



# CaCoSO diluted magnetic antiferromagnet semiconductor as efficient thermoelectric materials



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## ABSTRACT

We have reported the thermoelectric properties of the recently synthesized CaCoSO single crystal by Salter et al. in 2016. It is quite interesting to mention that CaCoSO single crystals exhibit a direct energy gap ( $\Gamma^v - \Gamma^c$ ) of about 2.187 eV for the spin-up ( $\uparrow$ ) channel, which turns out to be a ( $K^v - K^c$ ) direct gap of about 1.187 eV for the spin-down ( $\downarrow$ ) channel, resulting in an indirect gap ( $\Gamma^v - K^c$ ) of about 0.4 eV for the spin-polarized CaCoSO single crystal. Such a small gap makes CaCoSO a promising candidate for thermoelectric materials. Calculations reveal a remarkable finding that the CaCoSO single crystal exhibits high electrical conductivity, low thermal conductivity and a large Seebeck coefficient; therefore, based on these findings, the CaCoSO single crystal may be considered an efficient thermoelectric material. The electron clouds of  $\text{CaO}_3\text{S}_4$  and  $\text{CoS}_3\text{O}$  exhibit a planar shape with conjugated electron orbitals and exhibit a strong covalent Ca–O, Co–O bonding. This is another factor which makes CaCoSO a promising candidate for thermoelectric materials, since covalent bonding is more favorable for the transport of the carriers than ionic bonding.  $\text{CaO}_3\text{S}_4$  and  $\text{CoS}_3\text{O}$  are the main sources for the thermoelectric generator in CaCoSO. Therefore, based on the above findings, we can conclude that CaCoSO could be a promising thermoelectric material.

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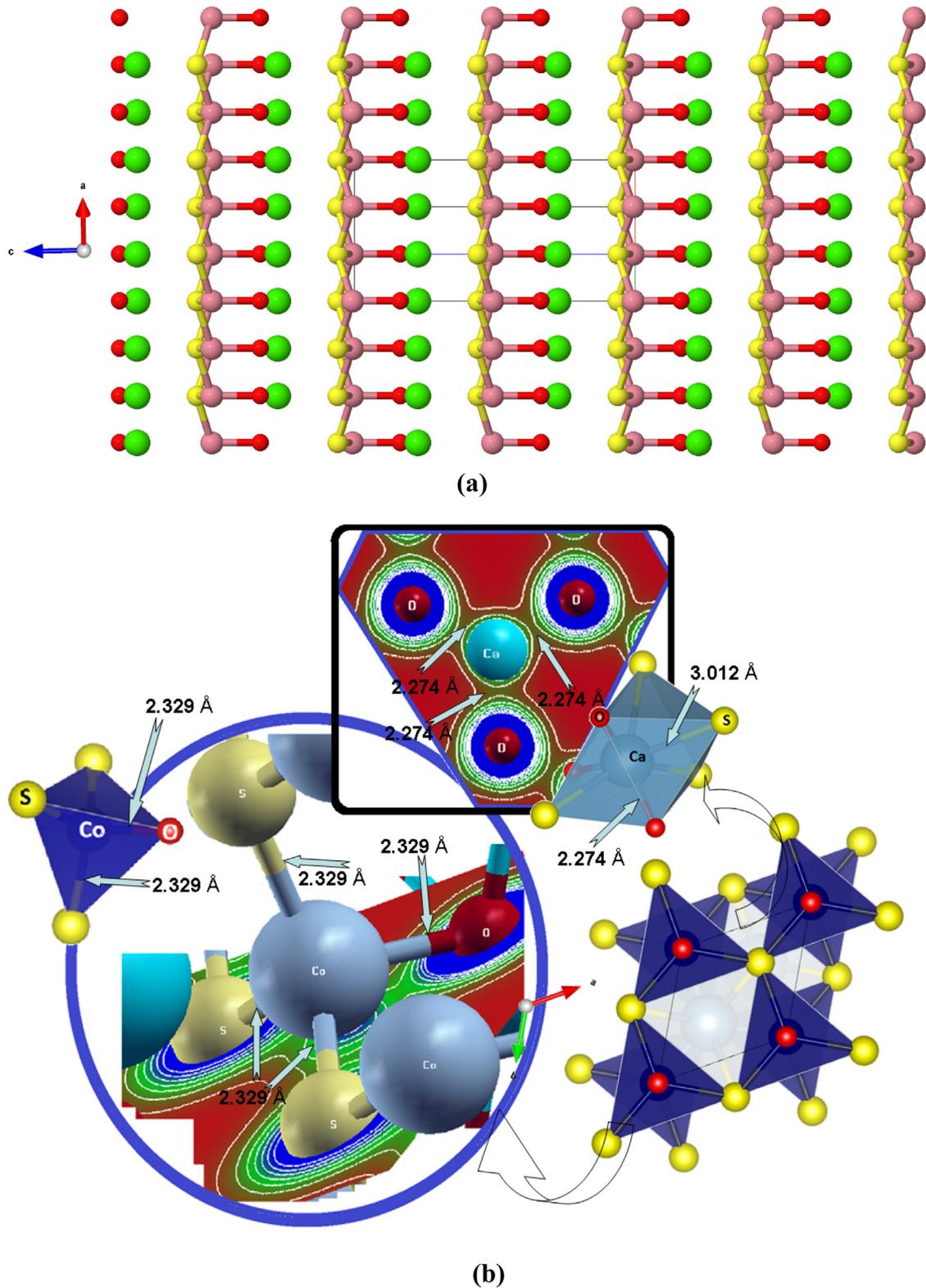
## 1. Introduction

