ELSEVIER

Journal of Magnetism and Magnetic Materials 242–245 (2002) 665–667

Journal of magnetism and magnetic materials

www.elsevier.com/locate/jmmm

Transport properties in Gd doped $La_{2/3}Ca_{1/3}MnO_3$

L.E. Hueso[a,*], P. Sande[a], F. Rivadulla[b], A. Fondado[a], J. Rivas[a], M.A. López-Quintela[b]

[a] *Departamento de Física Aplicada, Facultad de Fisica, Universidad de Santiago de Compostela, 15782 Santiago de Compostela, Spain*
[b] *Departamento de Química-Física, Universidad de Santiago de Compostela, 15782 Santiago de Compostela, Spain*

Abstract

The electronic transport in the paramagnetic range of mixed valence manganites is studied here through resistivity and thermopower of Gd^{3+} doped $La_{2/3}Ca_{1/3}MnO_3$. The analysis of the experimental results of the high temperature limiting value for the thermopower reveals a discrepancy with theory, which could be interpreted as a consequence of an increasing entropy term with lattice distortion. The polaron binding energy is found to be independent of the lattice distortion.

Keywords: Electrical resistivity,Thermal dependence; Thermoelectric transport; Magnetic oxides; Polaron

Electronic transport properties in manganites have been studied in detail since the rediscovery of colossal magnetoresistance (CMR), nearly 10 years ago. Although much effort has been expended to elucidate the relation between transport, magnetism and structure by microscopic analysis, the basic transport behavior is still the most intriguing part of these materials. Initially, it was explained qualitatively through double exchange (DE) theory, but further theoretical work indicated that an unusually high electron–phonon coupling is fundamental for a quantitative fit to basic results. Moreover, this seems to be the underlying mechanism in the new phase separation phenomena discovered recently (for a review see [1,2]). Translation of all the theoretical work developed has led to an agreement about considering nearest-neighbor hopping of small polarons as the right theory to explain high-temperature transport measurements in manganites [3]. Emin and Holstein calculated resistivity in the adiabatic regime and found that the mobility has a thermally activated form [4] that leads to:

$$\rho(T) = \rho_0 T \exp(E_\rho/kT), \tag{1}$$

where E_ρ is the activation energy, and the resistivity prefactor ρ_0 depends on the concentration of polarons, the hopping distance and the frequency of the longitudinal optical phonons. On the other hand, in a case of thermal activation of carriers, the thermopower takes the form

$$S = \frac{k}{e}\left(\frac{E_S}{kT}\right) + S_\infty, \tag{2}$$

where E_S is again the activation energy (that differs from the resistivity one, not as in the case of classical semiconductors) and S_∞ is the thermopower high-temperature limiting value [5]. From a careful study of both measurements, it is possible to understand the polaronic nature of conductivity in manganites and to elucidate some of the points that remain still unexplained.

In order to study the transport properties of manganites in the paramagnetic regime, we have prepared a series of samples with a fixed doping level and only changing one of the doping cation concentration to alter the crystallographic structure. As has been pointed out, the crystal symmetry plays a central role in the magnetotransport properties and it is one of our objectives to study this influence [6].

For this study, we synthesized a series of polycrystalline samples with nominal composition $(La_{1-y}Gd_y)_{0.67}Ca_{0.33}MnO_3$ ($y = 0$, 0.10, 0.25, 0.50, 0.75, 1). All of them were prepared by solid state

*Corresponding author. Fax: +34-981520676.
E-mail address: fahueso@usc.es (L.E. Hueso).

0304-8853/02/$ - see front matter
PII: S0304-8853(01)01009-5

reaction. X-ray Rietveld refinements show single-phase materials in all the cases. Resistivity was measured by the standard four-probe method with gold contacts. Measurements of thermoelectric power were performed with a home-made apparatus.

First of all, we analyze the electrical resistivity data of the whole series of samples prepared. The temperature where metal–insulator transition takes place (T_{M-I}) is reduced when Gd doping is increased, and for values greater than 10% it totally disappears from our experimental data range (see Fig. 1). Resistivity values also increase manifestly with Gd doping. These are well-known results in $La_{2/3}Ca_{1/3}MnO_3$ substituted manganites with Gd or other smaller size ions [1,6] and the reason for this is the different size of La^{3+} and Gd^{3+} ions. As Gd^{3+} percentage increases, the tolerance factor and the Mn–O–Mn bond angle in the perovskite structure diminishes. Since the electronic hopping between Mn sites depends strongly on the bonding angle, we easily produce a systematic increase in resistivity and a decrease in the metal–insulator and ferromagnetic–paramagnetic (T_C) transition temperatures. Although it is beyond the scope of this paper, magnetic transition temperatures in our different samples were determined experimentally and they fit perfectly into the phase diagram for manganites proposed by Hwang et al. [6]. Resistivity in the semiconductor range was satisfactorily fitted by small-polaron hopping equation (Eq. 1) and the activation energy (E_ρ) increases linearly with increase in the Gd percentage.

