Investigation of the electronic and thermoelectric properties of Fe$_2$ScX (X = P, As and Sb) full Heusler alloys by using first principles calculations

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Abstract

By using ab initio electronic structure calculations here we report the three new full Heusler alloys—Fe$_2$ScP, Fe$_2$ScAs and Fe$_2$ScSb. These alloys possess a very good thermoelectric behavior and are also expected to be synthesized in laboratories. The first two compounds are indirect band gap semiconductors and the last one shows a semimetallic ground state. The value of the band gap of Fe$_2$ScP and Fe$_2$ScAs is 0.3 eV and 0.09 eV, respectively. The presence of flat conduction bands along the $\Gamma-X$-direction suggest the large electron like effective mass and also promises a very good thermoelectric behavior of these compounds. At 200 K, the Seebeck coefficients of Fe$_2$ScP, Fe$_2$ScAs and Fe$_2$ScSb compounds are $-770$, $-386$ and $-192 \mu V K^{-1}$, respectively. The maximum power factor (PF) is expected for the $n$-type doping in these materials. The heavily doped Fe$_2$ScP and Fe$_2$ScAs have $PF > 60$ for a wide temperature range, which is comparable to the $PF$ of Bi$_2$Te$_3$—a well known and one of the most commercially used thermoelectric materials. The present work suggests the possible thermoelectric applicability of these materials in a wide temperature range.

Keywords: full Heusler alloys, thermoelectric materials, Seebeck coefficient, power factor, semiconductors

(Some figures may appear in colour only in the online journal)

1. Introduction

In recent years, the demand for the development of clean and renewable energy sources is growing at a very high rate, because the natural resources are diminishing and their burning contributes to global warming. Thermoelectric materials have attracted much attention because of their capability of converting heat directly into electricity and vice versa [1–4]. The efficiency of thermoelectric devices is determined by the dimensionless figure-of-merit ($ZT$), which depends on transport properties of the material such as the Seebeck coefficient ($S$), the electrical conductivity ($\sigma$) and thermal conductivity ($\kappa$), and is given by [5, 6]

\[ ZT = S^2\sigma T/\kappa \]  

This equation suggests that a high $ZT$ requires a large $S$ and $\sigma$ and a low $\kappa$. $S$ for a metal or degenerate semiconductor is related to the effective mass ($m^*$) by the following formula [7]:

\[ S = (8\pi^2k_B^2 / 3e^2) m^* T (2\pi / 3n)^{2/3} \]  

where the Boltzmann constant, $k_B$, and electronic charge, $e$, are constants and hence at a fixed temperature $T$, $S$ depend on the carrier concentration ($n$) and $m^*$. This equation implies that the $S$ will be greater in materials with a large $m^*$.

Most of the Heusler alloys have a half metallic ground state with $\sim 100\%$ spin-polarization at the Fermi level, ($E_F$), where majority and minority spin channels usually show metallic and insulating behaviors, respectively. The minority spin channel of these compounds normally shows the presence of
a flat conduction band (CB) along the $\Gamma - X$ direction [8–14]. The presence of a flat CB appears to be the generic property of full Heusler alloys. This flat band will give rise to a large value of $m^*$ and hence a large value for $S$ corresponding to the minority spin channel. Recently, we have explored this aspect for the Co$_2$MnGe half-metallic full Heusler alloy. Our results also show the presence of a flat CB along the $\Gamma - X$-direction in the spin down channel. At room temperature we achieved a calculated value of $S \approx 550 \frac{\mu V}{K}$ corresponding to the spin-down channel. This value was about 55 times more than that of the spin-up channel. However, the overall value of $S$ is found to be about $10 \frac{\mu V}{K}$ due to the presence of a $\sim 1000$ times larger $\alpha/\tau$ for the up spin channel in comparison to the down spin channel [8]. This result clearly suggests that full Heusler alloys with a semiconducting ground state could be very good thermoelectric materials.

However, the presence of semiconducting ground state in full Heusler alloys is very rare [15]. Interestingly, Yabuuchi et al. [10] have predicted the presence of a semiconducting ground state with a very large $S$ for Fe$_2$TiSn and Fe$_2$TiSi compounds. The presence of a semiconducting ground state also demands a nonmagnetic ground state because of the Slater-Pauling rule. For full-Heusler alloys this rule is given by the following equation [16, 17]

$$m = N_V - 24$$

where $N_V$ is the valence electron number per formula unit. It is clear from this formula that the magnetic moment vanishes for the compounds having a valence electron number equal to 24 and these compounds are semimetallic or semiconducting [16, 19]. Fe$_2$VAl is one of the most important examples of Heusler alloys with a 24 valence electron number and this compound shows interesting thermoelectric properties [18, 19].