Oxide chalcogenide compounds have become important candidates for several applications, for instance, as p-type transparent conductors [1–6]. Among these oxide chalcogenide compounds, the CaCoSO compound was recently synthesized in 2016 by Salter et al. [7]. It has been reported that the CaCoSO is isostructural with  $\text{CaZnSO}$ ,  $\text{BaCoSO}$  and  $\text{CaFeSO}$  [7–11]. The newly synthesized CaCoSO consists of  $\text{CaO}_3\text{S}_4$  and  $\text{CoS}_3\text{O}$  groups. The Ca and Co atoms form strong covalent bonding with O atoms [7]. It has been reported that covalent bonding is more favorable for the transport of the carriers than ionic bonding [12]. Therefore, the  $\text{CaO}_3\text{S}_4$  and  $\text{CoS}_3\text{O}$  groups are the main sources for the thermoelectric generator in CaCoSO. The search for new materials with very efficient thermoelectric properties is still challenging. Therefore, in the current work we aim to find new materials with efficient thermoelectric properties; for this we should find a new material with high electrical conductivity, low thermal

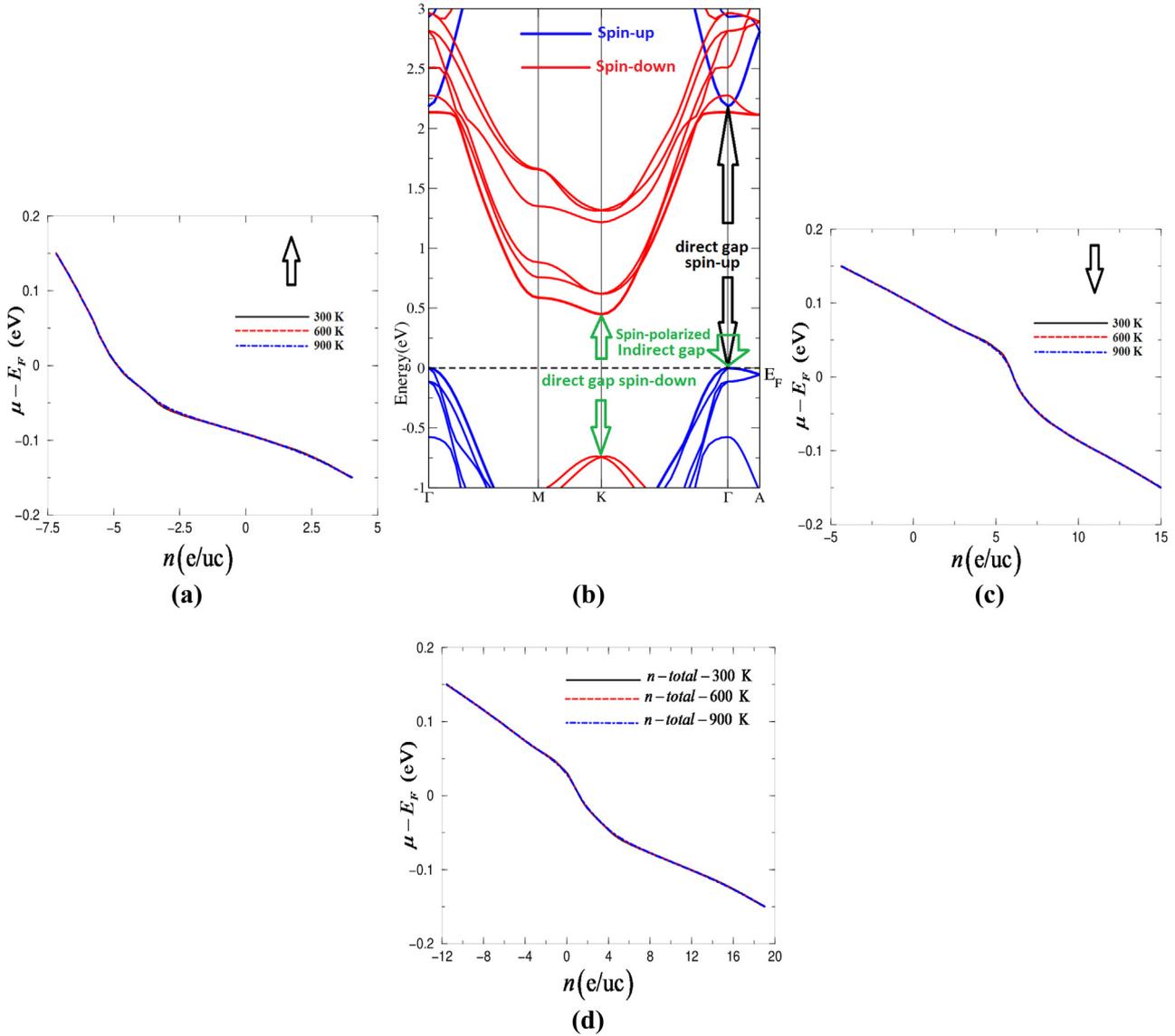
conductivity and a large Seebeck coefficient [13]. The starting point is the previous experimental research on several Diluted Magnetic Semiconductors (DMS), which state that the DMS are promising candidates as thermoelectric materials [14,15]. We decided to investigate the thermoelectric properties of the recently synthesized CaCoSO single crystal [7] based on the density functional theory and the transition from first- to second-principles methods.