In Fig. 2 is plotted the thermopower temperature dependence. Low doping rate samples present a transition almost coincident with T_C and T_{M-I} (see inset of Fig. 2). However, it is noticed that the change in the sign observed around that temperature is not related with a change in the carriers nature but on the competition between the entropy term and the energy transport term of the thermopower [5]. The values in the metallic range are constant and small, around a few μV/K, as is typical in these systems. If we study the paramagnetic span, the thermopower values are very high and coincident with the reduced carrier mobility viewed through resistivity. All the samples can be accurately fitted to Eq. (2). Activation energy values (E_S), as resistivity ones, also increase linearly with increase in the Gd doping level. Another important parameter we are going to study is the thermopower infinite values (S_∞), which are plotted in Fig. 3. It is unambiguous again the linear dependence between the doping level and S_∞. The quantities are always negative and reflect the combination of several contributions, generally [5]:

$$S_\infty = S_\sigma + S_{ME}. \tag{3}$$

The first term (S_σ) is determined by the configurational entropy of placing a spin σ_1 hole in a spin σ_0

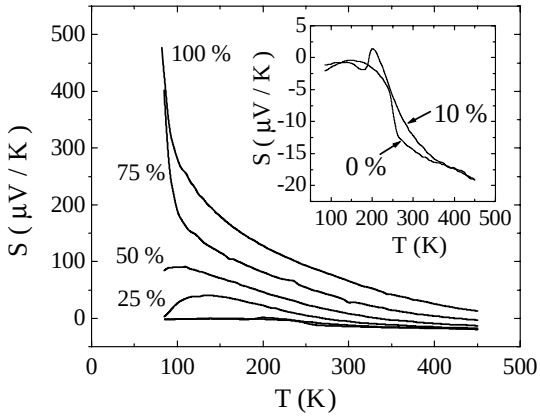

Fig. 2. Thermal dependence of thermopower for all the samples studied. (Inset) thermopower versus temperature curves for the samples with less Gd content.

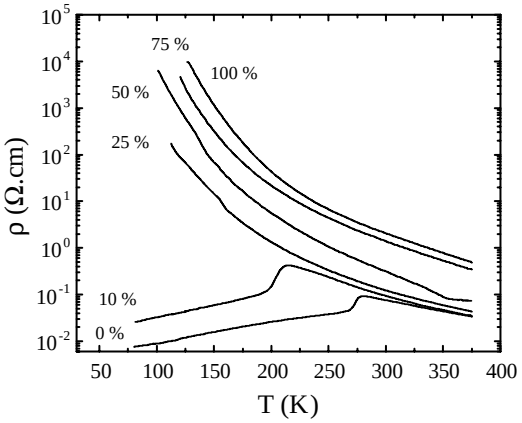

Fig. 1. Thermal dependence of resistivity for all the samples studied with different Gd content percentage.

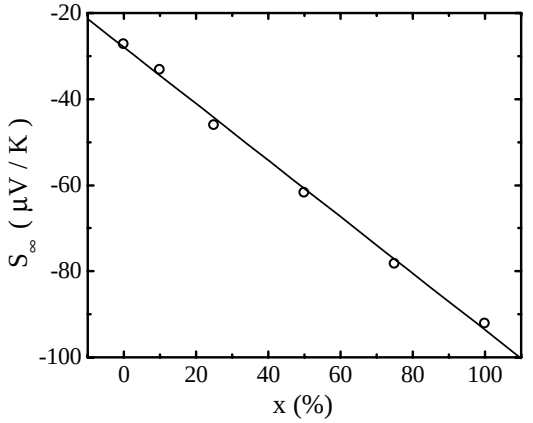

Fig. 3. Thermopower infinite temperature limiting value versus Gd content. The line is a linear fit to the data.

