Thermoelectric materials taking advantage of spin entropy: lessons from chalcogenides and oxides

Sylvie Hébert, Ramzy Daou, Antoine Maignan, Subarna Das, Aritra Banerjee, Yannick Klein, Cédric Bourgès, Naohito Tsujii, and Takao Mori

*Laboratoire de Cristallographie et Sciences des Matériaux (CRISMAT), Normandie Université, UMR6508 CNRS, ENSICAEN, UNICAEN, Caen, France;
Department of Physics, University of Calcutta, Kolkata, India;
IMPMC, Sorbonne Université, Paris, France;
International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science, Tsukuba, Japan;
Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Japan

ABSTRACT
The interplay between charges and spins may influence the dynamics of the carriers and determine their thermoelectric properties. In that respect, magneto-thermoelectric power (MTEP), i.e., the measurements of the Seebeck coefficient $S$ under the application of an external magnetic field, is a powerful technique to reveal the role of magnetic moments on $S$. This is illustrated by different transition metal chalcogenides: CuCrTiS$_4$ and CuMnTiS$_4$ magnetic thiospinels, which are compared with magnetic oxides, Curie-Weiss (CW) paramagnetic cobaltites, ruthenates, either ferromagnetic perovskite or Pauli paramagnetic quadruple perovskites, and CuGa$_{1-x}$Mn$_x$Te$_2$ chalcopyrite telluride and Bi$_{1.99}$Cr$_{0.01}$Te$_3$ in which diluted magnetism is induced by 3%-Mn and 1%-Cr substitution, respectively. In the case of a ferromagnet (below $T_C$) and CW paramagnetic materials, the increase of magnetization at low $T$ when a magnetic field is applied is accompanied by a decrease of the entropy of the carriers and hence $|S|$ decreases. This is consistent with the lack of MTEP in the Pauli paramagnetic quadruple perovskites. Also, no significant MTEP is observed in CuGa$_{1-x}$Mn$_x$Te$_2$ and Bi$_{1.99}$Cr$_{0.01}$Te$_3$, for which Kondo-type interaction between magnetic moments and carriers prevails. In contrast, spin glass CuCrTiS$_4$ exhibits negative MTEP like in ferromagnetic ruthenates and paramagnetic misfit cobaltites. This investigation of some chalcogenides and oxides provides key ingredients to select magnetic materials for which $S$ benefits from spin entropy.

KEYWORDS
Thermopower; chalcogenides; oxides; spins; entropy; magneto-resistance

CLASSIFICATIONS
50 Energy Materials; 203 Magnetics / Spintronics / Superconductors; 206 Energy conversion / transport / storage / recovery; 210 Thermoelectronics / Thermal transport / insulators, chalcogenides, magneto-thermopower
1. Introduction

Thermoelectric (TE) materials have the potential to be one of the green solutions towards today’s global energy crisis [1,2]. Over the years, to make TE devices a commercial success, many efforts have been made first to optimize material parameters like Seebeck coefficient (S) and electrical resistivity (ρ) through band engineering approaches, including band distortion [3], band convergence [4,5], and band nesting [6], to find a candidate with a large power factor PF as PF enters the TE Figure of merit \( ZT = S^2T/(\rho \kappa) = (PF)T/\kappa \), where \( \kappa \) and \( T \) are the thermal conductivity and absolute temperature, respectively. Many chalcogenides having transition metal cations with partially filled d orbitals in them exhibit fascinating TE properties. In most cases, their interesting transport properties cannot be described by standard models. Strong correlations between carriers and interplay between charges and spins can influence the dynamics of the carriers and determine their TE properties [7–9]. Magnetic field-dependent thermoelectric power (MTEP) along with magnetoresistance (MR) studies provide a tool to unveil the possible mechanisms of unconventional transport properties of such magnetic systems and subsequently find new TE materials with suitable parameters. As the Seebeck coefficient depends on both transport coefficients and entropy [10], the application of a magnetic field can affect both terms. A significant MTEP usually signifies large orbital or spin degrees of freedom of the carriers, which through increasing entropy can result in large \( S \), which is required for TE application [11]. At first, considering metal transition oxides, Wang et al., through MTEP measurement of \( Na_2CoO_2 \) samples with mixed valency of low spin \( Co^{3+} \) and \( Co^{4+} \), demonstrated that \( S \) is dominated by spin entropy in these layered oxides [8]. As for the latter system, the misfit cobalt oxides, another class of compounds containing \( CoO_2 \) layers of the \( CdI_2 \)-type (Figure 1), exhibit a temperature dependence of \( S \), which is not metal like. The low temperature slope of \( S \) in \( BiCaCoO \) misfit is strongly enhanced by the presence of paramagnetic spins as evidenced by its large negative MTEP below 20 K [12]. However, in oxides, the MTEP is not limited to \( CdI_2 \)-type structure in which the transition metal forms hexagonal layers but is also found in square lattices of 3D perovskites (Figure 1). A giant negative MTEP between \(-80\% \) and \(-100\% \) under 5 T in the 60–225 K temperature range was observed in the \( Nd_{0.75}Na_{0.25}MnO_3 \) perovskite manganite and was accompanied by a large MR, which can be correlated with magnetic field-induced collapse of antiferromagnetism (AFM) [13]. It is noteworthy to mention that large MTEP and MR can also be observed without the presence of any magnetic cation in some topological insulators and phases having Dirac states [14–

![Figure 1](image-url). Schematic structural representation example of a) \( CuCr_2S_4 \) Thiospinel structure-type, b) Misfit Cobaltite structure, c) \( SrRuO_3 \) Perovskite structure-type and d) \( CuGaTe_2 \) Chalcopyrite structure-type.
Such effects arise from non-trivial band structure and are not in the scope of this study.