In the search for semiconducting full Heusler alloys we come across with a new set of compounds: Fe$_2$ScP, Fe$_2$ScAs and Fe$_2$ScSb. These compounds have a valence electron number equal to 24 and thus their total magnetic moment is expected to vanish as per the Slater-Pauling rule. In the present work we have studied the electronic and transport properties of these compounds by using the full-potential linearized augmented plane-wave (FP-LAPW) method based on the density functional theory (DFT) along with the Boltzmann transport theory. The first two compounds are indirect band gap semiconductors whereas the last one has a semimetallic ground state. As expected these compounds show an almost flat conduction band along the $\Gamma - X$-direction. The indirect band gaps of about 0.3 eV and 0.09 eV are found in Fe$_2$ScP and Fe$_2$ScAs compounds. The undoped compounds show a very large and negative value of $S$, which suggests that these Heusler alloys are $n$-type thermoelectric materials. Additionally the power factor ($PF$) versus the chemical potential ($\mu$) plots give the qualitative information about the type of doping and suggest that the $n$-type doping can further enhance the $S$ of these compounds. The $PF$ of heavily doped Fe$_2$ScP and Fe$_2$ScAs is found to be closer to the $PF$ of Bi$_2$Te$_3$. These materials offer good thermoelectric properties in the wide temperature range.

Further calculations of the formation energy of these materials also suggests the possibility of synthesizing them in laboratories.

2. Computational details

By combining first principles calculations with the BoltzTraP code we have investigated the electronic and thermoelectric properties of new Heusler alloys: Fe$_2$ScP, Fe$_2$ScAs and Fe$_2$ScSb. The electronic properties have been investigated by using the full-potential linearized augmented plane-wave (FP-LAPW) method within the DFT implemented in WIEN2k code [20]. The exchange-correlation function has been treated by employing the recently developed PBEsol exchange-correlation function [21]. The muffin-tin radii were kept fixed to 2.0 Bohr (a$_0$) for all atoms, except for Sb, for which it was set equal to 2.2 a$_0$. The self-consistency iteration was achieved by demanding the convergence of the total energy/cell and charge/cell of the system to be less than $10^{-4}$ Ry and $10^{-3}$ electronic charge, respectively, in every system. Calculation of the transport properties requires a heavy k-point mesh in order to give more accurate results, hence the $50 \times 50 \times 50$ k-point mesh was used. To compute the transport properties of compounds, the BolzTrap code [22] under the constant relaxation time approximation for the charge carriers was employed. The lpfac parameter, which represents the number of k-points per lattice point was kept equal to 5. The chemical potential in the calculation of transport properties was fixed to the middle of the gap in every case.

3. Results and discussions

Normally, the full Heusler compounds crystallize in a L2$_1$ crystal structure, with space group Fm-3m. Therefore we have studied these compounds in the L2$_1$ phase. The crystal structure of Fe$_2$ScX, where X is an atom of P, As or Sb, is shown in figure 1. In this figure, Fe atoms are placed on the Wyckoff position 8c (1/4, 1/4, 1/4), Sc atoms are placed on the Wyckoff position 4a (0, 0, 0) and X atoms (i.e. P, As and Sb) are located...
at the Wyckoff position 4b (1/2, 1/2, 1/2). The cubic L2₁ structure consists of four interpenetrating fcc sub-lattices, two of which are equally occupied by Fe atoms. In these compounds the two Fe-site fcc sub-lattices combine to form a simple cubic sub-lattice. The Sc and X atoms alternatively occupy the centre of the simple cubic sub-lattice, resulting in a CsCl-type superstructure.