background, and it is given by

$$S_\sigma = \left(\frac{k}{e}\right)\ln\left(\frac{2\sigma_1+1}{2\sigma_0+1}\right) \quad (4)$$

in our specific case, the right values are $\sigma_1 = 3/2$ and $\sigma_0 = 2$, leading to a final value of $S_\sigma = -19,2\,\mu V/K$. The second term ($S_{ME}$) is the mixing entropy term that counts in how many different ways x holes can be distributed between n sites. There are several alternative models considered in the bibliography, but the one that seems to be most adequate for our case is the Chaikin–Beni limit [5,7]. That is given by

$$S_{ME} = \left(\frac{k}{e}\right)\ln\left(\frac{2(1-x)}{x}\right) \quad (5)$$

and supposes fermions with spin, but with on-site repulsion. For our constant doping ($x = 0.33$), this mixing entropy term contributes $S_{ME} = -120,0\,\mu V/K$ to the total thermopower infinite-temperature limit. So, the total result will be $S_\infty \approx -140\,\mu V/K$. This theoretical result is not in correspondence with the experimental ones. At a fixed doping value, all the models support a constant value, so they cannot predict the linear fit obtained from our experimental data. However, we could try to understand this behavior not forgetting the crystallographic distortion induced by Gd doping, that is not taken into account in the development of the theoretical expressions. The greater the distortion, the more important the entropy term which suggests the disorder of the system, as it is shown in our experimental result.

From the activation energies of resistivity and thermopower it is possible to obtain one of the fundamental parameters from the transport properties, that is, the small polaron formation energy in the paramagnetic range (W_P). In general, we can use the relation [5]:

$$W_P/2 = W_H = E_\rho - E_S, \quad (6)$$

where W_H is the polaron hopping energy. In this way, we have computed the polaron formation energy for all the samples studied (see Fig. 4). As is clearly seen, the obtained result is almost independent of the doping level, or in other words, of the distortion of the structure. Despite the great changes induced in the exchange interaction which transforms enormously the magnetism and the transport properties, this parameter seems to behave limitless from this dependence. This is an exciting result that has to be interpreted in a proper way. As a final comment, it is important to note that this system was first studied by Rubinstein et al. [8]. In our work, we complement that study as a result of the analysis of a greater range of compositions of the samples. This allows us to obtain clear tendencies from our experimental data.

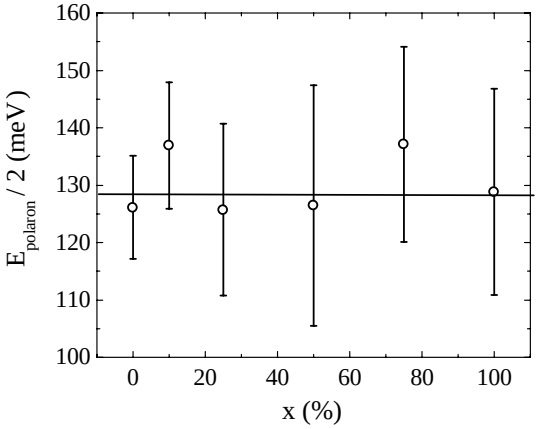

Fig. 4. Polaron hopping energy (W_H) or half of the polaron formation energy (W_P). The line is a linear fit to the data.

In summary, the transport properties in the paramagnetic range of the compound $(La_{1-y}Gd_y)_{0.67}Ca_{0.33}MnO_3$ have been studied through resistivity and thermopower measurements. The structural distortion induced by the smaller size of Gd^{3+} ion with respect to La^{3+} one induces huge changes in the transport behavior, but a study in detail will allow us to obtain more important information about materials of this kind. Thermopower data reveal a discrepancy between theory and experimental in the analysis of S_∞. This magnitude varies linearly with Gd doping, accounting for the progressive change in the high temperature entropy value due to lattice distortions. Furthermore, polaron binding energy seems to be a nearly constant parameter in spite of the great changes developed by other experimental quantities. This result, only briefly suggested by other groups, needs to be tested with further theoretical work in order to fully understand its consequences.

References

[1] J.M.D. Coey, M. Viret, S. von Molnar, Adv. Phys. 48 (1999) 167.
[2] E. Dagotto, T. Hotta, A. Moreo, cond-mat/0012117.
[3] M. Jaime, M.B. Salamon, M. Rubinstein, R.E. Treece, J.S. Horwitz, D.B. Chrisey, Phys. Rev. B 54 (1996) 11914.
[4] D. Emin, T. Holstein, Ann. Phys. 53 (1969) 439.
[5] M. Jaime, M.B. Salamon, in: T.A. Kaplan, S.D. Mahanti (Eds.), Physics of Manganites, Kluwer, Academic/Plenum Publishers, New York, 1999.
[6] H.Y. Hwang, S-W. Cheong, P.G. Radaelli, M. Marezio, B. Batlogg, Phys. Rev. Lett. 75 (1995) 914.
[7] P.M. Chaikin, G. Beni, Phys. Rev. B 13 (1976) 647.
[8] M. Rubinstein, D.J. Gillespie, J.E. Snyder, T.M. Tritt, Phys. Rev. B 56 (1997) 5412.