It is well known that the DFT approaches have the ability to accurately predict the ground state properties of materials, and the developed analysis tools are vital for investigating their intrinsic mechanisms. The understanding of the microscopic structure has further guided molecular engineering design for new crystals with novel structures and properties. It is anticipated that first-principle material approaches will remarkably improve the efficiency of the search and greatly help experiments save resources in the exploration of new crystals with good performance [16–27]. Recently, several researchers have used the DFT calculations for exploration of the thermoelectric properties of new thermoelectric materials and found good agreement with the experimental results. We would also like to mention that, in our previous works [28–31], we calculated the transport properties using the FP-LMTO method within the BoltzTraP code for several systems whose

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**Fig. 1.** (a) The crystal structure of the recently synthesized CaCoSO single crystal; (b) The electron cloud of the  $\text{CaO}_3\text{S}_4$  and  $\text{CoS}_3\text{O}$  exhibit planar shape with conjugated electron orbitals and exhibit a strong covalent Ca–O, Co–O bonding therefore, the  $\text{CaO}_3\text{S}_4$  and  $\text{CoS}_3\text{O}$  are the main source for the thermoelectric generator in CaCoSO.



**Fig. 2.** (a) calculated carriers concentration as a function of chemical potential ( $\mu - E_F = \pm 0.2$  eV) at three constant temperatures (300, 600 and 900) K for spin-up channel of CaCoSO single crystal; (b) Calculated electronic band structure for the spin-up, spin-down channels and the spin-polarized electronic band structure of CaCoSO single crystal; (c) calculated carriers concentration as a function of chemical potential ( $\mu - E_F = \pm 0.2$  eV) at three constant temperatures (300, 600 and 900) K for spin-down channel of CaCoSO single crystal; (d) calculated carriers concentration as a function of chemical potential ( $\mu - E_F = \pm 0.2$  eV) at three constant temperatures (300, 600 and 900) K for the spin-polarized CaCoSO single crystal.

transport properties are known experimentally and obtained a very good agreement with the experimental data. Thus, we believe that the calculations reported in this paper have produced very accurate and reliable results.

It should be emphasized that CaCoSO has been synthesized very recently (i.e. 2016) [7] and that no experimental or theoretical data for the thermoelectric properties of CaCoSO have been reported yet. For this reason, our results can serve as a reference for future investigations. Predicting and discovering new materials is always exciting, for the promise of new applications and properties [32,33]. Moreover, finding materials with new properties is always desirable.

**Table 1**

The calculated electron effective mass ratio ( $m_e^*/m_e$ ), effective mass of the heavy holes ( $m_{hh}^*/m_e$ ) and light holes ( $m_{lh}^*/m_e$ ).

| Effective mass ratio | Spin-up | Spin-down | Spin-Polarized CaCoSO |
|----------------------|---------|-----------|-----------------------|
| $m_e^*/m_e$          | 0.00545 | 0.03933   | 0.03933               |
| $m_{hh}^*/m_e$       | 0.06520 | 0.04395   | 0.06520               |
| $m_{lh}^*/m_e$       | 0.03282 | 0.02536   | 0.03282               |

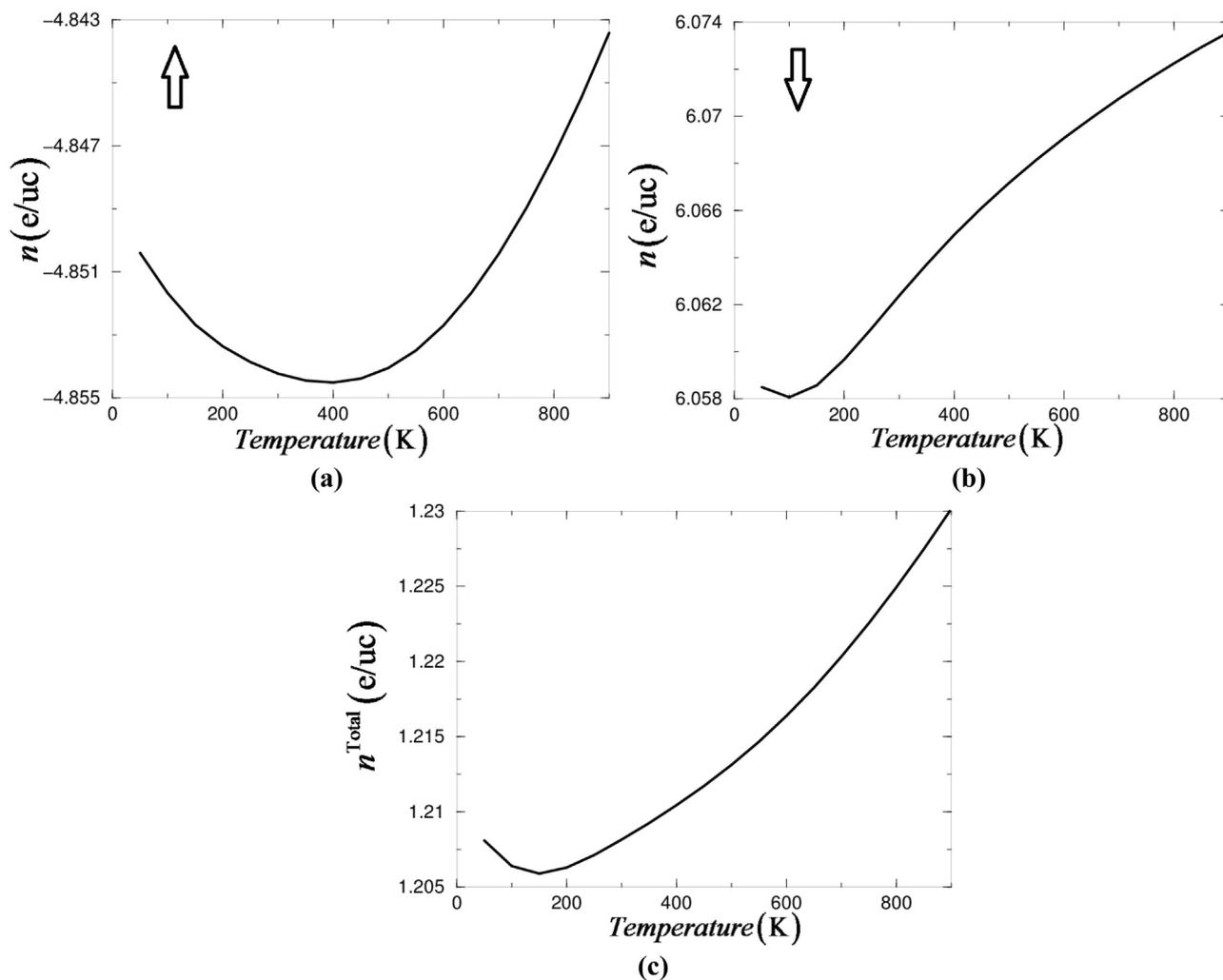
## 2. Density functional theory (transition from first- to second-principles methods)