In order to obtain the equilibrium lattice parameters we have optimized the total energy as a function of volume of the unit cell. The obtained equilibrium lattice parameters for Fe₂ScP, Fe₂ScAs and Fe₂ScSb are 5.662, 5.811 and 6.058 Å, respectively. The lattice parameter increases by about 7% on moving from Fe₂ScP to Fe₂ScSb. This is due to the fact that as one moves down a group in the periodic table, the atomic size increases and hence there is an increment in the lattice parameters. Using the equilibrium lattice parameters, firstly we have calculated the electronic properties of these compounds. The dispersion curves of Fe₂ScP, Fe₂ScAs and Fe₂ScSb are shown in the figure 2. It is clear from the figures 2(a) and (b) that Fe₂ScP and Fe₂ScAs are semiconductors with indirect band gaps of about 0.3 eV and 0.09 eV, where the top of the valence band (VB) and bottom of the conduction band (CB) are at Γ and X-point, respectively. In these materials the direct band gap is located at the Γ-point and is ~0.05 eV and 0.01 eV more than the value of the indirect band gap of Fe₂ScP and Fe₂ScAs, respectively. Thus at higher temperatures both the direct and indirect transitions are expected to contribute to the transport properties of these materials. The dispersion curve of Fe₂ScSb is shown in figure 2(c). The CB edge at the X-point is slightly lower in energy than the VB edge at the Γ-point (not visible from the scale shown here) which make this compound semimetallic. The value of the indirect band gap is found to decrease as one moves from the compound with P to the compound with Sb. This is because of the decrease in the electronegativity and the amount of orbital overlap due to moving down the group in the periodic table. In these materials, Sb is the least electronegative element and forms the weakest covalent bonding with Fe and thus the band gap decreases as one moves from the P to Sb containing compound. The top of the VB in all compounds is triply degenerate at the Γ-point. Along Γ to the X-direction the degeneracy is lifted and becomes doubly degenerate and non-degenerate at X-point. Along the L-direction the degeneracy is lifted to the doubly degenerate and non-degenerate band. Also along the Γ to X-direction there exists an almost flat conduction band in these compounds. Thus, these compounds surely have a large value of effective mass which suggests that these materials are good thermoelectric materials.

The total density of states (TDOS) and partial density of states (PDOS) plots for Fe₂ScP, Fe₂ScAs and Fe₂ScSb are presented in figure 3. It is clear from the TDOS, shown in figures 3(a)–(c) that Fe₂ScP and Fe₂ScAs are semiconductors, while in Fe₂ScSb there is very small TDOS at the Fermi level (E_F) which is due to the semimetallic behavior of the compound as discussed above. In the VB, there exists two broad peaks in the low energy region between ~7.0 eV to ~4.0 eV and two broad peaks with a comparatively high intensity in the high energy region between 0 eV to ~4.0 eV. The maxima of these peaks move towards the higher energy as going from Fe₂ScP to Fe₂ScSb. The PDOS of Fe atoms of Fe₂ScP, Fe₂ScAs and Fe₂ScSb are shown in figures 3(d)–(f). These plots show that the top of the valence band has a mainly t₂g character and the bottom of the conduction band has a e_g character. In the VB the t₂g with a very small contribution of e_g states are extended in two different regions from ~5 eV to ~4 eV and ~4 eV to 0 eV. In the region ~5 eV to ~4 eV the intensity of the peaks is very small and t₂g states have more of a contribution than the e_g states. The contribution from the t₂g(e_g) states of the Fe atom are 0.32 (0.14), 0.30 (0.13) and 0.26 (0.14) states/eV/atom in Fe₂ScP, Fe₂ScAs and Fe₂ScSb, respectively. On moving from Fe₂ScP to Fe₂ScSb these two regions become narrow and the maximum of the peak shifts slightly towards the higher energy. The PDOS of the Sc atom of Fe₂ScP, Fe₂ScAs and Fe₂ScSb are presented in figures 3(g)–(i). It is evident from the graphs that there is a small contribution from the d orbitals of the Sc atom than that of Fe atom. There are two broad peaks between ~6 eV to ~4 eV with smaller intensities and ~3.5 eV to 0 eV having larger intensities. The region nearer to the E_F has more contributions from the t₂g and the region away from it is dominated by the e_g states. The maximum of the peak shifts toward the higher energy from Fe₂ScP to Fe₂ScSb. The PDOS for p orbitals of P, As and Sb atoms

![Figure 2. Dispersion curves of (a) Fe₂ScP, (b) Fe₂ScAs and (c) Fe₂ScSb.](image-url)
are shown in figures 3(j)–(l). There are two broad peaks in the region between −7 eV to −4 eV and as one moves from P to Sb these peaks shift towards the higher energy. This trend is the same as that found in the atomic energy of p orbitals of these atoms. The trend in the atomic energies of 3p, 4p and 5p orbitals of P, As and Sb atom is −6.9 eV < −6.7 eV < −6.3 eV, respectively. In the PDOS plots of Fe and Sc atoms the very small peaks appear in the low energy region between −7 eV to −4 eV, which are essentially due to the hybridization between the p orbitals of P, As and Sb with the d orbitals of Fe and Sc. This can be understood from the crystal structure shown in figure 1. This figure shows that the Fe atom is lying in the Wyckoff position 8c (1/4, 1/4, 1/4), thus there is more hybridization between the \( t_{2g} \) of the Fe atom and p-orbitals of the X atom in comparison to the \( e_g \) orbitals. The Sc atoms are at the origin and As atoms are lying at 4b (1/2, 1/2, 1/2). Thus in comparison to the \( t_{2g} \) states of the Sc atom, more hybridization is taking place between the \( e_g \) orbitals of Sc and p-orbital of the X atom. This is evident from the PDOS plot for Fe and Sc atoms, where small peaks appear in the low energy region between −7 eV to −4 eV with dominating \( t_{2g} \) states in Fe and \( e_g \) states in the Sc atom.