Apart from oxides, there exists other metal transition magnetic compounds containing chalcogen anions like S, Se and Te, which show excellent TE parameters with or without MTEP effect. For sulphaides, considering the spinel structure first found in oxides, this is exemplified by the CuCrTiS\(_4\) thiostephanie (Figure 1), characterized by a large TEP absolute value (\(S_{300\text{K}} = -180\ \mu\text{V/K}\)), and for which MTEP was reported [17]. This large S absolute value is remarkable if one considers the low S values reported for the metallic behaviours of both end members CuCr\(_2\)S\(_4\) and CuTi\(_2\)S\(_4\) [17]. In some magnetic chalcopyrites also, where all metals are tetrahedrally coordinated to sulphur anions (Figure 1), magnetism was invoked to explain the large TEP. Compounds derived from AFM CuFeS\(_2\) chalcopyrite may exhibit a large power factor, by doping at the Cu site, or by creating S vacancies [18]. Indeed, a maximum power factor of \(10^{-3}\ \text{Wm}^{-1}\text{K}^{-2}\) was found for Cu\(_{0.97}\)Zn\(_{0.03}\)FeS\(_2\) where large TEP was explained through an enhancement of the effective mass m* due to the interaction between delocalized carriers and localized antiferromagnetic spins [19,20].

Here, we present an MTEP investigation of oxides and sulphides possessing different structures schematically described in Figure 1. The variety of their crystallographic structures, 2D or 3D, with magnetic cations forming hexagonal or cubic arrays and with very different metal coordinations, octahedral in misfit cobaltites and perovskite ruthenates, tetrahedral in chalcopyrites or both octahedral and tetrahedral coordinations in spinel, is at the origin of different electronic and magnetic states. In the following, the relationship between magnetism and thermopower is demonstrated in this diversity of thermoelectric compounds. Though fundamental, our comparative study will help to understand and correlate the interplay between spin and thermal transport in systems having different magnetic properties, which might be important for their further development towards better TE materials.

2. Experimental details

According to our previous studies [21–23], among magnetic chalcogenides, sulphides like CuCrTiS\(_4\) thiospinel and tellurides like CuGa\(_{1-x}\)Mn\(_x\)Te\(_2\) chalco-pyr-ite (0 ≤ x ≤ 0.03) and Bi\(_{1.99}\)Cr\(_{0.01}\)Te\(_2\) were chosen. The synthesis of these materials was carried out using solid state reaction technique by heating the constituent elements under vacuum. A CuMn\(_{0.5}\)Ti\(_{1.5}\)S\(_4\) ceramic sample was also prepared replacing Cr by Mn/Ti metal and using the same synthesis method as in Ref [21]. As for oxides, three families were investigated with different magnetic properties: SrRuO\(_3\) perovskite,

\[\text{DCu}_3\text{Ru}_2\text{O}_{12} \quad (D = \text{Na, Ca, Ca}_{0.5}\text{La}_{0.5}, \text{La})\]

quadruple perovskites, and misfit cobaltites like [Bi\(_2\)O\(_3\)][CoO\(_2\)]\(_{0.5}\)\(_{1/2}\) (\(A = \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}\); \(b_1/b_2 = \text{crystallographic misfit ratio}\)) were taken for investigation. These oxides were prepared by standard ceramic method. The details of synthesis of the samples along with their in-depth structural characterization and experimental details about magnetic property measurements can be found elsewhere [21–26].

Thermopower (TEP) measurements were performed using a homemade sample puck in a physical property measurement system (9 T-PPMS, Quantum Design, San Diego, USA) [27]. Measurements are performed using a four-point steady-state technique with separate measuring and power contacts. Bars of typical dimension of 2×2×10 mm\(^3\) were mounted using GE varnish on the heat sink of the cryostat, and two chromel-constantan thermocouples were attached to monitor the temperature gradient. The thermoelectric voltage was measured through the chromel wires. For MTEP measurements (Figure 2), magnetic field perpendicular to the temperature gradient was applied (Figure 2(a)). Measurements were done either in isothermal conditions by varying the magnetic field or as a function of temperature in an applied magnetic field. The thermoelectric properties of CuGa\(_{1-x}\)Mn\(_x\)Te\(_2\) and Bi\(_{1.99}\)Cr\(_{0.01}\)Te\(_2\) were measured using the TTO option from Quantum Design. For CuGa\(_{1-x}\)Mn\(_x\)Te\(_2\), magnetic fields were applied both parallel and perpendicular to the temperature gradient. As shown below, the two different configurations gave essentially the same results. Thus, for Bi\(_{1.99}\)Cr\(_{0.01}\)Te\(_2\), the magnetic field was applied parallel to the direction of heat gradient (Figure 2(b)).

MR was measured in the same instrument by a conventional four probe method by applying magnetic field perpendicular to the current flow. For CuGa\(_{1-x}\)Mn\(_x\)Te\(_2\) samples, MR measurements were performed by applying magnetic field both parallel and perpendicular to the current.

