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The universal relation between thermopower and magnetic susceptibility for a charge ordered manganite: $\text{Bi}_{1-x}\text{Sr}_x\text{MnO}_3$ ($0.5 \leq x \leq 0.8$)

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Abstract

The relation between the thermoelectric power (S) and magnetic susceptibility (χ) for $\text{Bi}_{1-x}\text{Sr}_x\text{MnO}_3$ ($0.5 \leq x \leq 0.8$) has been established empirically. A simple linear equation for the relation between the two transport coefficients is deduced from the experimental data. From this relation, we extract the Peltier heat and S for this material. They are composed of two terms: one has a magnetic origin and the other originates from the configuration entropy. The universality of this relation is found by applying the relation to other magnetically interacting systems including colossal magnetoresistance materials and high T_C cuprate.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Mixed valence manganites have been focused on during the last few years due to their colossal magnetoresistance (CMR) and charge ordering (CO) phenomena [1–3]. CO is usually considered as a spatially ordered distribution of $\text{Mn}^{3+}/\text{Mn}^{4+}$ ions in the lattice in a purely ionic picture accompanied by orbital ordering [2]. On the other hand the formation of ordered Zener polarons has been understood as a more realistic scenario for explaining CO phenomena of manganites. In the Zener polaron model, an e_g electron is trapped in and shared with an Mn–O–Mn trio instead of a single Mn cation. Two Mn ions in a trio maintain the mixed valence state and they are coupled ferromagnetically by double-exchange interaction [4]. Recently, Sr doped BiMnO_3 (BSMO) has attracted great attention due to having the highest charge ordering temperature (T_{CO}) among manganites. However, T_{CO} decreases with the increase

of Sr (from $T_{\text{CO}} \sim 475$ K for Sr = 0.5 to $T_{\text{CO}} \sim 435$ K for Sr = 0.8) [9]. The structure, magnetic and electrical transport properties of BSMO have been studied from low to high temperature regimes [5–9]. However one of the electrical transport properties, thermoelectric power (TEP), of the strongly correlated system as well as BSMO has been rarely investigated as compared with other properties because it is difficult to perform TEP measurements and analyse the results. Although TEP has these problems as mentioned above, it is a useful probe for investigating the intrinsic properties of polycrystalline samples; since TEP is a zero-current transport coefficient, it is less sensitive to defects compared to resistivity that is drastically altered by defects. TEP, S , is defined as the ratio of the temperature difference (ΔT) and the voltage difference (ΔV) caused by ΔT across the material, i.e. $\Delta V = S\Delta T$. S is related to the Peltier heat (Π) via $\Pi = ST$. Peltier heat is the ratio between heat current (J_Q) and electrical current (J). This implies that TEP is the entropy per carrier as follows:

$$S = \frac{\Pi}{T} = \frac{J_Q}{JT} = \frac{nvk_B T \ln g}{nevT} = \frac{k_B \ln g}{e} = \frac{\sigma}{e}, \quad (1)$$

where k_B , g , and σ are the Boltzmann constant, degeneracy, and entropy, respectively. Recently, the effect of spin and orbital degeneracy on the TEP was reported theoretically [10–13] and experimentally [14]. Furthermore, Koshibae *et al* [11, 12] and Wang *et al* [15] reported that the ratio between degeneracies of Co ions for the states of carrier in NaCo_2O_4 and spin entropy plays an important role in the enhancement of TEP. One can infer that there is a certain relation between TEP and spin interaction. In a metal, both the Pauli susceptibility and TEP are generally proportional to the density of states. In view of the thermodynamics, the Helmholtz free energy is represented by $F = -Nk_B T \ln[2 \cosh(\varepsilon/k_B T)]$ for the noninteracting two-level system ($J = 1/2$). Here $\varepsilon = \pm\mu_B H$ and H is a magnetic field. From the definition of entropy, the relation between the entropy and magnetization (M) can be obtained as

$$\sigma = Nk_B \ln \left[2 \cosh \left(\frac{\varepsilon}{k_B T} \right) \right] - \frac{\varepsilon}{\mu_B T} M. \quad (2)$$

