On peculiarities of the electron transport in doped manganites

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Abstract. A systematic experimental study of the temperature dependences of the resistivity and thermopower, $S$, in hole- and electron-doped manganites of the ReMnO$_3$ (Re = La, Ce) systems doped by strontium in a wide range of content was performed. The main specific features of the thermopower behavior at temperatures both below and above the temperature of the magneto-ordered transition were revealed and discussed. The $S(T)$ dependences were observed to be quite complicated in both temperature ranges. The $S(T = 300 \text{ K})$ values are negative for the Ce$_{1-x}$Sr$_x$MnO$_3$ samples, while for the La$_{1-x}$Sr$_x$MnO$_3$ ones they are positive for slightly doped samples (at $x < 0.2$), but negative for a high doping level ($x > 0.333$). The thermopower results are qualitatively discussed with respect to peculiarities of the conduction process.

1. Introduction

Although manganites have been known since 1950s, their intensive researches began after 1993 due to discovering the effect of the colossal magnetoresistance in these materials [1–3]. The specific feature of these materials influencing strongly their physical properties is a very complicated magnetic phase diagram [4]. As a result, when varying temperature and doping level different types of phase transitions can occur and manganite samples exhibit complex magnetic properties [5, 6]. Under varying sample composition the temperature of the magneto-ordered transition, $T_c$, can change in a wide range and the magneto-ordered state can be either ferromagnetic or antiferromagnetic of various types [4-6]. In spite of extensive discussions and a huge number of publications devoted to the study of different manganite properties, the nature of the colossal magnetoresistance effect remains unclear. However, unusual properties of these materials go well beyond this phenomenon. In particular, questions on the mechanism of the conduction process in different temperature ranges (both below and above $T_c$) and approaches allowing one to describe the experimentally observed behavior of the transport coefficients are still undetermined and call for further investigations of the electron transport peculiarities in manganites of different compositions.

Such a situation is related to the fact that the presence of strong correlation effects is characteristic of manganites. This affects all the experimentally observed properties of these materials and makes it impossible to use the classical models based on the single-electron approximation for their interpretation and analysis. For this reason, a lot of models were proposed to describe unusual properties of manganites (see, for example, reviews [5, 6]), but at present none of them can be considered as generally accepted. In particular, some proposed approaches have aimed to explain experimental results on a character of the temperature dependences of the resistivity and thermopower and their modifications under doping influence. One of the purposes of such studies was to clear up the conductivity type in manganites. It is well-known, that the charge-carrier type is usually...
determined from the experimental investigations of either the Hall coefficient or thermopower. However, these coefficients in manganites can often have different signs in different temperature ranges [7, 8]. Besides, contrary to the conductivity and magnetoresistance effect, the peculiarities of the behavior of other transport coefficients (in particular, the thermopower) have not been studied in details and most of the experimental results are related to a limited range of doping.

For the above reasons, this paper is devoted to a systematic experimental study of the specific features of the electron transport in manganites of different systems (both hole- and electron-doped) when changing the doping level in a wide range.

2. Samples and Experimental Details

The ceramic samples of La$_{1-x}$Sr$_x$MnO$_3$ ($x = 0.15, 0.2, 0.28, 0.333, 0.38, 0.5, 0.666$) and Ce$_{1-x}$Sr$_x$MnO$_3$ ($x = 0.5, 0.67$) were used for investigations. Such compositions were chosen to trace the modification of the electron transport in a wide range of doping and also to compare the effect of strontium influence in cases of different manganite systems. All the samples were prepared by the standard solid-state processing technique from the high-purity oxides mixed in the required proportions. X-ray diffraction analysis has shown them to be almost of single phase with amount of foreign impurities not exceeding 1-2%. The sample homogeneity was controlled by measuring the local values of the thermopower in various points on the sample surface at room temperature.

The resistance temperature dependences, $R(T)$, were measured by the standard four-probe low-frequency ac ($f = 20$ Hz) method. The thermopower, $S$, was measured by a differential method relative to copper electrodes at the temperature difference between the two ends of a sample of about 2K and then calculated by correcting for the absolute thermopower of copper. Both transport coefficients were measured in the temperature range of $T = 4.2–300$ K.

3. Experimental Results and Discussion

The $R(T)$ dependences are typical for ceramic manganite samples. As an example, figure 1 shows the results obtained for two samples of the La$_{1-x}$Sr$_x$MnO$_3$ system and Ce$_{1-x}$Sr$_x$MnO$_3$ samples. The $T_c$ value for the La$_{1-x}$Sr$_x$MnO$_3$ sample with $x = 0.15$ is about 270 K and at high temperatures ($T > T_c$) resistance increases exponentially with decreasing temperature, reaches a maximum at $T \approx T_c$; at lower temperatures the resistance decreases sharply at temperatures down to 140 K. At lower temperatures the resistance increases again, that is most likely associated with an influence of grain boundaries in a ceramic sample having a high resistance. For La$_{1-x}$Sr$_x$MnO$_3$ samples with a higher strontium content, the $T_c$ value exceeds 300 K in agreement with the data of other studies [9, 10]. For this reason, a sharp drop of the resistance becomes not observable and its value increases with decreasing temperature throughout the measured temperature range. Thus, most of the experimental results obtained for the La$_{1-x}$Sr$_x$MnO$_3$ system are related to temperatures below $T_c$, giving us a possibility to use these samples for revealing specific features of the thermopower behavior in the magneto-ordered state.

