Thermopower and thermal conductivity of the electron-doped manganite $La_{0.9}Te_{0.1}MnO_3$

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The thermal properties and their relationship to the charge transport properties of an electron-doped manganite $La_{0.9}Te_{0.1}MnO_3$ were investigated. The resistivity and the Hall effect were measured. The magnetic-field dependence of Hall resistivity indicates that the carriers in $La_{0.9}Te_{0.1}MnO_3$ are electrons. The thermopower S and thermal conductivity κ were also measured. Above the metal-insulator transition temperature T_P, a significant difference between the resistivity activation energy (E_ρ=128.3 meV) and the thermopower activation energy (E_S=14.7 meV) was observed, implying that the conductivity of $La_{0.9}Te_{0.1}MnO_3$ above T_P was dominated by the small-polaron hopping. In the ferromagnetic region, it is found that S shows $T^{3/2}$ dependence, suggesting that the electron-magnon scattering strongly affects the low-temperature thermopower of $La_{0.9}Te_{0.1}MnO_3$. The temperature dependence of thermal conductivity, $\kappa(T)$, reveals that the phonon component (κ_{ph}) is the major one. Moreover, in the paramagnetic region, a positive $d\kappa/dT$ is observed, i.e., $d\kappa/dT>0$, which might be related to the local anharmonic lattice distortions. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2402030]

I. INTRODUCTION

The hole-doped manganites $Ln_{1-x}A_xMnO_3$ (Ln=La–Tb, and A=Ca, Sr, Ba, Pb, etc.) have attracted much renewed attention due to the discovery of colossal magnetoresistance (CMR).[1–3] Many theories, such as the double exchange (DE) interaction,[4] the polaronic effects,[5] and the phase separation combined with percolation,[6] have been proposed to understand the underlying physics of the CMR effects. Recently, based on the development of spintronics, many researches have been focused on electron-doped compounds such as $La_{1-x}Ce_xMnO_3$ (Refs. 7 and 8) and $La_{1-x}Te_xMnO_3$.[9–11] These investigations also suggest that the CMR behavior might occur in the mixed-valence state of Mn^{2+}/Mn^{3+}.

For the hole-doped manganites, the DE alone cannot explain the temperature dependence of resistivity, and the small polarons play a major role in the conductivity in the high-temperature paramagnetic (PM) region.[12,13] The Hall-effect study also suggested the presence of small polarons in manganites.[14] On the other hand, some of the research groups reported the formation of large polarons or bipolarons to explain the high-temperature conductivity.[15,16] A salient question to ask is *what happens in the case of electron-doped manganites?* The relevant reports are very rare. Thermopower S and thermal conductivity κ measurements are important tools to investigate the transport properties of transition-metal oxides, since they are very sensitive to the nature of charge carriers and they can provide some information which cannot be obtained by the magnetization and the resistance measurements. In addition, the thermopower measurement is less affected by the presence of grain boundaries, and the thermal conductivity data also reveal the critical information regarding the various scattering processes of thermal carriers and aid to understand the complex physical properties of materials. To understand comprehensively the conductivity in an electron-doped manganite, $La_{0.9}Te_{0.1}MnO_3$, in this work, we will report our results of investigation on the thermal properties and their relationship to the charge transport properties of $La_{0.9}Te_{0.1}MnO_3$ using the resistivity, the Hall-resistivity, the thermopower, and the thermal-conductivity measurements.

II. EXPERIMENT

A ceramic sample of $La_{0.9}Te_{0.1}MnO_3$ was synthesized by the conventional solid-state reaction method in air. The powders mixed in the stoichiometric compositions of high-purity La_2O_3 (99.99%), TeO_2 (99.9%), and MnO_2 (99.9%) were ground, and then fired in air at 700 °C for 24 h. The powders obtained were ground, pelletized, and sintered at 1050 °C for 24 h with three intermediate grindings, and finally, the furnace was cooled down to 200 °C for 8 h and then cooled to room temperature. The crystal structure and the lattice constant were determined by powder x-ray diffraction (XRD) using Cu $K\alpha$ radiation at room temperature. The