3. Results and discussions

3.1. Paramagnetic systems

For spinel chalcogenides, magnetic and magnetotransport properties are determined by distribution and localization of metal ions in their tetrahedral as well as octahedral cationic sites and their oxidation states [28–30]. In this family, cubic thiospinel CuTi\(_2\)S\(_4\) having Ti\(^{3+}\) and Ti\(^{4+}\) mixed valence exhibits a Pauli paramagnetic behaviour whereas a double exchange between high spin Cr\(^{3+}\) and Cr\(^{4+}\) is reported to be responsible for ferromagnetism observed in CuCr\(_2\)S\(_4\) [31,32]. A solid solution exists between these two members, and the CuCrTeS\(_4\) thiospinel having half-filled t\(_{2g}\) Cr\(^{3+}\) and empty t\(_{2g}\) Ti\(^{4+}\) shows a paramagnetic
behaviour down to low temperature (Figure 3). A spin glass transition occurs at $T = 8$ K [33]. Fitting susceptibility data with Curie-Weiss law shows a slight upward deviation of the experimental data below $T = 75$ K (inset of Figure 3). This points to small antiferromagnetic fluctuations occurring due to magnetic interaction among Cr$^{3+}$ ions. While its magnetic properties are governed by Cr$^{3+}$, Ti ions mainly contribute to carriers conduction. To describe transport properties for $T < 75$ K, a variable range hopping model (VRH) was employed for this system [21]. Despite the metallicity and rather small $S$ value of both end members, i.e. ferromagnet CuCr$_2$S$_4$ ($S = +16$ $\mu$V/K) and Pauli paramagnet CuTi$_2$S$_4$ ($S = -12$ $\mu$V/K) [34], a thermopower as high as $-140$ $\mu$V/K at 300 K is observed in CuCrTiS$_4$ (Figure 4). Due to a small departure from the stoichiometry of the compound, a small fraction of Ti$^{3+}$ having slightly filled $t_{2g}$ orbitals remains in the system, which leads to large negative $S$. A giant MR, reaching $-95\%$ at 5 K for 9 T is observed [21] (top panel of Figure 5). This could be attributed to the gradual alignment of neighboring magnetic moments of Cr$^{3+}$ ions with the application of external magnetic field. Such a large negative MR in the VRH regime is similar to the behaviour observed in colossal magnetoresistive (CMR) manganites [35]. So MR in the whole $T$ range was scaled as a function of $(1 - B_j^2)$, where $B_j$ is the Brillouin function (in [21]), with $S = J = 3/2$. This confirms that paramagnetic Cr$^{3+}$

Figure 2. Schematic diagram of the MTEP set up in (a) homemade sample puck where direction of magnetic field is perpendicular to the direction of heat flow, as represented by the black circles (b) TTO option from Quantum Design where direction of heat flow and magnetic field is parallel to each other.

Figure 3. Temperature dependence of magnetic susceptibility ($\chi$) of CuCrTiS$_4$ and CuMn$_{0.5}$Ti$_{1.5}$S$_4$ in a field of $10^{-2}$ T. Inset: $\chi^{-1}$ $(T)$ of CuCrTiS$_4$ where the dashed line corresponds to the Curie-Weiss fitting.
ions progressively align themselves as the temperature is lowered and give rise to giant negative MR. The effect of external magnetic field on $S$ can be observed below 45 K as shown in Figure 6. A large MTEP with absolute $S$ decreasing from 34 µV/K at 0 T to 25 µV/K at 9 T for a typical temperature $T = 20$ K is obtained (inset of Figure 6). This $S$ lowering can be attributed to the gradual alignment of $\text{Cr}^{3+}$ spins, which decreases the magnetic entropy. For comparison, the properties of the metallic thiospinel $\text{CuMn}_{0.5}\text{Ti}_{1.5}\text{S}_4$ are reported. This compound was found to be isostructural to the cubic $\text{CuCrTiS}_4$ thiospinel. As shown in Figure 3, the susceptibility is smaller in the whole $T$ range, with a rapid increase at low $T$. A Curie-Weiss fitting to this $T$-dependent susceptibility in between 100 K and 300 K yields $\mu_{\text{eff}} = 5.7$ $\mu_B$/f.u. Such a value is consistent
with $S = 0$ for $\text{Ti}^{4+}$ and $S = \frac{5}{2}$ for high spin $\text{Mn}^{2+}$ as a theoretical value $\mu_{\text{eff}} = 5.9 \mu_B$ is calculated for a high spin $d^4$ cation. Thus, in both $\text{CuCrTiS}_4$ and $\text{CuMn}_{0.5}\text{Ti}_{1.5}\text{S}_4$, the Ti cations are tetravalent, whereas Cr is trivalent for the former and Mn divalent for the latter. $\text{CuMn}_{0.5}\text{Ti}_{1.5}\text{S}_4$ is metallic with a small upturn of electrical resistivity below 50 K (inset of Figure 4), the temperature below which the $\chi$ values strongly increase. In this T range, below 50 K, a small negative MR appears, reaching $\sim -2\%$ in 9 T at 5 K (bottom panel of Figure 5). For this metallic thiopinol, the thermopower, with values in between those of $\text{CuCrTiS}_4$ and $\text{CuTi}_{2}\text{S}_4$, exhibits negative values, varying almost linearly with temperature as expected for a metal (Figure 4). In clear contrast with $\text{CuCrTiS}_4$ which exhibits VRH transport, only a very small MTEP is detected (not shown), showing the major role of localized paramagnetic spins on MTEP.

The positive impact of localized spins on thermopower had already been evidenced in Bi-based misfit cobaltites like [Bi$_2$O$_3$]$_{0.1}$[CoO$_2$]$_{0.92}$/$\text{BiCaCoO}$ ($A = \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}$; $b_1/b_2 =$ crystallographic misfit ratio). They consist of a single layer of CdI$_2$ type [CoO$_2$], which is stacked with four layers of rocksalt (RS) type structure [24]. Cationic substitutions in the RS type layers are responsible for a doping of the [CoO$_2$] layer by a mechanism of charge transfer and a modification of the positive charge in RS type layer, which is manifested through a change in the misfit ratio ($b_1/b_2$). These materials do not show any magnetic ordering and remain paramagnetic down to 2 K [36]. Figure 7 depicts $S$(T) data for [Bi$_{1.7}$Co$_{0.3}$Ca$_{0.4}$][CoO$_2$]$_{1.67}$ abbreviated as BiCaCoO. Within the temperature range 20–125 K, a linear variation of $S$ is observed. The large value of the slope in the linear region below 20 K reflects strong electronic correlations in accordance with the high value of the Sommerfeld coefficient $\gamma$ and the universality of the ratio $S/$(T$\gamma$) [7,12]. As far as MTEP is concerned, a strong magnetic field dependence of $S$ is observed for BiCaCoO [24] below ~125 K: as shown in the inset of Figure 6, $S$ is dramatically reduced as the magnetic field is applied. This
Weiss a observed and of a align- (H). decrease 36 24 Sci. of magnetization BIBaCoO, misfit, no MTEP is observed [24,36], as discussed for thiospinels. MR and MTEP are observed only for localized carriers, with a large enough susceptibility associated with a Curie-Weiss behaviour.