The crystal structure of the recently synthesized CaCoSO single crystal is shown in Fig. 1, which shows that the structure contains  $\text{CaO}_3\text{S}_4$  and  $\text{CoS}_3\text{O}$  groups. The electron clouds of the  $\text{CaO}_3\text{S}_4$  and  $\text{CoS}_3\text{O}$  (Fig. 1) exhibit a planar shape with conjugated electron orbitals, which makes the  $\text{CaO}_3\text{S}_4$  and  $\text{CoS}_3\text{O}$  groups the main source for the thermoelectric generation in CaCoSO. The recently reported experimental geometrical data [7] are optimized by using the *ab-initio* LAPW + lo full-potential method within the generalized gradient approximation (PBE-GGA) [34]. The electronic band structure is calculated utilizing the DFT+U approach [35–39]. The U parameter is applied on Co-3d; after several attempts we found that  $U=0.20$  Ry is the optimal value which results in good agreement with experimental data. Based on the obtained results, the transport properties are calculated using the semi-classical Boltzmann theory as incorporated within the BoltzTraP code [40]; it is the second-principles method which solves the semi-classical Bloch-Boltzmann transport equations within the limits of Boltzmann theory [41–43] and the constant relaxation time approximation [40]. Therefore, calculating the thermoelectric properties is

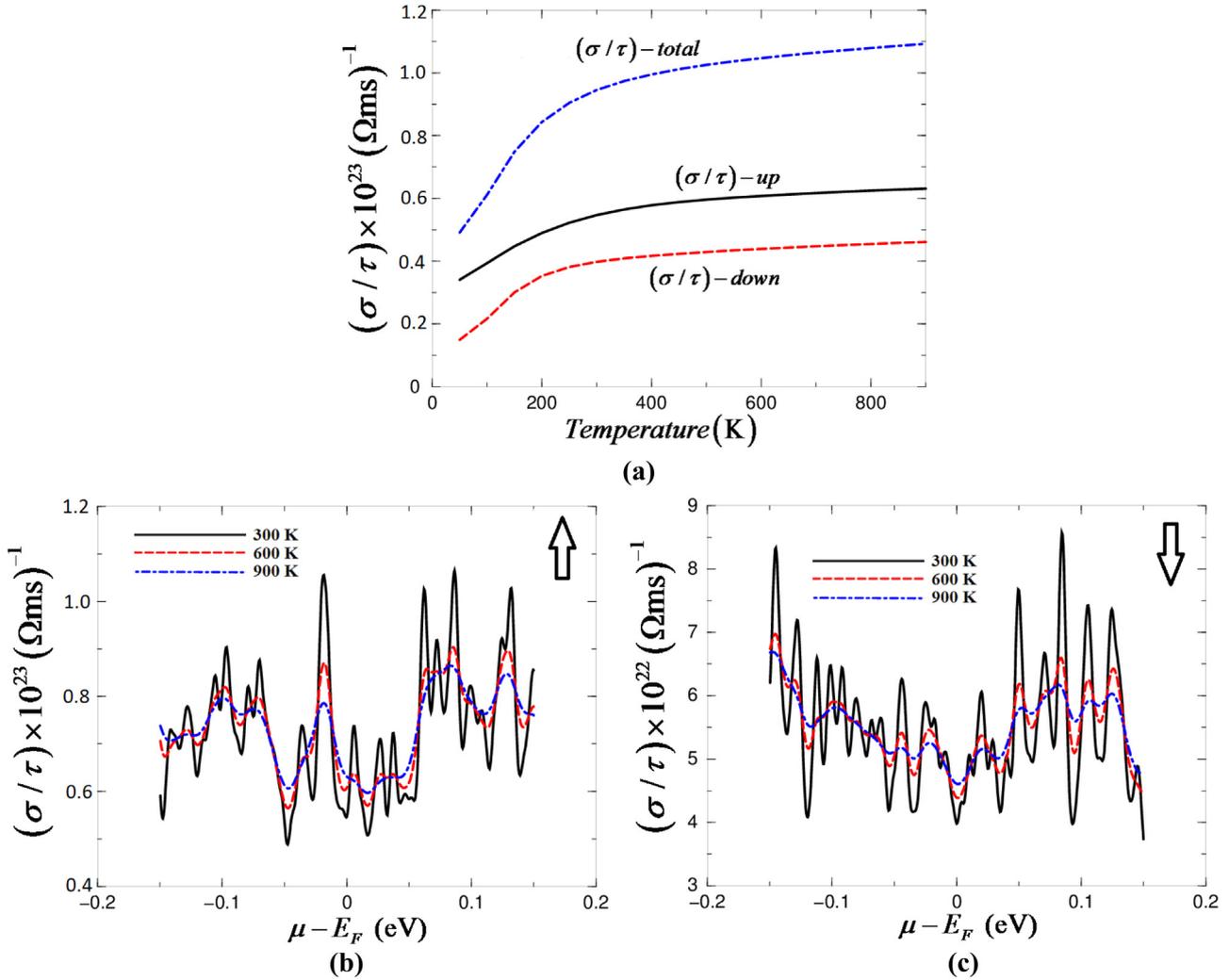
a transition from first- to second-principles methods. The self-consistency is obtained using 2000  $k$  points in the irreducible Brillouin zone (IBZ). The calculations are converged since the total energy of the system is stable within 0.00001 Ry. The spin-polarized electronic band structure and hence the transport properties are obtained using 25,000  $k$  points in the IBZ, as accurate calculations require a dense sampling of the BZ.