Equation (2) shows that the entropy of a noninteracting two-level system is composed of two terms; one is directly related to magnetization and the other is not. Moreover, Liu and Emin [16] reported theoretically that the Peltier heat of ferromagnetic (FM) one-dimensional chains and three-dimensional cubic lattices is the sum of the magnetic origin term and combinatorial (configurational) origin term. However, this relation has been uncovered in the strongly correlated system with experimental results. In this paper we show experimentally that there is a universal relation between TEP and magnetic susceptibility χ for a charge ordered manganite $\text{Bi}_{1-x}\text{Sr}_x\text{MnO}_3$ ($0.5 \leq x \leq 0.8$) (BSMO) and that the relation can be applied to strongly correlated systems $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$, $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ and $\text{La}_{1.9}\text{Sr}_{0.1}\text{CuO}_4$.

2. Experimental details

A polycrystalline sample of BSMO was prepared by a conventional solid-state reaction method. The sample was characterized using x-ray diffraction (Rigaku D-max) ($\text{Cu K}\alpha$). DC magnetic susceptibility measurements were carried out in a DC field using a SQUID magnetometer (MPMS, QUANTUM DESIGN). Temperature dependent resistivity was measured using a conventional four-probe method. The high temperature TEP was measured using a low frequency AC steady-state method in an oxygen atmosphere as described elsewhere [9].

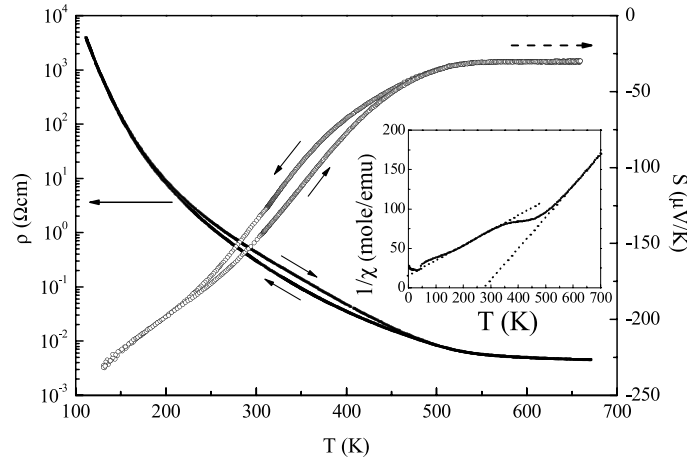


Figure 1. The transport properties of $\text{Bi}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$. Resistivity (ρ) (filled circle) shows that the material is insulating over the entire temperature range. The hysteretic behaviour exists in both ρ and S (opened circle), which indicates that there is a first-order phase transition (CO transition) at the onset temperature of the hysteresis. The inset shows the temperature dependence of the inverse magnetic susceptibility. The short arrows indicate heating and cooling processes.

3. Results and discussion

Since BSMO has the highest charge ordering (CO) temperature ($T_{\text{CO}} \sim 500$ K) among manganese compounds [9], it has been studied intensively. At T_{CO} , the slope of TEP and the resistivity changes abruptly and thermal hysteretic behaviour is shown in both TEP and resistivity (figure 1). An inverse magnetic susceptibility follows the Curie–Weiss law above and below T_{CO} and shows a plateau near T_{CO} (the inset of figure 1). This result indicates that local FM and antiferromagnetic (AFM) correlations exist in the high temperature and low temperature regimes, respectively.

Figure 2(a) shows that the temperature derivative of ST has good consistency with that of χ , which is evidence that $\chi(T)$ is strongly related to $S(T)$. The relation is represented by a simple linear equation:

$$\frac{d(ST)}{dT} = B_H \frac{d\chi}{dT} + S_J, \quad (3)$$

where χ is dimensionless and B_H and S_J are parameters whose units are voltage and TEP, respectively. Three sets of parameters (B_{H1} , S_{J1} and B_{H2} , S_{J2} in the charge ordered state and B_{H3} , S_{J3} in the high temperature regime) are needed to fulfil equation (3). They are separated at certain temperatures (T_P and T_H) represented by blue dotted lines in figure 2. The change in parameters is closely related to the variation of magnetic susceptibility as shown in figure 2(b). In particular, the signs of the parameters change; B_{H1} , S_{J1} and B_{H2} , S_{J2} are positive ($B_{H1} = 175$ V, $S_{J1} = 225 \mu\text{V K}^{-1}$ and $B_{H2} = 160$ V, $S_{J2} = 205 \mu\text{V K}^{-1}$) and B_{H3} , S_{J3} are negative ($B_{H3} = -220$ V, $S_{J3} = -165 \mu\text{V K}^{-1}$). The boundary temperature, T_H , between opposite-sign sets of parameters is the onset temperature of hysteretic behaviour (figure 2(c)). This temperature also corresponds to the onset of the first-order phase transition, i.e. the charge ordering phase transition. The charge ordered state and the normal state exist below and above T_H (for distinction from the definition of T_{CO} in [9], this temperature is denoted by T_H), respectively.

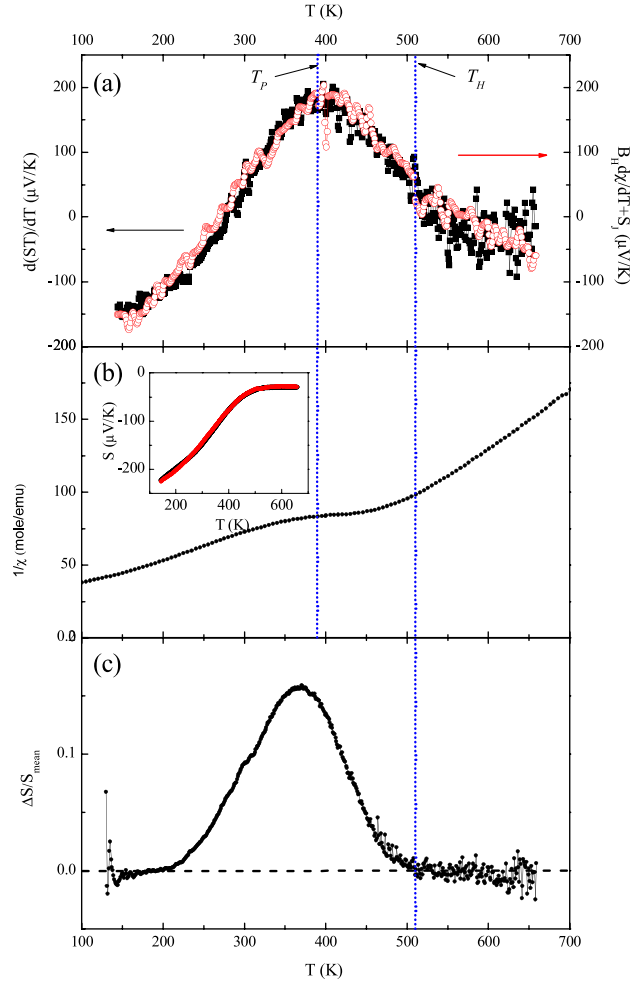


Figure 2. The relation between $S(T)$ and $\chi(T)$. Both coefficients are obtained during the heating process. (a) The temperature derivative of ST (black squares) is consistent with the linear equation of the temperature derivative of the magnetic susceptibility with parameters $B_{H1,2,3}$ (red circles) and $S_{J1,2,3}$. (b) The change of parameters is closely related to the temperature dependence of the magnetic susceptibility (blue dotted lines). T_P and T_H are temperatures corresponding to the change in parameters. The inset is the TEP from experiment (black circles) and from equation (4) (red circles). (c) The boundary temperature, where the sign change occurs, is the onset temperature of the hysteretic behaviour, i.e. the charge ordering temperature. Here, S_{mean} is $(S_{\text{cooling process}} + S_{\text{heating process}})/2$ and ΔS is $S_{\text{cooling process}} - S_{\text{heating process}}$. Since the magnetic field dependent TEP is constant up to, at least, 2 T (not presented in this paper), we used the zero-field TEP data.

