital to minimise the experimental tasks. **Figure 15** exhibits a plot of  $S$  versus  $\sigma/\tau$  at 1000 K for several Co-based and Mn-based full-Heusler compounds, as calculated by Li et al. [60]. Furthermore, recent advancements in machine learning dispel the difficulty in searching novel full-Heusler compounds [95, 96]. Combining such calculations with experiments, we can effectively discover magnetic full-Heusler compounds with much higher TE efficiency, which promises the realisation of high-efficiency TE power generation devices.

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## Conflict of interest

We declare that there is no conflict of interest.

## Nomenclatures

$\eta_{\max}$ [-]	maximum TE efficiency
$zT$ [-]	dimensionless figure-of-merit
$T$ [K]	absolute temperature
$S$ [V/K]	Seebeck coefficient
$\sigma$ [S/m]	electrical conductivity
$\kappa$ [W/Km]	thermal conductivity
PF [W/K <sup>2</sup> m]	power factor
$\varepsilon_i$ [eV]	electronic energy–wavenumber dispersion curve of the $i$ -th band
$k$ [m <sup>-1</sup> ]	wavenumber
$S$ [V/K]	Seebeck coefficient tensor
$\sigma$ [S/m]	electrical conductivity tensor
$\kappa_e$ [W/Km]	carrier thermal conductivity tensor
$e = 1.60217662 \times 10^{-19}$ C	elementary charge
$\varepsilon$ [eV]	electron energy
$\varepsilon_F$ [eV]	Fermi level
$f_{FD}$ [-]	Fermi-Dirac distribution function
$N_k$ [-]	total number of $k$ -points
$\tau$ [1/s]	relaxation time
$= 6.582119569 \times 10^{-16}$ eVs	Dirac constant
$\tilde{\sigma}$ [S/m]	conductance spectrum tensor
DOS [states/eV]	density of states
$M$ [-]	normalised magnetisation calculated by using molecular field theory
$\mu$ [eV]	chemical potential
$\kappa_e$ [W/Km]	carrier thermal conductivity
$L$ [W $\Omega$ /K <sup>2</sup> ]	Lorentz number
$\kappa_l$ [W/Km]	lattice thermal conductivity
$n$ [1/m <sup>3</sup> ]	carrier concentration

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