The presence of a semiconducting ground state and flat CB clearly suggests that there is potential for use as thermoelectric materials. Therefore we also studied the thermoelectric properties of these materials. The computed transport coefficients of Fe\(_2\)ScP, Fe\(_2\)ScAs and Fe\(_2\)ScSb for the chemical potential (\( \mu \)) ranging from −0.6 eV to 0.6 eV at different temperatures are shown in figure 4. The dashed line at \( \mu = 0 \) eV represents the chemical potential for pure compound and was fixed to the middle of the gap. The positive value of \( \mu \) represents the electron doping, whereas the negative \( \mu \) represents the hole doping. The Seebeck coefficient of Fe\(_2\)ScP, Fe\(_2\)ScAs and Fe\(_2\)ScSb at 200, 300 and 400 K, respectively, as a function of \( \mu \) is presented in figures 4(a)–(c). It is clear from these plots that at \( \mu = 0 \) i.e. for pure compounds, the maximum value of \( S \) is −770, −386 and −192 \( \mu \)V K\(^{-1} \) for Fe\(_2\)ScP, Fe\(_2\)ScAs and Fe\(_2\)ScSb, respectively. The large and negative \( S \) means that these compounds are of \( n \)-type. The \( S \) is found to be negative because of the presence of flat CB along \( \Gamma \)–X-direction as stated earlier. For Fe\(_2\)ScP and Fe\(_2\)ScAs in the selected range of \( \mu \), two peaks with a maximum value of \( S \) are obtained, one at positive \( \mu \) and another at negative \( \mu \). In Fe\(_2\)ScP at +14 meV the maximum values of \( S \) are ∼ 853 and −608 \( \mu \)V K\(^{-1} \) for 200 K and 300 K, respectively, however for 400 K the maximum \( S \) is ∼ 486 \( \mu \)V K\(^{-1} \) and is obtained at a comparatively higher \( \mu \) equal to +21 meV. The other maxima having \( S \) equal to ∼673, 433 and 316 \( \mu \)V K\(^{-1} \) were obtained at \( \mu = -50 \), −70 and −90 meV for 200, 300 and 400 K, respectively. It is also clear from these plots that when the temperature increases the
maximum value of $S$ decreases and shifts slightly towards the higher $\mu$ (in magnitude). A similar trend is found in Fe$_2$ScAs where the maximum $S$ is $\sim$ 390, −300 and $\sim$ 270 $\mu$V K$^{-1}$ at 200, 300 and 400 K, respectively for positive $\mu$. In Fe$_2$ScSb one maximum peak with the same $S$ equal to $\sim$ 70 $\mu$V K$^{-1}$ for all temperatures is found at negative $\mu$, while another maximum peak is obtained exactly at $\mu = 0$ eV having a value equal to $\sim$ 185 $\mu$V K$^{-1}$ for all temperatures. In Fe$_2$ScP and Fe$_2$ScAs, the large $S$ is found for the positive value of $\mu$, i.e. for electron doping. This suggests that the $n$-type doping will provide better thermoelectric behavior than the $p$-type doping in these compounds.

Figures 4(d)–(f) shows the plots of electronic conductivity ($\sigma$/$\tau$) versus $\mu$ at different temperatures for Fe$_2$ScP, Fe$_2$ScAs and Fe$_2$ScSb, respectively. The electronic conductivity increases with $\mu$ at the same rate for all values of temperature, as is evident from these plots. The conductivity of these compounds increases with doping because of the increase in carrier concentration with increasing $\mu$. The $\sigma$/$\tau$ is more for the positive $\mu$ in comparison to the negative value of $\mu$, which means that electron doped compounds will have a higher conductivity than hole doped compounds. However, as one move from the P to Sb containing compound the conductivity increases and a maximum is obtained at the lower $\mu$. In Fe$_2$ScP the conductivity is almost the same $\sim$ 10$^{14}$ ($\Omega$ m$^{-1}$ s$^{-1}$) in the region between $\sim$ 140 meV to $\sim$ 90 meV. The width of the region with the almost the same conductivity decreases in Fe$_2$ScAs. The electronic thermal conductivity ($\kappa$/$\tau$) as a function of $\mu$ for different values of temperature is presented in figures 4(g)–(i) for Fe$_2$ScP, Fe$_2$ScAs and Fe$_2$ScSb, respectively. From these plots it is evident that $\kappa$/$\tau$ increases with $\mu$ for all temperatures. However, at positive $\mu$, this value is found to be more than at negative $\mu$. This means that the largest value of $\kappa$/$\tau$ will be for electron doped compounds.

