Thermoelectric power of polycrystalline hole and electron doped manganites

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Abstract. The temperature dependence of the thermoelectric power $S(T)$ for polycrystalline hole-doped La$_{0.8}$Ca$_{0.2}$MnO$_3$ and electron doped La$_{0.8}$Ce$_{0.2}$MnO$_3$ perovskites have been investigated to determine the role of several scattering mechanism. In the ferromagnetic regime, the phonon drag $S(T)$ with scattering of phonons from defects, grain boundaries, phonons and charge carriers in these samples is computed within the relaxation time approximation. Later on, Mott expression is used to generate the carrier diffusive thermoelectric power. It is noticed that the behaviour of the $S(T)$ is determined by competition among the several operating scattering mechanisms for the heat carriers and a balance between carrier diffusion and phonon drag contributions in the hole-doped and electron doped samples.

1. Introduction

The complex phase diagrams and the fragile phase boundaries of the electron/hole doped rare earth manganites continue to attract intense theoretical and experimental attention [1]. The hole-doped manganites La$_{1-x}$Ca$_x$MnO$_3$ have been the purpose of numerous investigations in recent years owing to their colossal magnetoresistance properties. This behavior has been interpreted on the basis of the double-exchange theory [2] and of dynamic Jahn-Teller effect [3]. Relatively less studied in this respect are the electron-doped manganites of the form La$_{1-x}$Ce$_x$MnO$_3$. It is found that Ce enters into these compounds in 4+ valence state and therefore one expects these to have certain unique properties. Thus, a detailed understanding of the transport properties is essential for electron and hole doped manganites.

The purpose of the present investigation is to measure $S(T)$ in polycrystalline hole-doped La$_{0.8}$Ca$_{0.2}$MnO$_3$ and electron doped La$_{0.8}$Ce$_{0.2}$MnO$_3$ manganites as well to improve our understanding of the interplay of scattering processes between the heat carriers themselves and between the carriers and the impurities for the explanation of the observed behaviour of $S(T)$. Further it is relevant to study the relative magnitudes of these scattering processes, which lead to the anomalous behaviour.

2. Results and discussion

The thermopower measurement of the doped manganites compounds have been done down to 4 K using two stage close cycle refrigerator. The thermopower sample holder consists of two copper blocks electrically insulated from rest of the system but thermally connected to the cold head of close cycle refrigerator. The radiation shield and the vacuum of 10$^{-5}$ mbar ensure the minimal heat leak. The
temperature of the one block is measured using silicon diode sensor with Lakeshore temperature controller. A finite temperature difference of 1 - 2 K is maintained between the two copper blocks by manganin wire heater wounded on the copper blocks and controlled using Au-Fe (7%) Chromel thermocouple and Lakeshore temperature controller. The thermo emf thus developed across the sample is measured against copper. The absolute thermopower is then calculated by subtracting the measured thermopower from the copper thermopower.

The variation of thermopower with temperature is shown in figure 1 for both samples. It is inferred that the thermopower shows a metal - insulator phase transition, manifested by a jump between metal-like behavior at low temperature and semiconductor like behavior at high temperatures for La_{0.8}Ca_{0.2}MnO_3 and La_{0.8}Ce_{0.2}MnO_3. In the paramagnetic phase, on cooling, S increases, down to T_c, and then decreases very rapidly in the ferromagnetic state. Furthermore, in low temperature domain, S shows upturn in the ferromagnetic phase. The small upturn at low temperatures may be due to the weak localization. A linear term and a phonon-drag-type anomaly are clearly visible at low temperatures, further evidence of well-established metallic phases.

The measured thermopower is analysed following Kubo formula [4]. It has contributions from both the phonons and the carriers. We first explore the lattice part; in the continuum approximation

\begin{equation}
S_{\text{ph}}^{\text{drag}}(T) = -k_B \left[ \frac{T}{\theta_D} \right] ^3 \int_0^\infty d\omega (\beta \omega)^4 A(\omega)((\beta \omega)^4 \frac{e^{\beta \omega}}{(e^{\beta \omega} - 1)^2},
\end{equation}

with \( k_B \) is the Boltzmann constant, \( e \) is the charge of carriers, \( \omega_D \) is the Debye frequency and \( \beta = \hbar/k_BT \).

The relaxation time is inhibited in \( A(\omega) \) and is proportional to the imaginary part of the phonon self-energy. The phonon drag thermopower relaxation time \( A(\omega) \) is written as

\begin{equation}
A(\omega) = \frac{1/\tau_{\text{ph-d}} + 1/\tau_{\text{ph-\text{gb}}} + 1/\tau_{\text{ph-\text{ph}}} + 1/\tau_{\text{ph-c}}}{1/\tau_{\text{ph-d}} + 1/\tau_{\text{ph-\text{gb}}} + 1/\tau_{\text{ph-\text{ph}}}}.
\end{equation}

The various relaxation times are defined in terms of transport coefficients elsewhere [5]. Here, \( L \) is grain size; \( n_F \) is the Fermi-Dirac distribution function. The notation \( \tau_{\text{ph-d}}, \tau_{\text{ph-\text{gb}}}, \tau_{\text{ph-ph}} \) and \( \tau_{\text{ph-c}} \) are the phonon scattering relaxation time due to defects, grain boundaries, phonon and phonon-carrier interactions respectively. We note that to this order Mathiessen’s rule holds namely, that the inverse of the total relaxation time is the sum of the various contributions for the different scattering channels.