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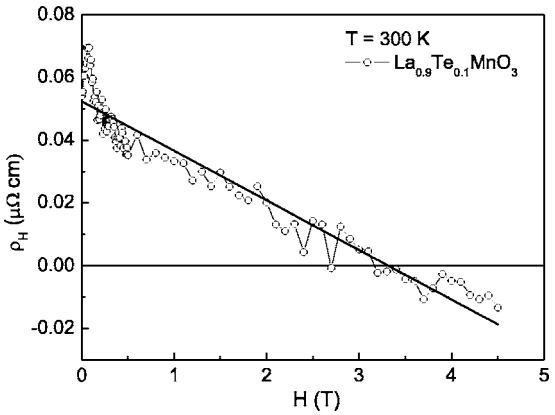

FIG. 1. Magnetic-field dependence of Hall resistivity of $La_{0.9}Te_{0.1}MnO_3$ at 300 K. The solid line is obtained by fitting the data at high magnetic fields.

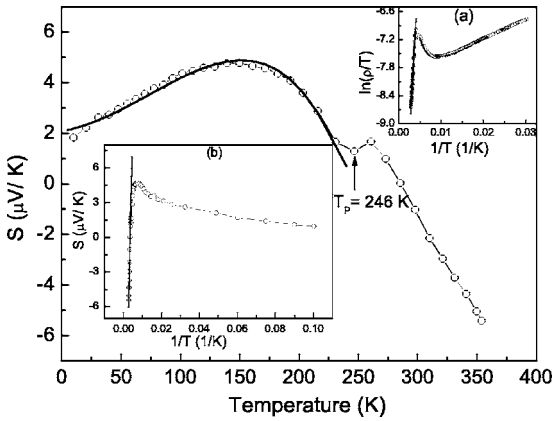

FIG. 2. Thermopower vs temperature for $La_{0.9}Te_{0.1}MnO_3$. The solid line is obtained by fitting the data in the FM region. Inset (a) shows the $\ln(\rho/T)$ vs $1/T$ plot, and the solid line is obtained by fitting the data according to the SPH model. Inset (b) includes S vs $1/T$ plot and the solid line is a fitting based on the data.

chemical composition of the sample was determined by energy dispersive spectroscopy (EDS) quantitative analysis using a scanning electron microscope (AMRAY 1000B). The resistance as a function of temperature was measured by the standard four-probe method from 25 to 350 K. The measurements of Hall resistance, thermopower, and thermal conductivity were performed by using a commercial Quantum Design Physical Property Measurement System (PPMS) ($1.8 \leqslant T \leqslant 400$ K, $0 \leqslant H \leqslant 5$ T).

III. RESULTS AND DISCUSSION

The powder XRD pattern taken at room temperature (not shown) reveals that the sample is a single phase with no detectable secondary phases. A quantitative analysis of the energy dispersive spectroscopy data indicates that the concentration is very close to the nominal $La_{0.9}Te_{0.1}MnO_3$ composition. The XRD patterns of the sample can be indexed by a rhombohedral lattice with the space group $R\bar{3}C$. The lattice parameters were refined by the standard Rietveld technique[17] to be $a=5.5241$ Å and $c=13.3572$ Å. The structural information has been described in detail in Ref. 18. In addition, the sample $La_{0.9}Te_{0.1}MnO_3$ undergoes a paramagnetic-ferromagnetic (PM-FM) transition at $T_C=239$ K and the metal-insulator transition (MIT) at $T_P=246$ K.[18] Figure 1 shows the magnetic field dependence of Hall resistivity ρ_H for $La_{0.9}Te_{0.1}MnO_3$ at the room temperature. In ferromagnets, ρ_H is the sum of the conventional term R_0B and the anomalous term proportional to the observed magnetization, $\rho_H=R_0B+\mu_0R_SM$. Here R_0 is the ordinary Hall coefficient, R_S the anomalous Hall coefficient, μ_0 the vacuum permeability, and $B=\mu_0[H+(1-N)M]$ is the magnetic induction of the sample. The solid line was obtained by fitting the data at high magnetic field. As it can be seen clearly in Fig. 1, the curve $\rho_H(H)$ exhibits a negative high-field slope, indicating that the main charge carriers are electrons. This is another evidence of $La_{0.9}Te_{0.1}MnO_3$ being the electron-doped manganite.