A good thermoelectric material is characterized by its power factor and in order to improve the electronic properties of a thermoelectric material one has to enhance its power factor (PF). Therefore we have also shown the PF as a function of $\mu$ for Fe$_2$ScP, Fe$_2$ScAs and Fe$_2$ScSb at 200, 300 and 400 K as shown in figures 4(j)–(l). It is clear from these plots that for every temperature there are two peaks having a maximum PF in the given range of $\mu$ and the highest PF is obtained at 400 K. Also it is clear from these plots that the maximum of these peaks shifts slightly towards the higher $\mu$ when the temperature is increased from 200 K to 400 K. The maximum PF at negative $\mu$ increases from $\sim$ 14–46, 11–32 and 12–30 (10$^{14}$ $\mu$W cm$^{-1}$ K$^{-2}$ s$^{-1}$) for Fe$_2$ScP, Fe$_2$ScAs and Fe$_2$ScSb, respectively, when the temperature is increased from 200 K to 400 K. The other maximum peak corresponding to large PF exists at positive $\mu$ for Fe$_2$ScP and Fe$_2$ScAs, whereas in Fe$_2$ScSb it exists at $\mu = 0$. The values of PF are almost the same for compounds with P and As and increase
from 32 to 64, whereas in Fe$_2$ScSb it increases from 30 to 60 (10$^{14}$ m$^{-1}$ W cm$^{-1}$ K$^{-2}$ s$^{-2}$) with increasing temperature from 200 K to 400 K. Thus plots of $PF$ versus $\mu$ provide the qualitative information that the $PF$ of the electron doped compounds is expected to be more. The position of the maximum peak also qualitatively shows that the maximum $PF$ can be obtained when these compounds are heavily doped.

In order to know the exact doping range to obtain the maximum $PF$ we have doped these compounds in the doping range between 10$^{17}$–10$^{21}$ cm$^{-3}$. From the above discussion it is clear that the $PF$ for electron doping will be more, however we have doped these compounds with electrons as well as holes. The transport coefficients versus temperature plots at different doping ranges are presented in figures 5 and 6. The $S$ versus temperature plots for p-type doping are shown in figures 5(a)–(e) and it is clear that the maximum peak of $S$ shifts towards the higher value of temperature as the concentration is increased. In Fe$_2$ScP and Fe$_2$ScAs, the maximum peak of $S$ exists at 150 K in Fe$_2$ScP and Fe$_2$ScAs for the carrier concentration of 10$^{17}$ cm$^{-3}$ and 10$^{19}$ cm$^{-3}$, respectively, whereas in Fe$_2$ScSb the maximum is at 500 K for the carrier concentration of 10$^{19}$ cm$^{-3}$. The maximum value of $S$ is ∼880, ∼460 and ∼80 μV K$^{-1}$ for Fe$_2$ScP, Fe$_2$ScAs and Fe$_2$ScSb, respectively. Also it is clear from these plots that at the highest carrier concentration the value of $S$ remains negative for the entire temperature range in all compounds. In Fe$_2$ScSb the value of $S$ is positive for the carrier concentration 10$^{17}$ cm$^{-3}$ to 10$^{19}$ cm$^{-3}$ and is almost same for all temperatures. The $S$ versus temperature plots show that the maximum $S$ is obtained when these compounds are doped with electrons and this is the same as conjectured above. Also the highest value of $S$ is found in Fe$_2$ScP at a low temperature for the carrier concentration of 10$^{17}$ cm$^{-3}$.