At room temperature, no MTEP is observed in any of these misfit materials. However, the presence of magnetic cations still plays a role, as S at room temperature is mainly dependent on the formal valency of Co in [CoO2] layers, and on the fact that these Co cations carry a spin as shown by the generalized Heikes formula [37,38]. The S data around 300 K can be described by:

\[ S = -\frac{k_B}{e} \ln \left[ \left( \frac{2S_n + 1}{2S_{n+1} + 1} \right) \left( \frac{1 - x}{x} \right) \right] + \frac{k_B}{e} \ln(\Gamma_{\text{orb}}) \]

where \( S_n \) and \( S_{n+1} \) are the spins of the transition metal \( M^{n+} \) and \( M^{(n+1)+} \), respectively, \( x \) is the carrier concentration and \( \Gamma_{\text{orb}} \) the orbital degeneracy. In the case of Bi-based misfits, both spin and orbital degeneracy terms related to low spin Co\(^{3+} \) (\( S = 0 \)) and low spin Co\(^{4+} \) (\( S = \frac{1}{2} \)) have to be taken into account to describe its room temperature \( S \) [39,40]. Taking into account the lifting of the \( t_{2g} \) degeneracy [40,41] the spin and orbital terms correspond to \( \ln(2) = \sim 60 \mu V/K \) [8,40], a sizable fraction of the thermopower, \( \sim 140 \mu V/K \) at 300 K for \( x = 0.33 \) (Figure 7).

### 3.2. Ferromagnetic ruthenates

In the case of ruthenium oxides, the role of the spin entropy and magnetism can be investigated for different magnetic states due to the diversity of magnetic behaviour in these most often metallic oxides. The Seebeck coefficients of different ruthenium oxides exhibiting ferromagnetism (SrRuO\(_3\)), paramagnetism (CaRuO\(_3\)) and Pauli paramagnetism (quadruple perovskites) have been measured. SrRuO\(_3\) is a ferromagnetic metal \( (T_C \sim 160 \text{ K}) \) where Ru takes a \( d^4 \) electronic configuration [42]. In this perovskite structure, a low-spin \( (S = 1) \) state of Ru\(^{4+} \) is favoured due to the large crystal field splitting between \( e_g \) and \( t_{2g} \) orbitals in the presence of octahedrally connected oxygens [43]. A close look at Figure 8 reveals that \( S(T) \) for SrRuO\(_3\) does not exhibit the expected linear dependence for a typical Drude metal, and that magnetism plays a role with an accident observed near \( T_C \sim 160 \text{ K} \). In the case of the paramagnetic CaRuO\(_3\) [44], the evolution is smoother up to high temperature.

Calculation of the spin only term in Heikes formula using spins of Ru\(^{5+} \) \( (S = 3/2) \) in matrix of Ru\(^{4+} \) \( (S = 1) \) and Ru\(^{3+} \) \( (S = 1/2) \) in the matrix of Ru\(^{4+} \) gives \( S \) value of 25 \( \mu V/K \) and 35 \( \mu V/K \), respectively, which is very close to the measured \( S \) for SrRuO\(_3\) and related ruthenates around 300 K [25]. Above \( T_C \), \( S \) is driven by a constant spin entropy. This model is much too simple, and a more rigorous calculation has shown that in the case of SrRuO\(_3\), the orbital entropy is quenched up to 1200 K, leading to a spin entropy-dominated Seebeck coefficient below 1200 K [45]. In addition, a negative MTEP is also observed below \( T_C \) for SrRuO\(_3\) (inset of Figure 8 for \( T = 20 \text{ K} \)). This field

![Figure 8](image-url)
dependence of S follows the magnetization curve M(H) (Figure 9): a gradual increase of external magnetic field makes the spins more aligned up to its saturation magnetization \(M_S\) (to be compared to M(H), inset of Figure 8), leading to a decrease of S. From the inset of Figure 8, when the saturation magnetization \(M_S\) is reached, the MTEP becomes constant. The magnitude of the SrRuO\(_3\) MTEP is similar to the one measured in the ferromagnetic CaRu\(_{0.8}\)Sc\(_{0.2}\)O\(_3\) (~15% at 30 K) [46].