While estimating the temperature dependent thermopower of these samples, we make use of the transport parameters, which are characterize the strengths of the phonon-defects \( D_{\text{ph-def}} = 5.73 \times 10^{-8} \text{ K}^{-1} \), phonon-grain boundary \( D_{\text{ph-\text{gb}}} = 3 \times 10^{-3} \), phonon-phonon \( D_{\text{ph-ph}} = 0.1 \times 10^{-4} \text{ K}^{-1} \text{Sec}^{-1} \) and phonon-carrier \( D_{\text{ph-c}} = 2.3 \times 10^{-3} \text{ Sec}^{-1} \) scattering process for Ca (Ce)-doped samples, respectively. These are indeed material dependent parameters for phonon drag thermopower in the present model. We have used the length of the sample is about 3 mm and \( v_s = 3 \times 10^7 \text{ cm sec}^{-1} \).

The main finding of phonon drag thermopower (\( S_{\text{ph}}^{\text{drag}} \)) in figure 2 is that at low temperatures, the quasi particle excitation condensed into the ground state and they cannot scatter phonons. \( S_{\text{ph}}^{\text{drag}} \), thus, increases exponentially with temperature in the absence of the other scattering mechanism. Although
Figure 1. Thermopower as a function of temperature

Figure 2. Variation of phonon thermoelectric power as function of temperature in presence of various phonons scattering mechanism for the La$_{0.8}$Ca$_{0.2}$MnO$_3$ (a) and La$_{0.8}$Ce$_{0.2}$MnO$_3$ (b).

Figure 3. Thermopower versus temperature along with experimental data.
the phonon drag thermopower experiences an exponential increase at low temperature, the presence of the defect, grain boundaries and the carriers set a limit on its growth, as a consequence the phonon drag thermopower diminishes as the temperature increases further.

First it is evident from figure 2 that at low temperatures, $S_{ph}^{drag}(T)$ is linear in temperature, which is common for most metals and change in a slope around 10 K. The departure from linearity at about 10 K depends on the relative magnitudes of the phonon defect and phonon-phonon interactions. Below 10 K, the grain boundary and defects become the effective phonon scatterers and the thermopower exhibits a typical $T^2$ behavior at even lower temperatures, grain-boundary scattering dominates and the usual Debye $T^3$ behaviour appears. $S_{ph}^{drag}(T)$ shows a saturating behaviour and shows slow negative $dS(T)/dT$ at higher temperatures. This kind of nature is attributed to the fact that the phonons mean free path decreases with the increase in temperature, as more and more carriers are available for scattering. Possible reason for the departure from linearity at about 10 K is mainly due to the competition between the increase in the phonon population and decrease in phonon mean free path due to phonon-phonon scattering as evident from equations (1) and (2).

We shall now proceed to include the effect of free carrier diffusion contribution towards thermoelectric power contribution employing the well-known Mott formula. The low temperature carrier diffusion thermoelectric power [6] is

$$S_c^{diff}(T) = -\frac{2\pi^2 k_B^2 T}{3|\varepsilon|} \left[ \frac{\partial \ln \sigma(\varepsilon)}{\partial \varepsilon} \right]_{\varepsilon=\varepsilon_F}$$

with $\sigma(\omega) = Ne^2\tau(\varepsilon_F)/m$ is the energy dependence of conductivity in the relaxation time approximation. For the sake of simplicity, the mean free path of the carriers ($\ell$) is assumed to be independent of temperature, the equation (3) becomes

$$S_c^{diff}(T) = -\frac{\pi^2 k_B^2 T}{3|\varepsilon|\varepsilon_F}.$$  

For constant mean free path, the method point to the scattering of carriers by impurities is dominant. Within the Fermi liquid picture the calculated electron parameter as the Fermi energy $\varepsilon_F \cong 0.6$ (0.4) eV for La$_{0.80}$Ca$_{0.20}$MnO$_3$ and La$_{0.80}$Ce$_{0.20}$MnO$_3$, respectively. In the present analysis, the elastic carrier-impurity contribution to the thermopower is plotted figure 3 for La$_{0.80}$Ca$_{0.20}$MnO$_3$ and La$_{0.80}$Ce$_{0.20}$MnO$_3$ along with the experimental data. The thermopower behavior depends on the competition among the various scattering mechanisms for the heat carriers and balance between the electron and phonon competition. Finally, it is worth stressing that the $S(T)$ decrease slowly above 25 K and is well reproduced from the present theoretical model (see figure 3), this phenomenon is attributed to shortened phonon mean free path as compared to that at low temperatures. It may be seen that the slope change in $S_{ph}^{drag}$ is much more pronounced than that in $S_c^{diff}$ below 15 K for both samples. The reason for being this change is due to the fact that the phonon-impurity scattering dominates and electron-impurity scattering is weaker.

Acknowledgments
Financial assistance from All India Council for Technical Education (AICTE), New Delhi and Madhya Pradesh Council of Science and Technology (MPCST), Bhopal is gratefully acknowledged.

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