The $R(T)$ dependences for Ce$_{1-x}$Sr$_x$MnO$_3$ samples are mainly characterized by the same peculiarities. In this case the magneto-ordered transition appears at much lower temperatures and $T_c$ value decreases slightly with increasing strontium content (from 105 K for the sample with $x = 0.5$ to 100 K for the one with $x = 0.67$, see figure 1). Thus, in cases of Ce$_{1-x}$Sr$_x$MnO$_3$ samples we can obtain the results characterizing their properties at temperature both below and above $T_c$. Note that the observed $T_c$ values correspond well to published results for manganites of the Ce-based system [11]. As for the temperature dependence of the resistance, in the Ce$_{0.33}$Sr$_{0.67}$MnO$_3$ sample a characteristic peak on the $R(T)$ dependence is clearly seen near $T \approx T_c$; at lower temperatures the resistance decreases. The values of resistance for Ce$_{0.5}$Sr$_{0.5}$MnO$_3$ are much higher (by about two orders of magnitude), besides the transition to the magneto-ordered state manifests itself significantly weaker and a drop in the resistance value at $T < T_c$ is weak enough when comparing to the sample with $x = 0.67$. These facts are probably the results of a grain boundaries influence. Nevertheless, for both Ce$_{1-x}$Sr$_x$MnO$_3$ samples the $R(T)$ dependences at $T > T_c$ are qualitatively similar to each other.
The main aim of our work was to study the thermopower behavior. This coefficient is well-known to be much less sensitive to an influence of grain boundaries and other defects compared to the resistance. As a result, the thermopower study in ceramic samples allows one to obtain the information on the electron properties of a material with a given composition eliminating (or at least minimizing) the effect of sample macrostructure.

The $S(T)$ dependence for La$_{1-x}$Sr$_x$MnO$_3$ samples are presented in figure 2 (a). One can see that in a wide rage of doping there is a systematic variation of the thermopower with increasing lanthanum content. For the sample with $x = 0.15$ the thermopower is positive and for temperatures near $T_c$ the $S(T)$ dependence corresponds qualitatively to the temperature dependence of resistance: at $T > T_c$ the thermopower increases slightly up to 24 $\mu$V/K and then falls sharply down to 9 $\mu$V/K at $T = 210$ K. In the low-temperature region (at $T < T_c$, i.e. in the magneto-ordered state) the thermopower shows a slight increase (up to 10.3 $\mu$V/K), demonstrates a broad maximum at $T = 115$ K, and then falls down to 2.8 $\mu$V/K at $T = 14$ K. For other samples with $x \leq 0.5$ having a high $T_c$ the thermopower at $T < 300$ K
does not demonstrate abrupt changes (like the case of the $R(T)$ dependences), but a character of its temperature dependence is completely similar to that observed for the sample with $x = 0.15$ at $T < T_c$. The only feature which can additionally be noted is that in case of $x = 0.5$ a slight decrease of the negative thermopower values is observed at $T < 90$ K.

With increasing strontium content, the $S(T = 300$ K) value decreases noticeably, becomes very close to zero for intermediate doping ($x = 0.28-0.333$) and negative for higher strontium contents (see figure 3). The experimental results obtained for two samples (with $x = 0.28, 0.333$) demonstrating very small thermopower values are additionally shown in figure 2 (b). It is seen that even in case of such small $S$ values the $S(T)$ dependences are very similar in shape. It should be noted that the thermopower for the La$_{0.667}$Sr$_{0.333}$MnO$_3$ sample shows the sign change at a temperature near $T = 300$ K. One can propose that the analogous property is characteristic of the La$_{0.72}$Sr$_{0.28}$MnO$_3$ sample, but at higher temperatures.

![Figure 3](image.png)

**Figure 3.** Thermopower value at $T = 300$ K vs strontium content for La$_{1-x}$Sr$_x$MnO$_3$ (La) and Ce$_{1-x}$Sr$_x$MnO$_3$ (Ce) samples.