In order to find the relation between $S(T)$ and $\chi(T)$, we interpreted equation (3) with definite integrals, then obtained the equation

$$S(T) = \begin{cases} \frac{B_{H1}}{T}[\chi(T) - \chi(0)] + S_{J1} & \text{for } T < T_P \\ \frac{1}{T}[B_{H2}\{\chi(T) - \chi(T_P)\} + C_P] + S_{J2} & \text{for } T_P \leq T < T_H \\ \frac{1}{T}[B_{H3}\{\chi(T) - \chi(T_H)\} + C_H] + S_{J3} & \text{for } T \geq T_H, \end{cases} \quad (4)$$

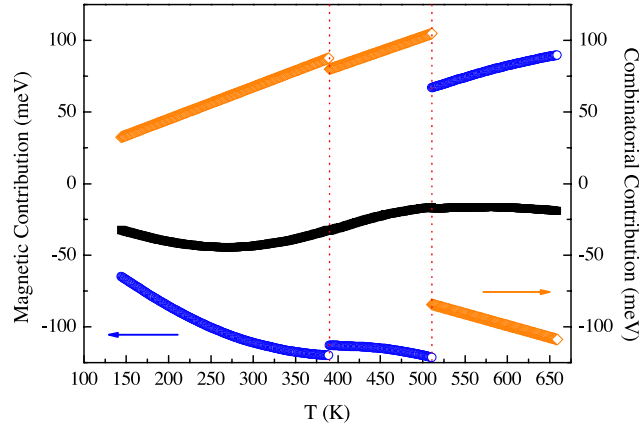


Figure 3. The Peltier heat of $\text{Bi}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ (black squares). The Peltier heat is composed of a magnetic origin term (blue circles) and a configurational origin term (orange diamonds). The sign of the magnetic origin term is suggested to be related to the local magnetic exchange interaction.

where $C_P = [S(T_P) - S_{J2}]T_P$ and $C_H = [S(T_H) - S_{J3}]T_H$ are constant. $\chi(0) = 0.00103 \pm 6.22 \times 10^{-6}$ for $T < T_P$ is very close to the χ at 2 K ($\chi(2) = 0.00104$) obtained from the experimental result. We fitted equation (4) to the experimental result. The inset of figure 2(b) shows that $B_{H1,2,3}$, $S_{J1,2,3}$ and $\chi(0)$ are well chosen. The temperature dependence of the TEP (black circles) is consistent with the data (red circles) obtained from the right-hand side of equation (4). Equation (4) indicates that the thermoelectric mechanism for the temperature of this material is directly related to the magnetic response to the temperature and shows that TEP (entropy per carrier) is composed of two terms as in equation (2).

Since the second term on the right-hand side of equation (4), $S_{J1,2,3}$ is independent of temperature, we applied the Heikes formula for TEP, $k_B \ln\{(1-c)/c\}$, which is the configuration entropy. Here c is the number of effective carriers (carriers per the number of site). In general, carriers are trapped in the CO state. As a result, a small number of effective carriers are expected. In the other case, for $T \geq T_H$, carriers are free to move. Thus the number of effective carriers increases. The values of S_J are $225 \mu\text{V K}^{-1}$ for $T < T_P$, $205 \mu\text{V K}^{-1}$ for $T_P \leq T < T_H$ and $-165 \mu\text{V K}^{-1}$ for $T \geq T_H$. The number of effective carriers obtained by the Heikes formula is smaller than 0.085 in the CO regime but 0.872 at high temperatures. The number of effective carriers in the high temperature regime is about ten times larger than that in the CO regime, which is consistent with the general behaviour of CO materials. Next, we obtained the Peltier heat by applying $\Pi = S T e$ (e denotes unit charge) to equation (4). It gives

$$S(T)T e = \begin{cases} B_{H1}[\chi(T) - \chi(0)]e + S_{J1}T e & \text{for } T < T_P \\ [B_{H2}\{\chi(T) - \chi(T_P)\} + C_P]e + S_{J2}T e & \text{for } T_P \leq T < T_H \\ [B_{H3}\{\chi(T) - \chi(T_H)\} + C_H]e + S_{J3}T e & \text{for } T \geq T_H. \end{cases} \quad (5)$$