## 3. Results and discussion

We make use of the spin-polarized electronic band structure (Fig. 2) to obtain the thermoelectric properties for spin-up and spin-down channels and hence the spin-polarized thermoelectric properties of the CaCoSO single crystal. It is interesting to mention that the CaCoSO single crystal exhibits a direct energy gap ( $\Gamma^v - \Gamma^c$ ) of about 2.187 eV for the spin-up ( $\uparrow$ ) channel, which turns out to be a ( $K^v - K^c$ ) direct gap of about 1.187 eV for the spin-down ( $\downarrow$ ) channel, resulting in an indirect gap ( $\Gamma^v - K^c$ ) of about 0.4 eV for the spin-polarized CaCoSO single crystal. This makes CaCoSO a promising thermoelectric material. Since the electron clouds of the  $\text{CaO}_3\text{S}_4$  and  $\text{CoS}_3\text{O}$  (Fig. 1) exhibit a planar shape with conjugated electron



**Fig. 3.** The temperature induced carrier concentration per unit cell (e/uc); (a) for spin-up electrons versus temperature; (b) spin-down electrons versus temperature; (c) spin-polarized CaCoSO single crystal.



**Fig. 4.** (a) The electrical conductivity for spin-up electrons versus temperature for spin-up, spin-down channels and the total electrical conductivity versus temperature; (b) The electrical conductivity for spin-up electrons as a function of chemical potential ( $\mu - E_F = \pm 0.15$  eV) at three constant temperatures (300, 600 and 900) K; (c) The electrical conductivity for spin-down electrons as a function of chemical potential ( $\mu - E_F = \pm 0.15$  eV) at three constant temperatures (300, 600 and 900) K.

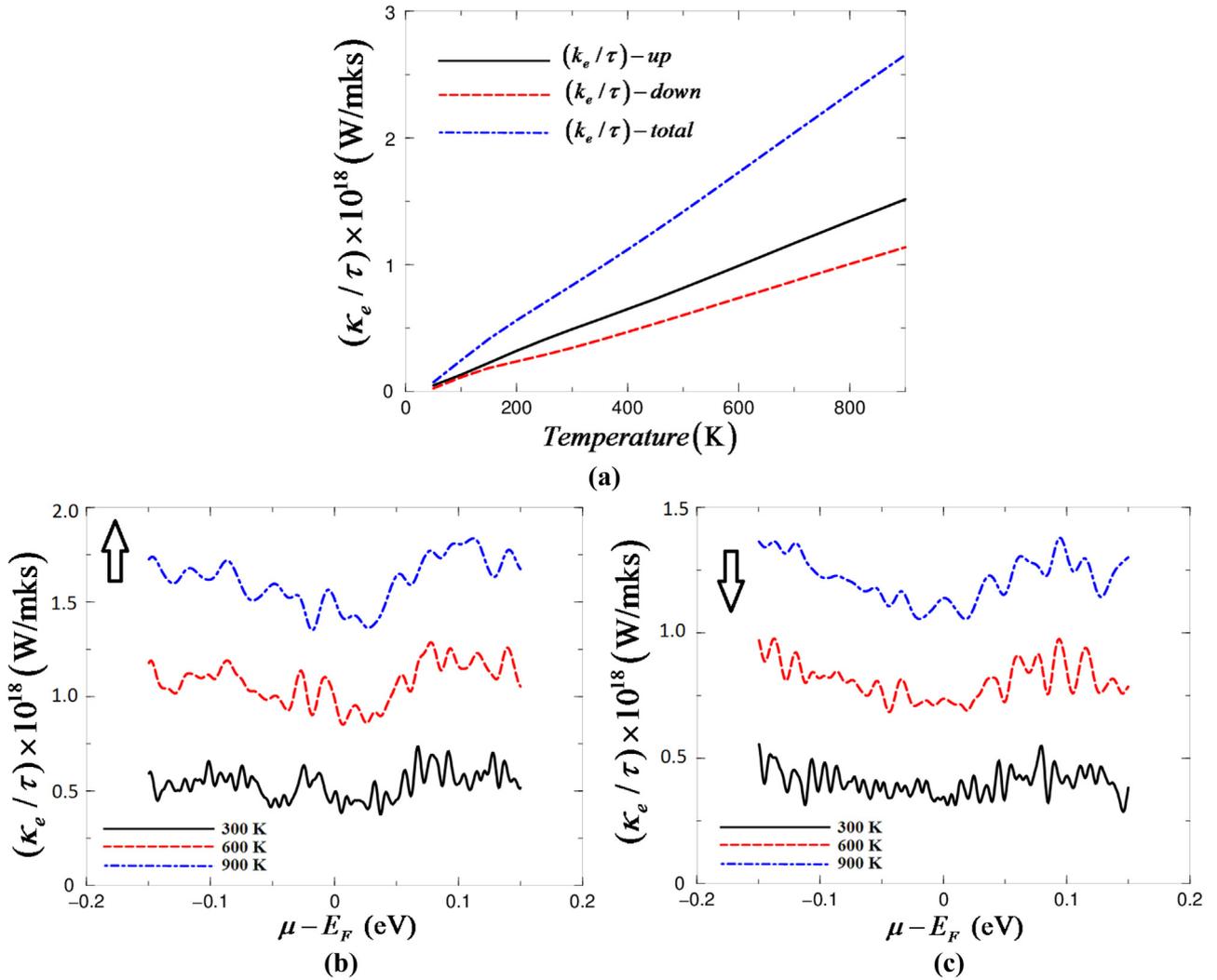
orbitals and exhibit a strong covalent Ca—O, Co—O bonding, the  $\text{CaO}_3\text{S}_4$  and  $\text{CoS}_3\text{O}$  are the main sources for the thermoelectric generator in  $\text{CaCoSO}$ . Wu et al. [12] reported that covalent bonding is more favorable for the transport of the carriers than ionic bonding. Therefore, based on the above-mentioned finding, we expect that  $\text{CaCoSO}$  is a promising thermoelectric material.