### 3.3. Pauli paramagnetic ruthenates

To compare with these perovskites, S and \(\rho\) measurements of a group of quadruple perovskite (QP) samples \(DCu_3Ru_4O_{12}\) (\(D=\ Na, Ca, Ca_{0.5}La_{0.5}, La\)) having Ru oxidation state ranging from 3.75 (\(D = La^{3+}\)) to 4.25 (\(D = Na^+\)) and presenting Pauli like behaviours (Figure 9) were performed. Density of states calculations in these materials shows that the influence of Cu states can only be observed far below \(E_F\), and hence have no effect on the transport properties [47]. \(\rho(T)\) measurements up to 900 K for LaCu\(_3\)Ru\(_4\)O\(_{12}\) exhibit a monotonic increase of \(\rho\), almost linearly with \(T\) without any saturation (Figure 2 in [26]), consistently with the bad metal behaviour observed in many ruthenates such as SrRuO\(_3\) or Sr\(_2\)RuO\(_4\) [48–50]. Even though S values of all these QP and single perovskite SrRuO\(_3\) are similar (~32 \(\mu V/K\)) at the highest temperature of 900 K, the evolution of S(T) differs with a gradual increase in the case of QP, with a much smaller slope than for SrRuO\(_3\) (Figures 10 and Figures 8). In fact, the saturation S value of 32 \(\mu V/K\) for SrRuO\(_3\) is reached at \(T \sim 200\) K whereas around this temperature all the S curves of the QP group almost merge to 12 – 15 \(\mu V/K\). At lower temperatures,
there is a substantial change in the value of $S$ of $DCu_3Ru_4O_{12}$ and the values of $S$ depend on the $M$ value of the samples, with the smallest Seebeck coefficient measured for $NaCu_3Ru_4O_{12}$ (Figure 11) which possesses the smallest Pauli susceptibility. For $T > 200$ K, all $S$ curves converge and almost a similar $S$ value of all the samples is observed in the temperature range 200–900 K. So formal Ru oxidation state has no effect on $S$ in these samples. A monotonic increase in $S$ up to high temperature can be rather related to classical metal-like picture following Mott’s formula, where band structure plays a significant role. MTEP measurements show no significant effect of external magnetic field on $S$ in these Pauli paramagnets as exemplified for $CaCu_3Ru_4O_{12}$ in the inset of Figure 10.

3.4. Diluted paramagnetism in a telluride, a Kondo effect?

The last example is $CuGa_{1-x}Mn_xTe_2$ which is a paramagnetic system with no evidence of magnetic order observed at least down to 5 K (Figure 12). $Mn^{2+}$ doping in the pristine system increases hole concentration. As a result, smaller electrical resistivity $\rho$ is observed in $x = 0.03$ as compared to $x = 0$. But in spite of increasing in carrier concentration, relatively high
TEP is observed in Mn-doped sample. Figure 13 shows the effective mass enhancement $m^*/m_0$ of CuGa$_{1-x}$Mn$_x$Te$_2$, which has been derived from the Seebeck coefficients and the carrier concentrations at $T = 325$ K based on a parabolic band model. The effective mass enhances from $0.6m_0$ for $x = 0$ to $1.5m_0$ for $x = 0.03$ [51]. It has been demonstrated that the interactions between holes and the magnetic ions play a pivotal role in enhancing $m^*$. Strong correlation between magnetic ions and holes is inferred from the magnetoresistance (MR) shown in Figure 13. At $T = 10$ K, transverse magnetoresistances $MR_T$ shown in Figure 14(a) decrease significantly, reaching almost −40% for $x = 0.01$ and −20% for $x = 0.02$ and 0.03. Shown in Figure 14(b) is the longitudinal magneto resistance $MR_L$ of $x = 0.03$ with field parallel to current, measured at various temperatures. $MR_L$ at $T = 10$ K almost agrees with $MR_T$ of $x = 0.03$ in Figure 14(a), which means that the large MR is intrinsic to the coupling of carriers and magnetic moments. The strong coupling has also manifested itself as the unusually large anomalous Hall effect (AHE), observed in $x = 0.03$ for $T \leq 20$ K [22]. Calculation revealed a negative value of AHE constant $R_H$ which also indicates antiferromagnetic coupling between Mn$^{2+}$ and carriers. It is notable that the magnetoresistance in Figure 14(a) is most significant in the diluted limit ($x = 0.01$), suggesting that the on-site interaction between hole and Mn$^{2+}$ moment is responsible, rather than the Mn-Mn inter-site couplings.

This interpretation is in accordance with the results of magnetic susceptibility. Magnetic susceptibility was fitted with Curie-Weiss function, $\chi = \frac{C}{T - \theta} + \chi_0$ where $C$, $\theta$ and $\chi_0$ is Curie constant, Weiss temperature and the temperature-independent term, respectively. The effective magnetic moment of 5.35μ$_{B}$ obtained for $x = 0.03$ sample is close to the Mn$^{2+}$ moment (5.92μ$_{B}$) with $S = 5/2$ and $g = 2$. In addition, the Weiss temperature comes out to be negative (−108.5 K), which indicates AFM interaction on Mn spins. One of the reasons of getting large negative $\theta$ can be AFM exchange between Mn$^{2+}$ ions. But at such low Mn concentration, Mn-Mn distance is much longer, and it is difficult to imagine that Mn–Mn interaction would give rise to this large negative $\theta$. In addition, the possibility of a direct overlap of 3d states of Mn is quite low in this case which rules out the contribution of Mn-3d impurity band to the large $S$ (Figure 15). This large negative $\theta$ and large $S$ can

**Figure 13.** Effective mass $m^*$ with respect to the free electron mass $m_0$ of CuGa$_{1-x}$Mn$_x$Te$_2$ derived from a parabolic band model. Broken line is guide for eye.

**Figure 14.** (a) Transverse magnetoresistance ($MR_T$) of CuGa$_{1-x}$Mn$_x$Te$_2$ measured at $T = 10$ K, where magnetic field is perpendicularly applied to current. (b) Longitudinal magnetoresistance ($MR_L$) of CuGa$_{0.97}$Mn$_{0.03}$Te$_2$ where magnetic field is parallel to current.
arise due to Kondo-type interaction between magnetic impurities and carriers [52]. The Kondo model was applied by Osinniy et al. to explain large TEP of ferromagnetic Ga1−xMnxAs [53]. Kondo interaction is a process of compensating the magnetic moments of impurities by forming spin-singlet states with carrier electrons. In the low temperature limit, this effect eliminates the magnetic entropies of impurities, while the entropies are transferred to carrier electrons with enhanced effective mass. As a result, the Seebeck coefficient increases with the Kondo-type interaction. Indeed, enhanced effective carrier mass m∗ has been observed in CuGa1−xMnxTe2, as shown in Figure 12.