The $\sigma/\tau$ versus temperature plots are shown in figures 5(g)–(l). These plots show that with increasing temperature the conductivity also increases in all these compounds and is almost same for the carrier concentration 10$^{17}$–10$^{20}$ cm$^{-3}$. However, for p-type doping the maximum value of $\sigma/\tau$ is obtained at low temperature with 10$^{21}$ cm$^{-3}$ carrier concentration in all these compounds and its value is 0.33, 0.4 and 0.39 (10$^{20}$ Ω$^{-1}$ m$^{-1}$ s$^{-1}$) at 150 K for Fe$_2$ScP, Fe$_2$ScAs and Fe$_2$ScSb, respectively. Also in n-type doping the maximum conductivity
corresponds to the \(10^{21} \text{ cm}^{-3}\) carrier concentration in all these compounds. \(\text{Fe}_2\text{ScP}\) and \(\text{Fe}_2\text{ScAs}\) both have the same value of \(\sigma/\tau \sim 0.15 \times 10^{20} \Omega^{-1} \text{ m}^{-1} \text{ s}^{-1}\) at 150 K and for \(\text{Fe}_2\text{ScP}\) this value corresponds to maximum conductivity. The maximum value of \(\sigma/\tau\) for \(\text{Fe}_2\text{ScAs}\) and \(\text{Fe}_2\text{ScSb}\) is \(0.2\) and \(0.3 \times 10^{16} \Omega^{-1} \text{ m}^{-1} \text{ s}^{-1}\), respectively at 1200 K.

Figure 6 represents the \(\kappa/\tau\) versus temperature and \(PF\) versus temperature plots at different carrier concentrations. The trend in the value of \(\kappa/\tau\) with temperature is more or less the same for \(p\) and \(n\)-type doping. The thermal conductivity found to increase with temperature and have a maximum value at the highest temperature under consideration. Among these compounds the maximum thermal conductivity is found in \(\text{Fe}_2\text{ScSb}\) for \(n\)-type doping. The thermal conductivity found to increase with temperature and have a maximum value at the highest temperature under consideration.

The \(PF\) versus temperature plots are presented in figures 6(g)–(l). It is clear from these plots that the \(PF\) increases slowly with temperature for the carrier concentration \(10^{17} \text{ cm}^{-3}\) to \(10^{19} \text{ cm}^{-3}\). The value of highest \(PF\) is \(\sim 10\) and \(7 \times 10^{14} \mu \text{W cm}^{-1} \text{ K}^{-2} \text{ s}^{-1}\) for \(\text{Fe}_2\text{ScP}\) and \(\text{Fe}_2\text{ScAs}\), respectively at 1200 K when these compounds are doped with holes or electrons. However, in \(\text{Fe}_2\text{ScSb}\), the maximum \(PF\) is obtained in the temperature range between 400–600 K with the value of \(PF\) closer to \(\sim 1.5 \times 10^{14} \mu \text{W cm}^{-1} \text{ K}^{-2} \text{ s}^{-1}\). With the carrier concentration of \(10^{20} \text{ cm}^{-3}\), \(p\)-doped \(\text{Fe}_2\text{ScP}, \text{Fe}_2\text{ScAs}\) and \(\text{Fe}_2\text{ScSb}\) have the maximum \(PF\) equal to \(22, 10\) and \(5 \times 10^{14} \mu \text{W cm}^{-1} \text{ K}^{-2} \text{ s}^{-1}\) for the temperature range between 700–800 K, 600–1200 K and 350–550 K, respectively. However, at same carrier concentration the \(n\)-type doped \(\text{Fe}_2\text{ScP}, \text{Fe}_2\text{ScAs}\) and \(\text{Fe}_2\text{ScSb}\) have the maximum \(PF\) equal to \(23, 16, 7 \times 10^{14} \mu \text{W cm}^{-1} \text{ K}^{-2} \text{ s}^{-1}\), respectively for the temperature range between 400–500, 200–300 and 100–150 K. In all these compounds the highest \(PF\) is obtained for the carrier concentration of \(10^{21} \text{ cm}^{-3}\) which corresponds to the heavy doping of these compounds and this is also as per expectation. The heavy doping is expected to be achieved easily by replacing either 2.5% of Co or 1.25% Ni or even less percentage of Cu at the Fe sites. In moving from \(\text{Fe}_2\text{ScP}\) to \(\text{Fe}_2\text{ScSb}\), the \(PF\) decreases from \(\sim 90–24 \times 10^{14} \mu \text{W cm}^{-1} \text{ K}^{-2} \text{ s}^{-1}\) for \(p\)-type doping and \(\sim 85–53 \times 10^{14} \mu \text{W cm}^{-1} \text{ K}^{-2} \text{ s}^{-1}\) for \(n\)-type doping. In \(p\)-doped \(\text{Fe}_2\text{ScP}\) and \(\text{Fe}_2\text{ScAs}\) the maximum \(PF\) is obtained for the temperature range 1050–1200 K, whereas in \(\text{Fe}_2\text{ScSb}\)
it is obtained for the temperature ranging from 900–1050 K. The maximum $PF$ in $n$-doped Fe$_2$ScP, Fe$_2$ScAs and Fe$_2$ScSb is obtained at lower temperatures, ranging from 600–900, 400–700 and 400–600 K, respectively.