Figure 2 shows the temperature dependence of thermopower $S(T)$ of $La_{0.9}Te_{0.1}MnO_3$. The temperature marked by an arrow corresponds to T_P. The $S(T)$ curve of $La_{0.9}Te_{0.1}MnO_3$ is quite complicated, which is consistent with many other reports.[19–22] The value of thermopower is in the range of a few μV/K. These small values seem to be the reminiscence of metallic systems; however, the change of sign from positive to negative with increasing temperature is observed, which can be commonly observed in hole-doped semiconductors. As discussed in Ref. 23, for the hole-doped semiconductors, the thermopower value at higher temperatures is negative due to the excitation of the electrons from the valence band to the conduction band (CB), and the mobility of electrons in the CB is high, leading to a negative thermopower. Here the negative thermopower at higher temperatures is attributed to the electron doping in $La_{0.9}Te_{0.1}MnO_3$. One possible origin of the sign change of S for $La_{0.9}Te_{0.1}MnO_3$ crystal is the change of electronic state.[21] The degeneracy of the e_g band seems to be gradually lifted as temperature is lowered below T_P and the S changes its sign from negative to positive with the increase of the spin polarization. However, the exact origin is not clear at present and needs to be further investigated.

There have been extensive discussions on the polaronic transport behavior in the PM phase for the hole-doped manganite.[13,20,21] and then a salient question to ask is *what is the case in the electron-doped manganites?* Tan *et al.* found that the resistivity of $La_{0.9}Te_{0.1}MnO_3$ in the PM phase can be fitted with either small-polaron hopping (SPH) or variable-range hopping (VRH).[24] Sometimes, it is difficult to determine the real transport mechanism of the carriers merely based on the fitting results of $\rho(T)$ data. Therefore, it is necessary to perform the fitting of $S(T)$. For $T_C \leqslant T \leqslant 350$ K, the T dependences of ρ and S of $La_{0.9}Te_{0.1}MnO_3$ are described by

$$\rho = \rho_0 T \exp(E_\rho/k_BT) \quad (E_\rho = 128.3 \text{ meV}) \tag{1}$$

and

$$S(T) = \frac{k_B}{e}\left(\alpha + \frac{E_S}{k_BT}\right) \quad (E_S = 14.7 \text{ meV}), \tag{2}$$

respectively, as shown in insets (a) and (b) of Fig. 2, where ρ_0 is a constant, E_ρ the resistivity activation energy, k_B Boltzmann's constant, e the electron's charge, E_S the activation energy obtained from the thermopower data, and α a constant. Therefore, we can estimate the resistivity activation

energy E_ρ(=128.3 meV) and the thermopower activation energy E_S(=14.7 meV). It was found that the activation energy deduced from the resistivity data is one order of magnitude larger than that obtained from the thermopower data E_S(=14.7 meV). Such a large difference in the activation energies is the hallmark of the SPH conduction. According to the polaron model, the measured activation energy of the resistivity E_ρ is the sum of the activation energy needed for the creation of the carriers and activating them hopping, and E_S is the energy required to activate the hopping of carriers. Therefore, the activation energy E_ρ is larger than E_S at the high-temperature range, and thus we can calculate the polaron binding energy $E_P=2(E_\rho-E_S)=227.2$ meV. When the temperature decreases to T_C, the sample $La_{0.9}Te_{0.1}MnO_3$ undergoes the PM-FM transition leading to an abrupt expansion of polarons, resulting in the formation of metallic conductivity. The carriers are polarons in zero magnetic field, but become delocalized carriers under an applied magnetic field at the same temperature, which leads to the increase of conductivity resulting in the magnetoresistance (MR) of the sample.