Figure 15 depicts the temperature dependence of S and electrical resistivity measured under zero and applied field of 7 T. Electrical resistivity ρ increases rapidly at low temperatures. Under magnetic field of μ0H = 7 T, this increase is significantly suppressed, as shown in the insets of Figure 15(a,b). This infers that the contribution of magnetic moment and carriers through Kondo-like mechanisms plays an important role in the transport properties of CuGa1−xMnxTe2. It was suggested that the Kondo-type interaction can lead the temperature dependent Seebeck coefficient as: S(T) = aT + S0(T + T0), with a, S0, and T0 are parameters [52,53]. The broken line in Figure 15(a) is the fit with the Kondo model. The model appears to explain the overall behaviour. On the other hand, as shown in the main panel of Figure 15, S is hardly affected by the application of field, possibly because of the too small Zeeman energy of the field of 7 T compared to the antiferromagnetic coupling between carrier and Mn2+ moment, of the order of θ = −100 K. This contradicting behaviour has recently also been observed in Sr2Fe1+xRe1−xO4 double perovskites [54]. It must be emphasized that the thermopower depends on the entropy and on a transport term associated with the band structure [10]. As shown in all the examples presented here, MTEP is associated with MR, but on the other hand the presence of MR is not sufficient to ensure a MTEP effect due to the complex interplay between the entropic and transport terms.

A second similar example is the Cr-doped Bi2Te3 tetradymite system. Bi2Te3 with diluted Cr doping, as well as with transition-metal TM atoms (V, Mn and Fe), have been found to exhibit ferromagnetic transitions, with Cr doping exhibiting relatively high transition temperatures near ~240 K. An effective magnetic moment of 3.53μB is obtained for Bi1.99Cr0.01Te3 consistent with the Cr3+ moment (3.87 μB). In contrast to the Mn2+ doping in CuGa1−xMnxTe2, the Cr3+ doping does not affect the carrier concentration, as predicted theoretically and confirmed experimentally [23,55]. But a TEP enhancement is observed in the case of Bi1.99Cr0.01Te3 compared to the pristine composition and is associated with an increase of the weighted mobility μw from 73.6 cm2 V−1 s−1 to 76.3 cm2 V−1 s−1 in the doped sample with 1%mol Cr. This representative quality parameter of the charge transport can be defined as μw = μ(m∗/m0) 3/2, where μ is the electron mobility, m∗ is the effective mass and m0 is the electron mass, and the increasing of this parameter supported that an additional mechanism, such as the carrier-magnetic moment interaction, was effective and increased the TEP. As evidence, the non-magnetic isovalent Ga3+ ions substitution for Bi3+ is compared with the same doping level with magnetic Cr3+. Only the magnetic doping with Cr led to an increase of the TEP. Bi1.99Cr0.01Te3 is reported to have a narrow hysteresis loop for the magnetization curves [23]. The relatively small coercivity, (μ0Hc = 0.2 T), and saturation magnetization indicates that the sample is a weak ferromagnet similar to Mn-doped Bi2Te3 [56]. However, the temperature-dependent S(T) of Bi1.99Cr0.01Te3 measured at 0 T, 5T and 9 T (Figure 16)
revealed that the TEP is not affected by the magnetic field. It is suggested that the Bi\(_{1.99}\)Cr\(_{0.01}\)Te\(_3\) TEP enhancement is not likely due to a spin fluctuation effect, as reported for the Fe\(_2\)V\(_{0.9}\)Cr\(_{0.1}\)Al\(_{0.9}\)Si\(_{0.1}\) [57], but by a localized electron-magnetic moment coupling promoting a heavier effective mass \(m^*\) as experimentally observed [23].

4. Conclusions
A comparative study of MTEP in magnetically doped chalcogenides showing different magnetic behaviour was performed. A significant negative MTEP is observed in ferromagnetic perovskite ruthenates and paramagnetic misfit cobaltites. In the case of ferromagnetic material, below \(T_C\), the increase of magnetization is accompanied by a decrease of the entropy of the carriers and hence \(|\Sigma|\) decreases. On the other hand, no MTEP is observed in quadruple perovskites indicating that Pauli paramagnetism with a very small susceptibility value is less effective in inducing MTEP. In addition, significant MTEP is absent in CuGa\(_{1-x}\)Mn\(_x\)Te\(_2\) and Bi\(_{1.99}\)Cr\(_{0.01}\)Te\(_3\) where Kondo-type interaction between magnetic impurities and carriers is indicated to prevail. Spin glass system CuCrTiS\(_4\) thiospinel also exhibits negative MTEP like in ruthenates and misfit cobaltites. Variable range hopping behaviour of the thiospinel along with negative MR makes the system similar to mixed-valence manganites [35]. Our MTEP study reveals that, in Pauli paramagnetic materials having smallest magnetic susceptibility values, the effect of spin on \(S\) is negligible. In contrast magnetism contributes to enhance \(S\) in ferromagnetic and some paramagnetic systems, whereas, when diluted, paramagnetism induces MR through

a Kondo effect at very low \(T\), but does not induce MTEP. The low temperature magnetic susceptibility of the different materials ranges from \(\sim 4.10^{-3}\) emu/mol for Pauli quadruple perovskites and CuGa\(_{1-x}\)Mn\(_x\)Te\(_2\) to 0.06–0.2 emu/mol for paramagnetic misfits and thiospinels, respectively, up to 4 emu/mol in SrRuO\(_3\). These very different values give a lower limit (\(\sim 10^{-2}\) emu/mol) below which MTEP has not been observed.

This investigation suggests that one route to enhance \(S\) for TE applications is to find new materials where localized or weakly coupled magnetic ions introduce spin entropy to the system. It is interesting to notice that for such a negative MTEP, the impact of magnetism is maximum in zero magnetic field which is very important for potential applications. The presence of MTEP is a strong indicator of the role these ions play. In that respect, ferrimagnetic systems would also be of interest for MTEP measurements as they combine non-compensated antiferromagnetically coupled ferromagnetic sublattices.