The different band dispersion and the energy band gap values between the spin-up channel, the spin-down channel and hence the spin-polarized  $\text{CaCoSO}$  (Fig. 2b) cause to vary the carrier concentration in the vicinity of Fermi level ( $E_F$ ) (Fig. 2a,c,d). It was found that the spin-polarized  $\text{CaCoSO}$  exhibits a maximum carrier concentration in the vicinity of  $E_F$  at three constant temperatures as a function of chemical potential. Fig. 2b shows that the spin-up, spin-down channels and the spin-polarized  $\text{CaCoSO}$  possess parabolic bands in the vicinity of  $E_F$ ; therefore, the carriers exhibit low effective mass and hence high mobility, which leads to a large gain in electrical conductivity. The effective mass ratio of the electrons  $m_e^*/m_e$ , heavy holes ( $m_{hh}^*/m_e$ ) and light holes  $m_{lh}^*/m_e$  for the spin-up, spin-down channels and the spin-polarized  $\text{CaCoSO}$  are listed in Table 1. Thus, we expect that  $\text{CaCoSO}$  can give high

thermoelectric efficiency provided that it has a large Seebeck coefficient and low thermal conductivity [13].

The carrier concentration ( $n$ ) as a function of temperature ( $T$ ) at fixed chemical potential ( $\mu = E_F$ ) for the spin-up, spin-down channels and the spin-polarized  $\text{CaCoSO}$  are shown in Fig. 3(a–c). It was noticed that the spin-up channel possesses n-type conduction and  $n$  shows exponential behavior with  $T$ , whereas the spin-down channel exhibits a p-type conduction which increases almost linearly with increasing  $T$ . As it is clear that the concentration of the p-type conduction is higher than that of the n-type, the spin-polarized  $n$  (total  $n$ ) exhibits p-type conduction and increases almost linearly with increasing  $T$ . Following Fig. 3(a–c), we can conclude that the p-type conduction is the dominant in  $\text{CaCoSO}$ , which agrees well with the previous finding that the oxide chalcogenide compounds are p-type transparent conductors [1–6].

The electrical conductivity ( $\sigma/\tau$ ) at  $\mu = E_F$  as a function of  $T$  for spin-up/down channels are shown in Fig. 4a. It is clear that the spin-up channel exhibits higher  $\sigma/\tau$  than that of the spin-down channel, resulting in a considerable spin-polarized  $\sigma/\tau$  (Fig. 4a). Overall, the spin-up/down and total  $\sigma/\tau$  show a similar tendency.



**Fig. 5.** (a) The electronic thermal conductivity for spin-up electrons versus temperature for spin-up, spin-down channels and the total electronic thermal conductivity versus temperature; (b) The electronic thermal conductivity for spin-up electrons as a function of chemical potential ( $\mu - E_F = \pm 0.15$  eV) at three constant temperatures (300, 600 and 900) K; (c) The electronic thermal conductivity for spin-down electrons as a function of chemical potential ( $\mu - E_F = \pm 0.15$  eV) at three constant temperatures (300, 600 and 900) K.

To ascertain the finding that the spin-up channel exhibits higher  $\sigma/\tau$  than that of the spin-down channel,  $\sigma/\tau$  as a function of chemical potential at three constant T for spin-up/down channels were investigated as shown in Fig. 4b,c. It was found that 300 K shows the highest  $\sigma/\tau$  in both channels and the spin-up channel exhibits higher values than those of the spin-down channel for all temperatures.