The Peltier heat of this material is composed of two terms of magnetic origin (blue circles in figure 3) and configurational origin (orange diamonds in figure 3). In particular, the magnetic origin term is divided into two terms for $T \geq T_P$: one is $B_{H2,3}[\chi(T) - \chi(T_{P,H})]e$ and the other is $C_{P,H}e = T_{P,H}[S(T_{P,H}) - S_{J2,3}]e$ which is the magnetic origin term for Peltier heat at $T_{P,H}$. It is worth noting that the sign of the magnetic origin term changes at T_H . Twenty years ago, Liu and Emin [16] reported the magnetic effect on Peltier heat via exchange interaction between the carriers and the surrounding magnetic sites in the magnetic ordered and paramagnetic (PM)

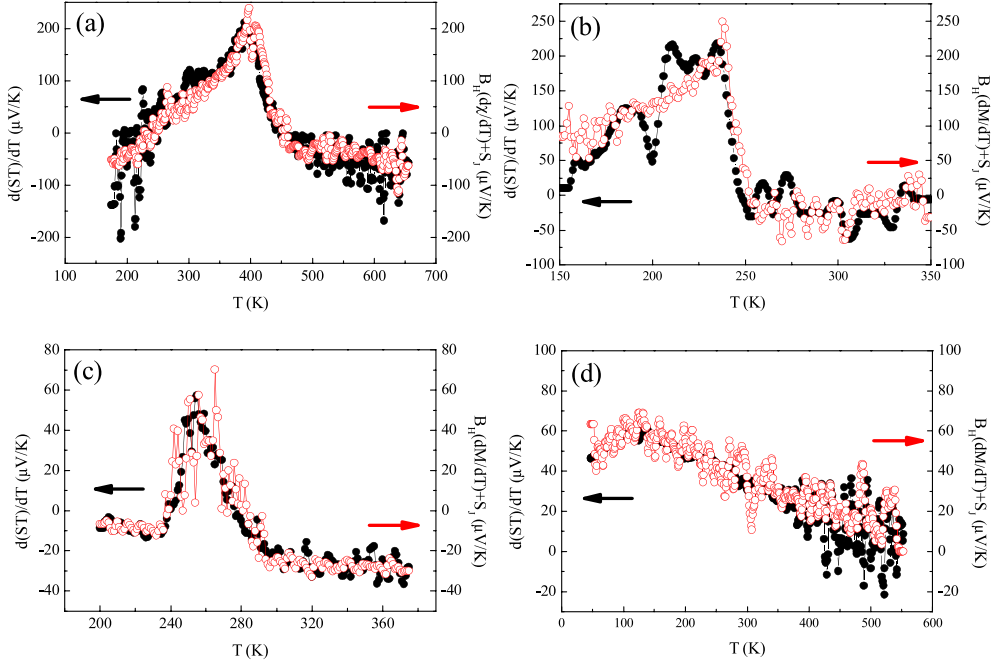


Figure 4. The universal relation between $S(T)$ (filled circles) and $\chi(T)$ (open circles). The black and red circles indicate $d(S(T))/dT$ and $B_H \cdot d\chi$ (or $M)/dT + S_J$, respectively. (a) $\text{Bi}_{0.2}\text{Sr}_{0.8}\text{MnO}_3$ from this work. (b) $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ from [18] and [19]. (c) $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ from [20]. (d) $\text{La}_{1.9}\text{Sr}_{0.1}\text{CuO}_4$ from [21] and [22].

regime, under the assumption that carriers are severely localized. Above all, they showed that the Peltier heat is composed of a magnetic origin term and combinatorial term, and the signs of the magnetic origin term in the ordered regime and that in the disordered regime are opposite. They proposed that the positive sign for $T \geq T_C$ (T_C is the transition temperature between ordered and disordered states) is caused by lining up the spin of the added electron with the host spin and that the negative sign for $T_C < T$ comes from the reduction of the occupation of excited energy levels due to the added exchange interactions. From experiment, we have observed similar results, as shown in figure 3. In the low temperature regime, the first term of the right-hand side of equation (5) (the magnetic origin term) shows a negative contribution to the Peltier heat but contributes with a positive sign to the Peltier heat at high temperatures. Local FM ($T \geq T_H$) and AFM ($T_P > T$) exchange interactions are observed in the inset of figure 1. Therefore we suggest that the magnetic origin term could be related to the local magnetic exchange interaction. In particular, we suggest a possible reason for two sets of parameters being necessary to satisfy the relation between TEP and magnetic susceptibility in the charge ordered regime. We focused on the temperature regime $T_P \leq T < T_H$. Consider the spin state in this temperature regime. The spin is not aligned completely with FM or AFM ground states; the spin is being changed from the FM to AFM ground state with the decrease of temperature. Next, we think about the structural transition. It occurs from cubic to orthorhombic [17]. Note that this structural transition process can be divided into three regions of temperature as shown in figure 3 (the temperature dependence of lattice parameters) of [17]: cubic structure, the process of transition from cubic to orthorhombic and orthorhombic structure. The boundary temperatures for three regions are similar to our results T_P and T_H , and the structural transition is in progress for $T_P \leq T < T_H$. These spin and structural