It is clear from the above discussion that the highest $PF$ is found in the heavily doped compounds, $p$-doped Fe$_2$ScP and $n$-doped Fe$_2$ScP and Fe$_2$ScAs have $PF < 60$ for the temperature ranging from 700–1200, 400–1000 and 400–650 K, respectively. Also the obtained values of $PF$ for Fe$_2$ScP and Fe$_2$ScAs are comparable with the Bi$_2$Te$_3$ [22]. The figure of merit of this compound is $\sim 1$ at room temperature and is known as the one of the most commercially used thermoelectric materials. Thus, it is expected that Fe$_2$ScP and Fe$_2$ScAs can also have a high value of the figure of merit like Bi$_2$Te$_3$ and can be the potential thermoelectric materials in the wide temperature range. It must be noted here that the high power factor should not be the only criterion for judging a material to be a good thermoelectric material. One has to consider the lattice thermal conductivity which should be low. The lattice thermal conductivity of the full Heusler alloys is normally found to be more than that of Bi$_2$Te$_3$. However, this can be reduced by doping and fabricating nanostructures as done in many cases [23, 24].

Therefore the above results, suggest that when these compounds are heavily doped with electrons, the maximum $PF$ is obtained in the broad temperature range, which is very important for various applications. However, at this stage it is important to keep in mind that the LDA/GGA based DFT calculations normally underestimate the band gap of the semiconductor. This can affect the temperature dependent behaviour of the Seebeck coefficient and electrical conductivity as these quantities depend on the carrier concentration ($n$) and $n$ depends on the band gap and temperature. The underestimation of the band gap normally gives the peak at a lower temperature and hence the peaks in the power factor curve are expected to be at higher temperatures for the real materials. Another important aspect for choosing good thermoelectric materials in a particular range of temperatures is the relation between the band gap and the working temperature. The rule of thumb for this is that the band gap should be of the order of $\sim 10$ $k_B T$ where $k_B$ is the Boltzmann constant. Thus the value of $S$ is also expected to be affected by the underestimation of the band gap in a particular range of temperatures. This has also been seen by Yabuuchi et al [10] where one can see a small change in the value of $S$ along with shifting in the peak with varying the band gap. But the final conclusion about the utility of these materials in a wide temperature range is not going to be affected much, if at all, by the underestimation of the band gap in the present work. Another important aspect one should keep in mind that the BoltzTrap code uses a constant relaxation time approximation and at sufficiently high temperature constant relaxation time approximation is not a good approximation as it becomes temperature dependent due to phonon scattering. Thus at high temperatures one expects a modification in the predicted values of the Seebeck coefficient and electrical conductivity. The modification in the values of $S$ and $\sigma$ may be larger at higher temperature if these compounds show strong temperature dependence of scattering. Thus the detailed study in this direction is desirable to understand the high temperature transport behaviour of these compounds.

From the above discussion, it is evident that electron doped compounds have the potential to be used as good thermoelectric materials. However, to the best of our knowledge, nobody has synthesized these compounds. In order to know whether these compounds will be synthesized or not we have calculated the formation energy ($FE$) of these compounds by using the following formula

$$FE = E\text{(compound)} - [2E(Fe) + E(Sc) + E(X)]$$

where $E\text{(compound)}$ is the energy of a compound and $E(Fe)$, $E(Sc)$ and $E(X)$ are the energies of the respective elements per atom. $X$ represents the atom of P, As and Sb. Here we have considered the body centered cubic, face centered cubic and orthorhombic structure of Fe, Sc and P atom, while the crystal structure of As and Sb is hexagonal as given in Myncryst database [25]. These energies are obtained computationally by minimizing the total energy as a function of the volume of the unit cell which corresponds to the above mentioned structures. The $FE$ comes out to be $-2.2$, $-1.6$ and $-1.4$ eV/formula unit for Fe$_2$ScP, Fe$_2$ScAs and Fe$_2$ScSb, respectively, which clearly suggests that these compounds can be synthesized in laboratories. Our formation energy calculations suggest the possibility of synthesizing these compounds in laboratories. However, based on present work one cannot guarantee the formation of 100% pure phase of these compounds. At this stage we can not rule out the possibility of the presence of impurity phases consisting of various constituent elements such as Fe, Sc, P, As and Sb. In order to rule out any such possibility the detailed studies in line with [26] are desirable.