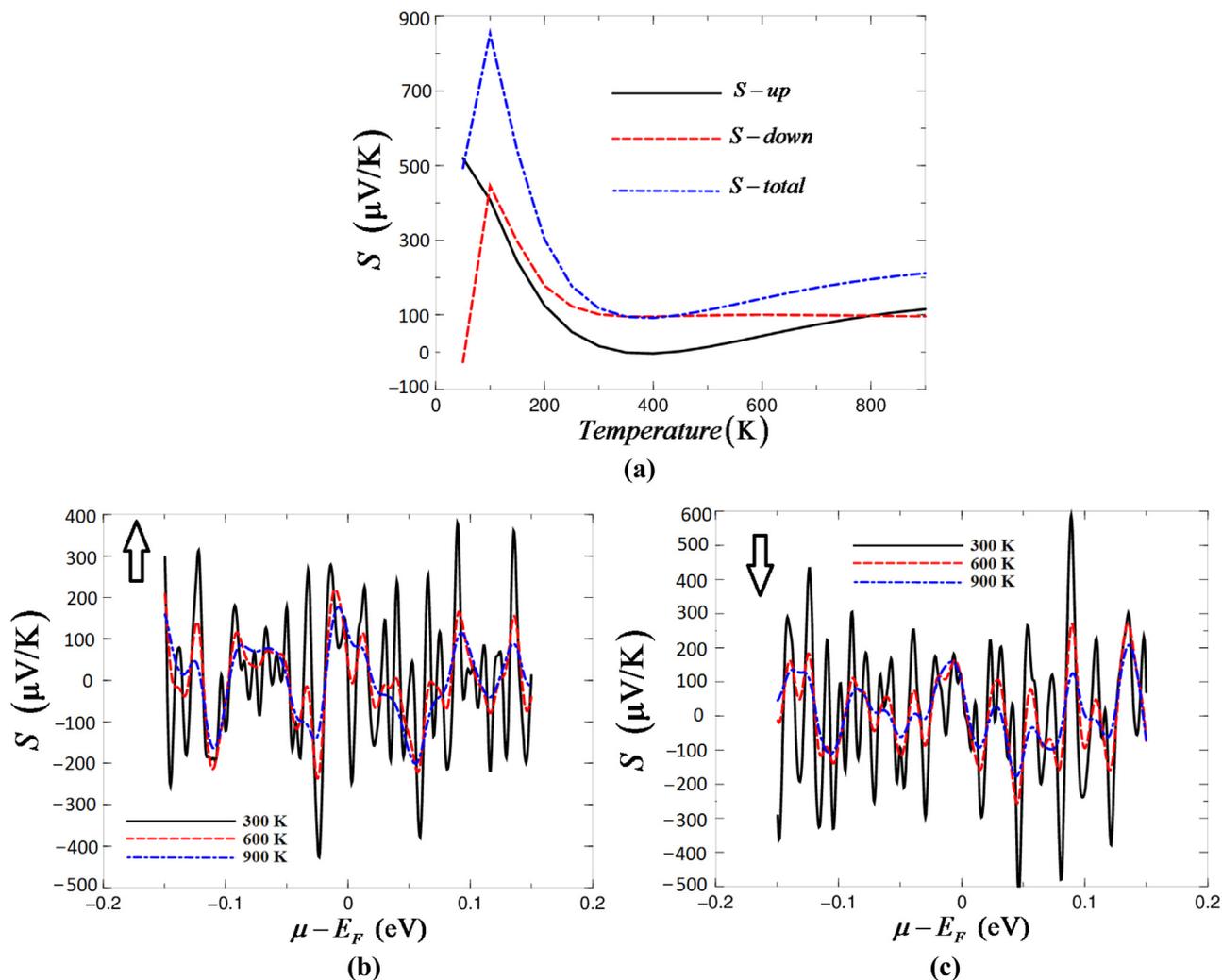
To gain high thermoelectric efficiency, a material should exhibit low thermal conductivity; therefore, the electronic thermal conductivity ( $k_e/\tau$ ) of CaCoSO was investigated as a function of T at fixed chemical potential ( $\mu = E_F$ ), as shown in Fig. 5a. This figure shows that  $k_e/\tau$  increases linearly with T, which implies that CaCoSO exhibits low  $k_e/\tau$  at room temperature for  $\mu = E_F$ . To support this finding, we investigated  $k_e/\tau$  as a function of chemical potential  $\mu - E_F$  between  $\pm 0.15$  eV for three temperatures, as shown in Fig. 5b,c. These figures confirm that CaCoSO exhibits the lowest  $k_e/\tau$  at 300 K, which implies that this material could be an efficient thermoelectric material, provided that it exhibits high electrical conductivity and a large Seebeck coefficient [13]. From the above, it was found that CaCoSO exhibits large electrical

conductivity and low thermal conductivity. Thus, we should investigate whether CaCoSO exhibits a large Seebeck coefficient or not.

Fig. 6a illustrates the calculated Seebeck coefficient (S) as a function of T at  $\mu = E_F$ , which clearly shows the highest values for S are achieved between 100 K and 250 K for a particular value of chemical potential  $\mu = E_F$ . Furthermore, we investigated S as a function of  $\mu - E_F = \pm 0.15$  eV at three temperatures, which shows that for all the values of  $\mu - E_F$  that confined between  $\pm 0.15$  eV, the largest value of S occurs at 300 K.

Based on the above results, we can conclude that CaCoSO exhibits high electrical conductivity, low thermal conductivity and a large Seebeck coefficient. Therefore, it is an efficient thermoelectric material.

The calculated power factor ( $P = S^2\sigma/\tau$ ) further supported the above-mentioned finding. Fig. 7a shows that the highest power factor values are achieved between 100 K and 250 K for a particular value of chemical potential  $\mu = E_F$ , whereas Fig. 7 b,c shows that the highest power factor values are achieved at 300 K for the chemical potentials confined between  $\pm 0.15$  eV. This is another confirmation



**Fig. 6.** (a) The Seebeck coefficient for spin-up electrons versus temperature for spin-up, spin-down channels and the total Seebeck coefficient versus temperature; (b) The Seebeck coefficient for spin-up electrons as a function of chemical potential ( $\mu - E_F = \pm 0.15$  eV) at three constant temperatures (300, 600 and 900) K; (c) The Seebeck coefficient for spin-down electrons as a function of chemical potential ( $\mu - E_F = \pm 0.15$  eV) at three constant temperatures (300, 600 and 900) K.

which supported the statement that CaCoSO is an efficient thermoelectric material.