Now let us investigate the transport mechanism in the FM state. Snyder *et al.*[25] analyzed the resistivity data in the FM phase for Sr- and Ca-doped $LaMnO_3$ using the expression $\rho=\rho_0+\rho_2T^2+\rho_{4.5}T^{4.5}$, where ρ_0 is the residual resistivity, the second term is due to the electron-electron scattering, and the additional $T^{4.5}$ term is due to the electron-magnon scattering. For the electron-doped manganite $La_{0.9}Te_{0.1}MnO_3$, we found that the resistivity in the FM region could also be fitted by the above expression, indicating that the electrical transport was mainly attributed to the electron-electron and electron-magnon scatterings. In ferromagnets, electrons can be scattered by spin waves. Analogous to the phonon drag effects, the electron-magnon interaction produce the magnon drag. The theory of magnon drag follows precisely that of the phonon drag. Since the magnon drag effect is approximately proportional to the magnon specific heat, one expects a $T^{3/2}$ contribution in S at low temperature for FM systems. We have analyzed the thermopower data below T_C using the expression[19]

$$S = S_0 + S_{3/2}T^{3/2} + S_4T^4, \tag{3}$$

and found that S exhibits the $T^{3/2}$ dependence, suggesting that the electron-magnon scatterings strongly affect the low-temperature thermopower of manganites. It is worth noting that there exists a broad peak below T_C. The peak in thermopower due to the phonon drag is usually seen at low temperature ($\approx\theta_D/5$), where θ_D is the Debye temperature. Since the Debye temperature for these systems is about 375 K, the peak in S due to the phonon drag is expected to appear at around 75 K, which is much lower than that we observed at ~170 K. This suggests that the electron-phonon scattering does not dominate the temperature dependence of thermopower for the manganites in the low-temperature FM metallic region. The broad peak below T_C can be understood on the basis of electron-magnon scattering as predicted for itinerant ferromagnets.

Heat is transferred primarily by electrons and phonons in crystalline materials. Figure 3 shows the temperature dependence of thermal conductivity $\kappa(T)$ of $La_{0.9}Te_{0.1}MnO_3$ at zero field. Usually the κ can be expressed by the sum of phononic component (κ_{ph}) and mobile-charge-carrier component (κ_{ch}) as $\kappa=\kappa_{ph}+\kappa_{ch}$. The κ_{ch} value can be estimated from Wiedemann-Franz law, i.e., $\kappa_{ch}=L_0T/\rho$, where $L_0=2.44\times10^{-8}$ V^2 K^{-2} is the Lorenz number. Such an estimate for our sample indicates a κ_{ch} contribution of 0.05%–0.2% of the measured κ. Consequently, the predominant contribution to the measured κ comes from κ_{ph} with the negligibly small contribution of κ_{ch}. The magnitude of $\kappa(T)$ lies in the range of 1–9 W/mK, which is typical for amorphous materials.[26] For a crystalline solid, this low value of thermal conductivity could be originated from random, noncentral distortions of the lattice, resulting in high degree of disorder. In the case of manganites, such a scenario may be attributed to the Jahn-Teller (JT) distortions of the MnO_6 octahedra. Below T_P (corresponding to the Curie temperature T_C), κ increases with increasing temperature, then decreases above ~200 K, and an anomaly at T_P appears. κ increases with decreasing temperatures in $200\text{ K}<T<T_P$. As we know, the local MnO_6 JT lattice distortions due to Mn^{3+} JT ions can scatter the phonon, which gives rise to the decrease in κ. Therefore, the small rise in κ below T_P suggests that the JT distortions become delocalized along with the charge carriers when the temperature is lowered below T_P and thereby reduces the phonon-phonon scattering. In the region of above T_P, $\kappa(T)$ displays the behavior of an amorphous solid, i.e., $d\kappa/dT>0$, similar to the cases of hole-doped manganites.[27,28] Generally speaking, a positive $d\kappa/dT$ above T_P is unusual since the high-temperature thermal conductivity in crystalline insulators is mostly a decreasing function of temperature and cannot be attributed to usual high-temperature electron or phonon processes. Local anharmonic distortions may be a possible cause for the observation of $d\kappa/dT>0$ above T_P. Moreover, above T_P, κ can be parametrized by the expression $\kappa=\kappa_0\exp(T/T_\kappa)$, where $\kappa_0=1.2608$ W/mK and $T_\kappa=190$ K, as shown by the solid line in Fig. 3.