Thus, for all samples with $x \leq 0.5$ the main peculiarities of the $S(T)$ curves at $T < T_c$ remain qualitatively unchanged, namely, the thermopower in the magneto-ordered state changes slightly with decreasing temperature and demonstrates a maximum whose position depends on the strontium content. However, the $S(T)$ dependence obtained for the La$_{0.334}$Sr$_{0.666}$MnO$_3$ sample is characterized by the presence of additional features. In this case the thermopower, being negative in the whole measured temperature range, changes slightly at high temperatures ($T > 190$ K), falls (in absolute value) sharply enough as temperature decreases from 190 K to 115 K, and changes slightly again at lower temperatures. Such distinctive features of the thermopower behavior are most probably related to the fact that the type of the magneto-ordered state in the La$_{1-x}$Sr$_x$MnO$_3$ system changes with increasing strontium content. The samples with $x = 0.28-0.5$ are of ferromagnetic phase in the whole measured temperature range, while the La$_{0.334}$Sr$_{0.666}$MnO$_3$ sample is paramagnetic at high temperatures and antiferromagnetic at low temperatures [9, 12]. Besides, in this sample a transition from the tetragonal to the orthorhombic structure occurs with decreasing temperature [9, 12]. These peculiarities result in the observed modification of the thermopower temperature dependence.

The results on the $S(T)$ dependences obtained by us for samples of the La$_{1-x}$Sr$_x$MnO$_3$ system are in qualitative agreement with the published data for hole-doped manganites of different systems. For example, a decrease in the thermopower value with increasing sodium content in La$_{1-x}$Na$_x$MnO$_3$ was
observed in [13], a change in the thermopower sign in the magneto-ordered state was observed in Nd$_{1-x}$(Sr,Pb)$_x$MnO$_3$ [14] and La$_{0.66}$Eu$_{0.02}$Sr$_{0.33}$MnO$_3$ [15]. The experimental $S(T)$ dependences for La$_{0.67}$- $R$,Sr$_{0.33}$MnO$_3$ ($R$ = Eu, Gd) [7] look to be similar to those obtained by us for the La$_{1-x}$Sr$_x$MnO$_3$ samples with $x = 0.28, 0.33$. This suggests that the specific features of the thermopower behavior in the magneto-ordered state including both a character of the $S(T)$ dependences and the thermopower variation under doping observed for samples of the La$_{1-x}$Sr$_x$MnO$_3$ system are typical for hole-doped manganites as a whole. Besides, these results clearly indicate that to describe the thermopower in the magneto-ordered state one should involve a two-band model and take into account a contribution of both hole and electrons in the conduction process.

The $S(T)$ dependences for Ce$_{1-x}$Sr$_x$MnO$_3$ samples are shown in figure 4. The thermopower at $T = 300$ K is negative, increasing strontium content leads to a decrease in the $S(T = 300)$ value like the case of the La$_{1-x}$Sr$_x$MnO$_3$ system (see figure 3). As temperature decreases, the absolute value of $S$ changes at first slightly, but in the temperature range from 190 K to 115 K for the sample with $x = 0.5$ and from 250 K to 150 K for the one with $x = 0.67$ falls sharply down to very small values. The latter points to an existence of two types of charge carriers (electrons and holes) at $T > T_c$, the relationship between whose concentrations changes strongly with decreasing temperature. Note that analogous results (a negative thermopower at $T = 120-350$ K and a sharp decrease in its absolute value at temperatures from 200 K to 120 K) was obtained for the Sr$_{0.5}$Ce$_{0.5}$MnO$_3$ sample [16].

![Figure 4. Temperature dependences of the thermopower for Ce$_{1-x}$Sr$_x$MnO$_3$ samples](image)

It should be noted that despite a minor change in the $T_c$ value in the studied Ce$_{1-x}$Sr$_x$MnO$_3$ samples (being about 5 K) obtained from the resistance data (see figure 1), the temperature range of a sharp thermopower decrease shifts upwards by about 50 K with increasing $x$. This clearly shows that strontium doping influences strongly the concentrations of free electrons and holes or their ratio at temperatures above $T_c$.

At low temperatures (below $T_c$) the thermopower for both samples changes insignificantly, while specific features of its behavior depend on the strontium content in Ce$_{1-x}$Sr$_x$MnO$_3$. For the sample with $x = 0.5$ a slight increase in the negative thermopower values is observed in the range from $T_c$ to 20 K, while for the one with $x = 0.67$ the thermopower becomes positive at $T \approx 145$ K and decreases weakly at further temperature decrease. The observed peculiarities of the thermopower behavior give evidence of a strong modification of the conduction process at $T \approx T_c$. 
4. Conclusions
In summary, this paper presents the results of the systematic study of the thermopower behaviour in manganites of the La$_{1-x}$Sr$_x$MnO$_3$ and Ce$_{1-x}$Sr$_x$MnO$_3$ systems. Increasing strontium content was observed to result in a decrease of the thermopower value for both investigated systems. In Ce$_{1-x}$Sr$_x$MnO$_3$ samples the thermopower at room temperature is negative, while in La$_{1-x}$Sr$_x$MnO$_3$ it is positive for a low doping level, very close to zero for intermediate doping ($x = 0.28–0.333$), and negative for a higher doping level. The peculiarities of the temperature dependences of the thermopower in different temperature ranges (both below and above the temperature of the magneto-ordered transition) characteristic of hole- and electron-doped manganites are revealed and discussed. The observed specific features of these dependences indicate that both below and above $T_c$ two types of charge carriers (electrons and holes) give contributions to the conduction process, so that an interpretation of the electron transport in manganites requires applying two-band models.

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