Acknowledgments
The authors acknowledge the support received through ‘Raman-Charpak Fellowship 2019’ jointly funded by the Department of Science and Technology (DST), Government of India and the French Institute in India (IFI), French Embassy in India, Ministry for Europe and Foreign Affairs, Government of France. CB, NT and TM acknowledge support from JST Mirai Program JPMJMI19A1.

Disclosure statement
No potential conflict of interest was reported by the author(s).
Funding
This work was supported by the JST Mirai Program [JPMJMI19A1].

References
[1] Bell LE. Cooling, heating, generating power, and recovering waste heat with thermoelectric systems. Science 2008;321:1457–1461.
[2] Petsagkourakis I, Tybrandt K, Crispin X, et al. Thermoelectric materials and applications for energy harvesting power generation. Sci Technol Adv Mater. 2018;19:836–862.
[3] Heremans JP, Jovovic V, Toberer ES, et al. Enhancement of thermoelectric efficiency in PbTe by distortion of the electronic density of states. Science. 2008;321:554–557.
[4] Pei Y, Shi X, LaLonde A, et al. Convergence of electronic bands for high performance bulk thermoelectrics. Nature. 2011;473:66–69.
[5] Li W, Chen Z, Lin S, et al. Band and scattering tuning for high performance thermoelectric Sn1–xMnxTe alloys. J Materiomics. 2015;1:307–315.
[6] Jang H, Abbey S, Nam WH, et al. Order-disorder transition-induced band nesiification in AgBiSe2–CuBiSe2 solid solutions for superior thermoelectric performance. J Mater Chem A. 2021;9:4648–4657.
[7] Behnia K, Jaccard D, Fluquet J. On the thermoelectricity of correlated electrons in the zero-temperature limit. J Phys: Condens Matter. 2004;16:5187–5198.
[8] Wang Y, Rogado NS, Cava RJ, et al. Spin entropy as the likely source of enhanced thermopower in NaCaZnO4. Nature. 2003;423:425–428.
[9] Mori T. Novel principles and nanotechnostrategies for enhanced thermoelectrics. Small. 2017;13:1702013.
[10] Peterson MR, Mukerjee S, Sriram Shastry B, et al. Dynamical thermal response functions for strongly correlated one-dimensional systems: hubbard and spinless fermion t–V model. Phys Rev B. 2007;76:125110.
[11] Koshibae W, Maekawa S. Effects of spin and orbital degeneracy on the thermoelectricity of strongly correlated systems. Phys Rev Lett. 2001;87:236603.
[12] Limlette P, Hébert S, Hardy V, et al. Scaling behavior in thermoelectric misfit cobalt oxides. Phys Rev Lett. 2006;97:046601.
[13] Repaka DVM, Mahendiran R. Giant magnetothermopower in charge ordered Nd0.75Na0.25MnO3. Appl Phys Lett. 2013;103:162408.
[14] Wang K, Petrovic C. Large linear magnetoresistance and magnetothermopower in layered SrZnSb2. Appl Phys Lett. 2012;101:152102.
[15] Niemann AC, Gooth J, Sun Y, et al. Magneto-thermoelectric characterization of a HfTe5 micro-ribbon. Appl Phys Lett. 2019;115:072109.
[16] Hu J, Caputo M, Guedes EB, et al. Large magnetothermopower and anomalous Nernst effect in HfTe5. Phys Rev B. 2019;100:115201.
[17] Ito M, Yamashita T, Ebisu S, et al. Thermodynamic and electrical properties of CuCrTiS4. J Alloys Compd. 2014;598:133–136.
[18] Li J, Tan Q, Li JF. Synthesis and property evaluation of CuFeS2-x as earth-abundant and environ mentally-friendly thermoelectric materials. J Alloys Compd. 2013;551:143–149.
[19] Tsujii N, Mori T. High thermoelectric power factor in a carrier-doped magnetic semiconductor CuFeS2. Appl Phys Exp. 2013;6:043001.
[20] Ang B, Khan AU, Tsujii N, et al. Thermoelectricity generation and electron-magnon scattering in a natural chloropizate mineral from a deep-sea hydrothermal vent. Angew Chem Int Ed. 2015;54:12909–12913.
[21] Berthebaud D, Lebedev OL, Maignan A, et al. Magnetothermalpower and giant magnetoresistance in the spin-glass CuCrTiS4 thiospinel. J Appl Phys. 2018;124:063905.
[22] Ahmed F, Tsujii N, Mori T. Thermoelectric properties of CuGa1–xMnxTe2: power factor enhancement by incorporation of magnetic ions. J Mater Chem A. 2017;5:7545–7554.
[23] Vaney JB, Yamini SA, Takaki H, et al. Magnetism-mediated thermoelectric performance of the Cr-doped bismuth telluride tetradymite. Mat Today Phys. 2019;9:100090.
[24] Maignan A, Hébert S, Hervieu M, et al. Magnetoresistance and magnetothermalpower properties of Bi/CaCa/O and Bi(Pb)/Ca/Co/O misfit layer cobaltites. J Phys: Condens Matter. 2003;15:2711–2723.
[25] Klein Y, Hébert S, Maignan A, et al. Insensitivity of the band structure of substituted SrRuO3 as probed by Seebeck coefficient measurements. Phys Rev B. 2006;73:052412.
[26] Hébert S, Dauq R, Maignan A. Thermopower in the quadruple perovskite ruthenates. Phys Rev B. 2015;91:045106.
[27] Hejtmánek J, Jiráček Z, Maryško M, et al. Interplay between transport, magnetic, and ordering phenomena in Sm1–xCaxMnO3. Phys Rev B. 2000;60:14057.
[28] Koroleva LI, Kessler YA, Lukina LN, et al. New magnetic semiconductors Fe1–xCr2(1–x)Sn2xS4. J Magn Magn Mater. 1996;157:148–476.
[29] Abramovich AI, Koreleva IJ, Lukina LN. Spin-glass and reentrant spin-glass states in iron sulfosplines having dilute A and B sublattices. Phys Solid State. 1999;41:73–79.
[30] Ito M, Furuta T, Terada N, et al. Relaxation of magnetization in spinel CuCrZnS4. Physica B. 2012;407:1272–1274.
[31] Lötgering FK. Ferromagnetism in spinels: cuCr2S4 and CuCr2Se4. Solid State Commun. 1964;2:55–56.
[32] Matsumoto N, Hagino T, Taniguchi K, et al. Electrical and magnetic properties of CuTi2S4 and CuZr2S4. Physica B. 2000;284-288:1978–1979.
[33] Nagata S, Koski N, Ebisu S. Spin-glass in the spinel-type CuCrTiS4. Philos Mag B. 2012;92:2957–2969.
[34] Snyder GJ, Caillat T, Fleural JP. Thermoelectric properties of chalcogenides with the spinel structure. Mater Res Innovations. 2001;5:67–73.
[35] Viret M, Ranno L, Coey JMD. Magnetic localization in mixed-valence manganites. Phys Rev B. 1997;55:8067.
[36] Bobroff J, Hébert H, Lang G, et al. Interplay between magnetic properties and thermoelectricity in misfit and Na cobaltates. Phys Rev B. 2007;76:100407.
[37] Doumerc JP. Thermoelectric power for carriers in localized states: a generalization of Heikes and...
[38] Koshitae W, Tsutsui K, Maekawa S. Thermopower in cobalt oxides. Phys Rev B. 2000;62:6869.