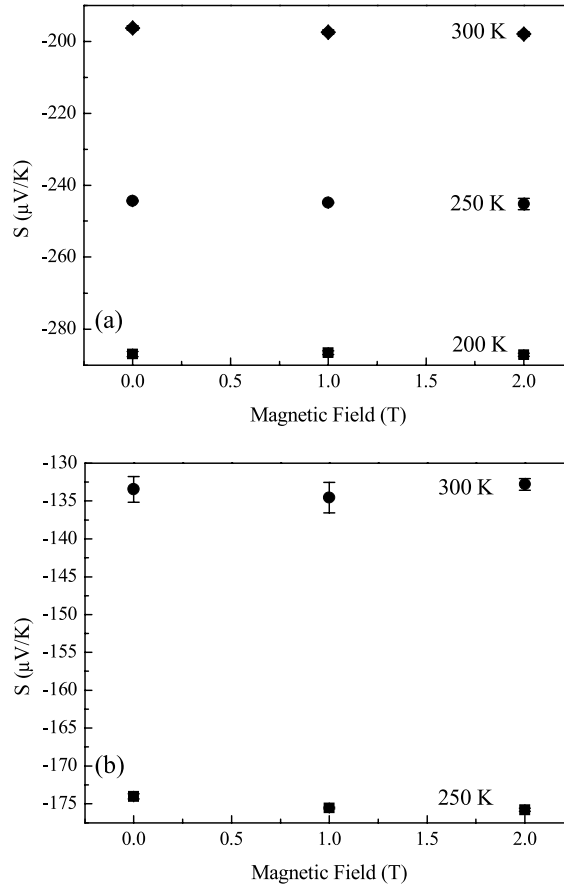


Figure A.1. The magnetic field dependence of TEP for BSMO. (a) $\text{Sr} = 0.6$. (b) $\text{Sr} = 0.8$.

transitions in $T_P \leq T < T_H$ help us understand the indispensability of two parameter sets in the charge ordering regime. At high temperatures, TEP is temperature independent (figure 1). In particular, the magnetic origin term of TEP is less dependent on temperature above $T > 580$ K. From this result we obtained the spin entropy per carrier at high temperatures. We used the average value of the magnetic origin term ($136.8 \pm 0.1582 \mu\text{V K}^{-1}$) in equation (4) and the fact that TEP represents entropy per carrier (equation (1)), $S = k_B \ln g_s g_c / e$ (here g_s and g_c denote, respectively, the spin and configurational degeneracy). Therefore, it is possible to get the spin degeneracy at high temperatures, i.e. $g_s = 4.89$. We adopt the scenario from [15] to explain this value of the spin degeneracy. If the e_g electron of the Mn^{3+} ion moves on the t_{2g} spin sea, then the degeneracy of e_g electron becomes 4, close to the experimentally obtained value, $g_s = 4.89$.