4. Conclusions

In the present work we have reported three new full-Heusler alloys Fe$_2$ScP, Fe$_2$ScAs and Fe$_2$ScSb, which can be synthesized in laboratories and expected to work as good thermoelectric materials. The electronic and transport properties of these compounds are studied by using the first principles calculations with the Boltzmann transport theory. Fe$_2$ScP and Fe$_2$ScAs are indirect band gap semiconductors, whereas Fe$_2$ScSb is semimetallic. The value of the band gap in Fe$_2$ScP and Fe$_2$ScAs is found to be 0.3 eV and 0.09 eV, respectively. We have observed the flat CB in these compounds along the $\Gamma$ to X-direction which is mainly responsible for the large value of Seebeck coefficients observed in these compounds. The power factor of $n$-doped Fe$_2$ScP and Fe$_2$ScAs comes out to be <60 above room temperature and this value is comparable with Bi$_2$Te$_3$, which is a well known thermoelectric material. Our work shows that these materials have the potential to be used as good thermoelectric materials which can operate over a wide temperature range.

References

[1] Tan X J, Liu W, Liu H J, Shi J, Tang X F and Uher C 2012 Phys. Rev. B 85 205212

[2] Pei Y, Wang H and Snyder G J 2012 Adv. Mater. 24 6125
[3] Pei Y, Wang H, Gibbs ZM, LaLonde AD and Snyder GJ 2012 NPG Asia Mater. 4 e28
[4] Akasaka M, Iida T, Matsumoto A, Yamanaka K, Takanashi Y, Imai T and Hamada N 2008 J. Appl. Phys. 104 013703
[5] Pei Y, Shi X, LaLonde A, Wang H, Chen L and Snyder GJ 2011 Nature 473 66
[6] LaLonde AD, Pei Y, Wang H and Snyder GJ 2011 Mater. Today 14 526
[7] Snyder GJ and Toberer ES 2008 Nat. Mater. 7 105
[8] Sharma S and Pandey SK 2014 J. Phys.: Condens. Matter 26 215501
[9] Sharma S and Pandey SK 2014 arXiv: 1406.3505v1
[10] Yabuuchi S, Okamoto M, Nishide A, Kurosaki Y and Hayakawa J 2013 Appl. Phys. Express 6 025504
[11] Barth J et al 2011 Phil. Trans. R. Soc. A 369 3588
[12] Graf T, Fecher GH, Barth J, Winterlik J and Felser C 2009 J. Phys. D: Appl. Phys. 42 084003
[13] Barth J et al 2010 Phys. Rev. B 81 064404
[14] Picozzi S, Continenza A and Freeman AJ 2002 Phys. Rev. B 66 094421
[15] Meinert M, Geisler MP, Schmalhorst J, Heinze M, Arenholz E, Heta M, Stöger-Pollach M, Hüttner A and Reiss G 2014 and references therein
[16] Galanakis I, Dederichs PH and Papanikolaou N 2002 Phys. Rev. B 66 174429
[17] Graf T, Felser C and Parkin SSP 2011 Prog. Solid State Chem. 39 1
[18] Nishino Y, Deguchi S and Mizutani U 2006 Phys. Rev. B 74 115115
[19] Lee CS, Chen CF, Lin Y, Yu YT and Kuo YK 2007 Phys. Rev. B 75 064204
[20] Blaha P, Schwarz K, Madsen GK, Kvasnicka D and Luitz J 2001 WIEN2k, an Augmented Plane Wave Plus Local Orbitals Program for Calculating Crystal Properties (Vienna: Vienna University of Technology)
[21] Perdew JP, Ruzsinszky A, Csonka GI, Scuseria GE, Constantin IA, Zhou X and Burke K 2008 Phys. Rev. Lett. 100 136406
[22] Madsen GK and Singh DJ 2006 Comput. Phys. Commun. 175 67
[23] Mikami M, Kinemuchi Y, Ozaki K, Terazawa Y and Takeuchi T 2012 J. Appl. Phys. 111 093710
[24] Takiguchi H, Aono M and Okamoto Y 2011 Japan. J. Appl. Phys. 50 041310
[25] http://database.iem.ac.ru/mincryst
[26] Watson RE, Weinert M and Alatalo M 1998 Phys. Rev. B 57 12134