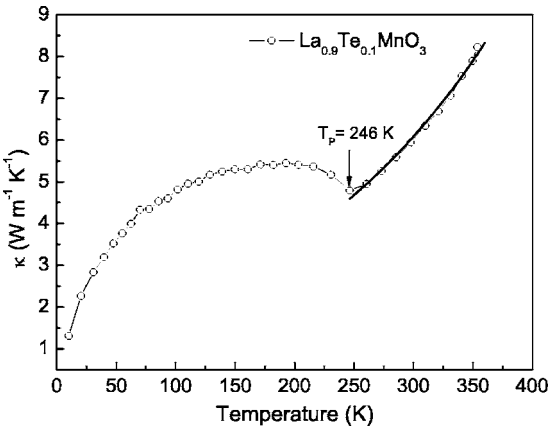

FIG. 3. Thermal conductivity as a function of temperature, $\kappa(T)$, for $La_{0.9}Te_{0.1}MnO_3$. The solid line represents the exponential temperature dependence, $\kappa=\kappa_0\exp(T/190)$.

It is well known that the thermoelectric materials are ranked by a figure of merit, ZT, which is defined as $ZT=S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity, and T is the absolute temperature.[29] According the above expression, we

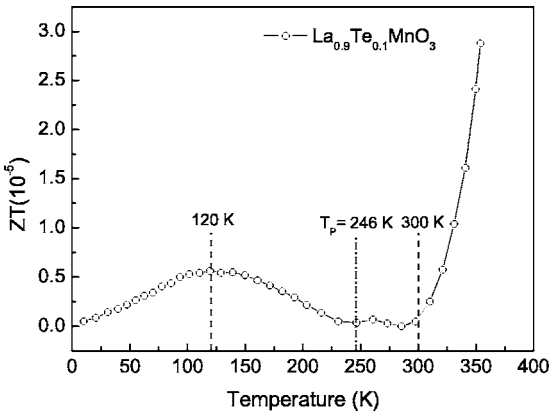

FIG. 4. Temperature dependence of figure of merit for $La_{0.9}Te_{0.1}MnO_3$. The line is drawn as a guide to the eyes only.

also plotted the temperature dependence of ZT for $La_{0.9}Te_{0.1}MnO_3$ in Fig. 4. ZT increases slightly when T changes from 5 to 120 K, and decreases abruptly from 120 K to T_P, but is stabilized for $T_P \leqslant T \leqslant 300$ K, and then ZT increases rapidly with the increase of temperature. Unfortunately, we found that the figure of merit of the electron-doped manganite $La_{0.9}Te_{0.1}MnO_3$ was very low, implying that those manganites were not candidate materials for thermoelectric materials. However, we think that the thermoelectric properties of manganites can be improved by doping and/or nanostructuralizing. In fact, the improvement of thermoelectric properties is challenging, since S, σ, and κ are interrelated, i.e., one alters the others, making optimization extremely difficult.

IV. CONCLUSIONS

The thermal and the transport properties of $La_{0.9}Te_{0.1}MnO_3$ have been studied by measuring the resistivity, the thermopower, and the thermal conductivity. The large difference between E_ρ and E_S provides an evidence for the small-polaron transport mechanism in the high-temperature PM region. In the FM region, a broad peak below T_C in the S vs T plot and the thermopower of $La_{0.9}Te_{0.1}MnO_3$ can be understood on the basis of electron-magnon scattering. In addition, from the results of $\kappa(T)$, it is found that the phononic component (κ_{ph}) contributes mainly to the measured κ.

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