Is this relation between TEP and magnetic susceptibility universal? In order to answer this question we investigated several materials to see whether they follow equation (3) or not. For $\text{Bi}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x = 0.6, 0.7,$ and 0.8), they all follow equation (3) and the behaviour of the parameters is same as that for the $x = 0.5$ sample (see figure A.2 in the appendix), i.e. three sets of parameters are needed to satisfy the equation (3) and the sign of parameter is opposite at T_H . The relation for one of the BSMO series, $\text{Bi}_{0.2}\text{Sr}_{0.8}\text{MnO}_3$, is presented in figure 4(a). We also investigated this relation for $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ [18, 19], the ferromagnetic manganite

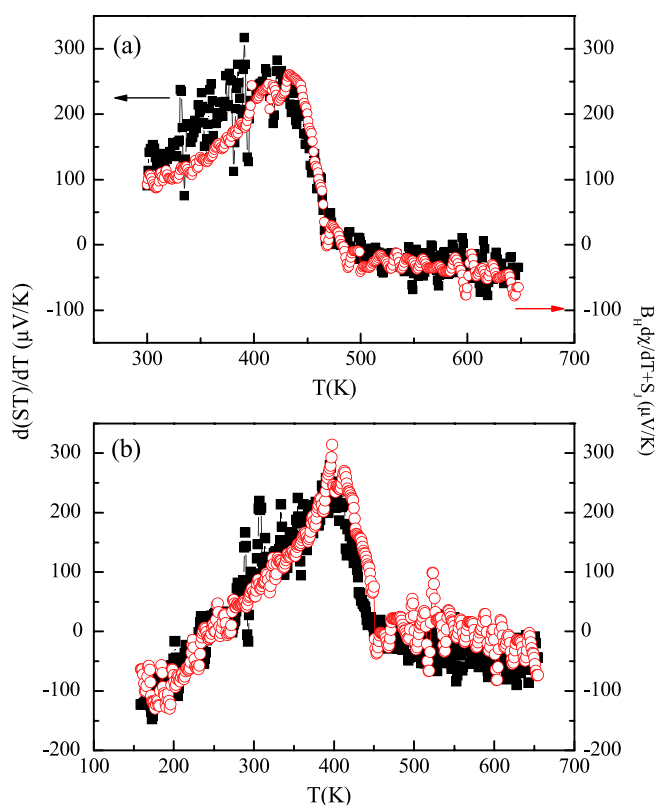


Figure A.2. The relation between the TEP and magnetic susceptibility of BSMO. (a) Sr = 0.6 and (b) Sr = 0.7.

$\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ [20] and the normal state of the superconductor $\text{La}_{1.9}\text{Sr}_{0.1}\text{CuO}_4$ [21, 22] (see figure 4). These compounds are consistent with the relation.

Although more theoretical work is needed to understand the physical meaning of this relationship between TEP and the magnetic susceptibility, we found a simple scaling relation by empirical means. This scaling relationship states that the magnetic response to the temperature, $\chi(T)$, for several charge ordered compounds and superconductors, is closely related to that of the transport coefficient, TEP, composed of a magnetic and a configurational term over the full temperature range. This scaling relationship between TEP and the magnetic susceptibility is universal, at least for strongly correlated systems, including colossal magnetoresistance materials and high T_C cuprates.

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Appendix

Measurement of the temperature dependent magnetic susceptibility of BSMO was performed in a 1 T magnetic field but measurement of that of TEP was performed at 0 T. Therefore,

we show that TEP and magnetic susceptibility measurements of BSMO in 1 T magnetic field are compatible with those for 0 T. One of the electrical transport properties, the resistivity, of BSMO is independent of the applied magnetic field, at least up to 8 T [7, 8]. In the case of half-doped BSMO, the change of magnetization with the field is very small as compared to the case for other half-doped manganese compounds [23]. And it was reported that a strong magnetic field ($\mu_0 H_C \sim 50$ T) is necessary to induce an FM state in BSMO [24]. This evidence indicates that another electrical transport property, TEP, may be unchanged by applied magnetic field. Moreover we presented the magnetic field dependent TEP of BSMO ((a) is for Sr = 0.6 and (b) is for Sr = 0.8) in figure A.1. The magnetic field dependent TEP of BSMO in the charge ordered regime shows that the TEP value is almost constant with changing applied magnetic field as shown in figure A.1. Hence the comparison between the zero-field thermopower and 1 T DC magnetic susceptibility is meaningful.

Figure A.2 shows the relation between the TEP and magnetic susceptibility of BSMO (Sr = 0.6 and 0.7). They also follow equation (3).

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