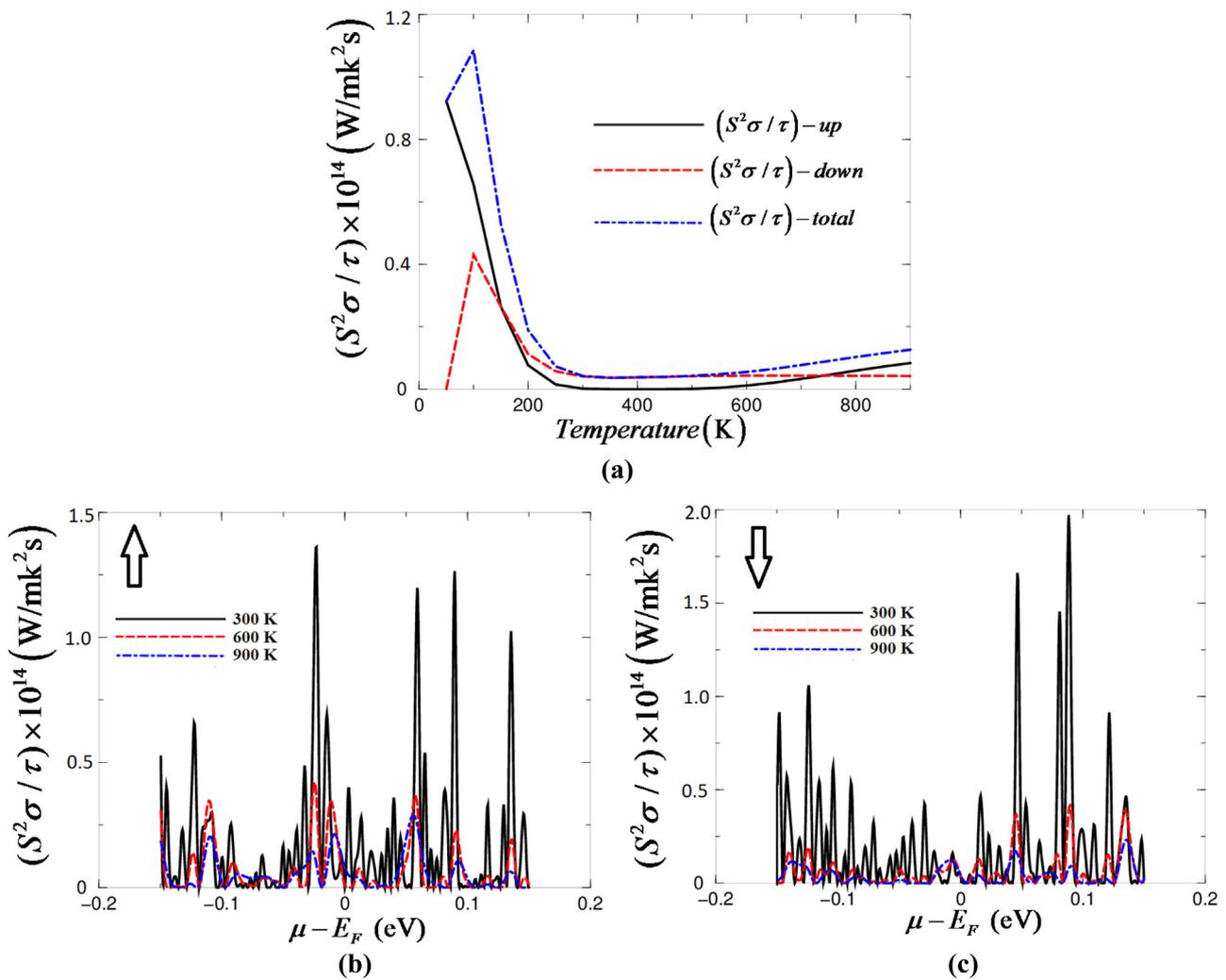
#### 4. Conclusions

We investigated the thermoelectric properties of the recently synthesized CaCoSO single crystal based on the density functional theory and the transition from first- to second-principles methods. The calculations reveal some interesting findings. The first finding is that the CaCoSO single crystal exhibits a high electrical conductivity, low thermal conductivity and a large Seebeck coefficient. Based on these findings, the investigated crystal can be considered an efficient thermoelectric material. The second finding is that the CaCoSO single crystal exhibits a direct energy gap ( $\Gamma^v - \Gamma^c$ ) of about 2.187 eV for the spin-up ( $\uparrow$ ) channel, which turns out to be ( $K^v - K^c$ ) direct gap of about 1.187 eV for the spin-down ( $\downarrow$ ) channel, resulting in an indirect gap ( $\Gamma^v - K^c$ ) of about 0.4 eV for the spin-polarized CaCoSO signal crystal. Such a small

gap makes the material a promising candidate for thermoelectric application. The third finding is that the electron clouds of the  $\text{CaO}_3\text{S}_4$  and  $\text{CoS}_3\text{O}$  exhibit a planar shape with conjugated electron orbitals and exhibit a strong covalent Ca—O, Co—O bonding. This is another factor which makes CaCoSO a promising candidate for thermoelectric materials, since covalent bonding is more favorable for the transport of the carriers than ionic bonding. Therefore, based on the above findings, we can conclude that CaCoSO is, in fact, a promising thermoelectric material.

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**Fig. 7.** (a) The power factor for spin-up electrons versus temperature for spin-up, spin-down channels and the total power factor versus temperature; (b) The power factor for spin-up electrons as a function of chemical potential ( $\mu - E_F = \pm 0.15$  eV) at three constant temperatures (300, 600 and 900) K; (c) The power factor for spin-down electrons as a function of chemical potential ( $\mu - E_F = \pm 0.15$  eV) at three constant temperatures (300, 600 and 900) K.

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