[39] Hébert S, Kobayashi W, Muguerra H, et al. From oxides to selenides and sulﬁdes: the richness of the CdII type crystallographic structure for thermoelectric properties. Phys Status Solidi A. 2013;210:69–81.

[40] Pollet M, Doumerc J-P, Guilmeau E, et al. Does the orbital degeneracy play any role in the high thermopower of lamellar cobaltites? J Appl Phys. 2007;101:083708.

[41] Landron S, Lepetit MB. Importance of t2g–eg hybridization in transition metal oxides. Phys Rev B. 2008;77:125106.

[42] Cao G, Chikara S, Lin XN, et al. Itinerant ferromagnetism to insulating antiferromagnetism: a magnetic and transport study of single crystal SrRu1−xMnxO3 (0<x<0.60). Phys Rev B. 2005;71:035104.

[43] Kobayashi H, Nagata M, Kanno R, et al. Structural characterization of the orthorhombic perovskites: [ARuO3 (A = Ca, Sr, La, Pr)]. Mater Res Bull. 1994;29:1271.

[44] Cao G, McCall S, Shepard M, et al. Thermal, magnetic, and transport properties of single-crystal Sr1−xCaxRuO3 (0<x<1.0). Phys Rev B. 1997;56:321.

[45] Mravlje J, Georges A. Thermopower and entropy: lessons from Sr2RuO4. Phys Rev Lett. 2016;117:036401.

[46] Yamamoto TD, Taniguchi H, Yasui Y, et al. Magnetothermopower in the weak ferromagnetic oxide CaRu0.8Sc0.2O3: an experimental test for the kelvin formula in a magnetic material. J Phys Soc Jpn. 2017;86:104707.

[47] Xiang H, Liu X, Zhao E, et al. First-principles study on the conducting mechanism of the heavy-fermion system CaCu3Ru4O12. Phys Rev B. 2007;76:155103.

[48] Allen PB, Berger H, Chauvet O, et al. Transport properties, thermodynamic properties, and electronic structure of SrRuO3. Phys Rev B. 1996;53:4393.

[49] Klein L, Dodge JS, Ahn CJ, et al. Transport and magnetization in the badly metallic itinerant ferromagnet SrRuO3. J Phys Condens Matter. 1996;8:10111–10126.

[50] Tyler AW, Mackenzie AP, Nishizaki S, et al. High-temperature resistivity of Sr2RuO4: bad metallic transport in a good metal. Phys Rev B. 1998;58:R10107.

[51] The values m* shown here are larger than those reported in ref. [17], where the degenerate limit has been assumed. The present calculation based on a parabolic band model suggested that the Lorenz numbers of CuGa1−xMnTe2 are L = 1.5 to 1.8×10−8 ΩK−2, thereby suggesting the degenerate limit was not appropriate for this case.

[52] Kondo J. Theory of dilute magnetic alloys. Solid State Phys. 1970;23:183–281.

[53] Osinniy V, Dybko K, Jedrzejczak A, et al. Thermoelectric studies of electronic properties of ferromagnetic GaMnAs layers. Semicond Phys, Quantum Electron Optoelectron. 2008;11:257–265.

[54] Maignan A, Martin C, Lebedev OI, et al. Sr2Fe1+xxRe1−xO6 double perovskites: magnetoresistance and (magneto)thermopower. Chem Commun. 2019;55:5878–5881.

[55] Zhang JM, Ming W, Huang Z, et al. Stability, electronic, and magnetic properties of the magnetically doped topological insulators Bi2Se3, Bi2Te3, and Sb2Te3. Phys Rev B. 2013;88:235131.

[56] Hor YS, Roushan P, Beidenkopf H, et al. Development of ferromagnetism in the doped topological insulator Bi2−xMnxTe3. Phys Rev B. 2010;81:195203.

[57] Tsuji N, Nishide A, Hayakawa J, et al. Observation of enhanced thermopower due to spin fluctuation in weak itinerant ferromagnet. Sci Adv. 2019;5:5935.