MAGNETORESISTANCE AND HOPPING CONDUCTIVITY IN LaMnO$_{3+\delta}$

R. Laiho$^1$, K. G. Lisunov$^2$, E. Lahderanta$^{1,3}$, V. N. Stamov$^2$, V. S. Zakhvalinskii$^2$, P. A. Petrenko$^2$ and Yu. P. Stepanov$^4$

$^1$Wihuri Physical Laboratory, University of Turku, FIN-20014 Turku, Finland;
$^2$Institute of Applied Physics, Academiei Str. 5, MD-2028 Kishinev, Moldova;
$^3$Physics, University of Vaasa, P. O. Box 700, FIN-65101 Vaasa, Finland;
$^4$A. F. Ioffe Physico-Technical Institute, 194021 St. Petersburg, Russia.

Abstract

Resistivity, $\rho (T)$, of LaMnO$_{3+\delta}$ displays between $\delta = 0 - 0.154$ an activated behavior both above and below the paramagnetic (PM) to ferromagnetic transition temperature, $T_C$. The relative magnetoresistance at 8 T reaches the values of $\sim -88\%$ near $T_C$ and $\sim -98\%$ at $T \approx 20$ K. In the PM phase $\rho (T)$ satisfies between $T_C \sim 130 - 160$ K and $T_v \sim 250 - 270$ K the Shklovskii – Efros-like variable-range hopping conductivity law, governed by a complex energy dependence of the density of the localized states near the Fermi level.

1. Introduction

LaMnO$_{3+\delta}$ belongs to the hole-doped mixed-valence perovskites, which have attracted much attention due to the colossal magnetoresistance (CMR) effect accompanied with a metal-insulator transition (MIT) [1 – 3]. These compounds have a rich magnetic phase diagram, exhibiting the high-temperature paramagnetic (PM), the ferromagnetic (FM) and the canted antiferromagnetic spin orderings [2, 3], as well as spin-glass or cluster-glass behavior [4]. The electronic properties of the manganite perovskites are governed by competing Mn$^{3+}$ - Mn$^{3+}$ superexchange and Mn$^{3+}$ - Mn$^{4+}$ double exchange interactions, by local Jahn-Teller distortions and formation of the mobile small-polaron state [2, 3].

Until now the electronic properties of LaMnO$_{3+\delta}$ are investigated much less than e.g. for its close analog La$_{1-x}$Ca$_x$MnO$_3$. On the other hand, since both materials are obtained by hole doping from the same parent compound, LaMnO$_3$, the electronic properties of non-stoichiometric LaMnO$_{3+\delta}$ are expected to be no less interesting than those of La$_{1-x}$Ca$_x$MnO$_3$ [2, 3]. In this paper we investigate the resistivity and magnetoresistance as a function of $\delta$ in LaMnO$_{3+\delta}$.

2. Results and analysis

Ceramic LaMnO$_{3+\delta}$ was prepared by the standard solid-state reaction method. A set of samples with $\delta = 0$, 0.065, 0.100, 0.112, 0.125, 0.133, 0.140 and 0.154 (marked below as S000, S065, ..., S154) was obtained by combining Ar and oxygen treatments and annealing in air using different temperatures and annealing times (for details see [4]).

According to the room temperature x-ray diffraction investigations our LaMnO$_{3+\delta}$ samples fall into three groups: (i) S000 with orthorhombic $Pbnm$ structure, (ii) S065, S100 and S112 having cubic $Pm3m$ structure with small rhombohedral distortions and (iii) S125, S133, S140 and S154 with the rhombohedral $R-3c$ structure.
Investigations of $\rho (T)$ were made using the four-probe technique in the transverse magnetic field configuration ($\mathbf{B} \perp \mathbf{j}$) for $B = 0 - 10$ T between 4.2 - 350 K.

As shown in Fig. 1 the resistivity decreases with increasing $\delta$. The dependence of $\rho$ on $T$ exhibits a weak inflection near $T_C$ (indicated by the open triangles in Fig. 1 and the other figures below) [4]. This inflection disappears when $B$ is increased, as typical of the PM – FM transition. The resistivity has an activated character for all $\delta$ (and the relative hole concentration $c = 2\delta = 0 - 0.308$) in the whole temperature range, without exhibiting any sign of the MIT with lowering $T$.

The magnetoresistance (MR) of S000 is negligible, which is connected to the absence of Mn$^{4+}$, whereas all the hole-doped samples S065 – S154 exhibit the CMR effect as evident from Fig. 2. The relative MR defined as $\Delta \rho / \rho_0 \equiv [\rho (B) - \rho (0)] / \rho (0)$ attains a minimum of -67 %, -64 %, -72 % and -88 % at $B = 8$ T in S065, S100, S125 and S154, respectively, at a temperature $T_m$ close to $T_C$ (see Fig. 2). Another feature in Fig. 2 is a complicated temperature dependence of MR below $T_C$ or $T_m$, constituting of a maximum at $T \approx 80 - 110$ K and an additional minimum with $\Delta \rho / \rho_0 = -62 \%$ at $T \approx 50$ K in S100 and -79 % at $T \approx 40$ K in S125. In S154 the second MR minimum is not observed and below $T \approx 100$ K the MR decreases monotonically with lowering the temperature, reaching at $T \approx 20$ K the value of $\Delta \rho / \rho_0 \approx -98 \%$, more typical for optimally doped La$_{0.67}$Ca$_{0.33}$MnO$_3$ films near the MIT [2, 3].

Hence, having the property of CMR near $T_C$ common with La$_{1-x}$Ca$_x$MnO$_3$, the resistivity and MR of LaMnO$_3$+$\delta$ exhibit a set of new features, including (i) absence of MIT at Mn$^{4+}$/Mn$^{3+}$ as high as $c \approx 0.3$, (ii) non-monotonic dependence of $T_C$, $T_m$ and $\Delta \rho / \rho_0$ on the hole concentration $c$ (more strictly, on $\delta$ connected to $c$) and (iii) a complicated temperature dependence of MR below $T_C$. 

Figure 1. Resistivity vs. $T$ in the investigated samples

Figure 2. The relative resistivity vs. $T$ in the field of 8 T
Above $T_C$ we analyze the resistivity with the law
\[
\rho(T) = \rho_0(T) \exp\left[\left(\frac{T_0}{T}\right)^p\right].
\] (1)

Here $T_0$ is a characteristic temperature and $p = 1$ for the nearest-neighbor hopping, $p = 1/4$ for the Mott [5] (corresponding to the constant density $g(\varepsilon)$ of the localized states, or DOS, around the Fermi level, $\mu$) and $1/2$ for the Shklovskii-Efros, or SE (corresponding to the soft Coulomb gap in the DOS spectrum around $\mu$) variable-range hopping (VRH) regimes [6]. In Eq. (1) $\rho_0 = AT^m$ (where $A$ and $m$ are constants depending on the hopping mechanism), $T_0 = T_{0M}$ or $T_{0SE}$ for $p = 1/4$ or $1/2$, respectively, where $T_{0M} = \beta_M / [k g(\mu) \alpha^3]$ and $T_{0SE} = \beta_SE e^2 / (\kappa\kappa_b)$, $\delta$ is the localization radius, $\kappa$ is the dielectric constant, $\beta_M = 21$ and $\beta_SE = 2.8$ [6]. Presence of the rigid gap $\gamma < \Delta$ in the DOS spectrum, as found in La$_{1-x}$Ca$_x$Mn(Fe)O$_3$ [7, 8] modifies the SE-VRH by changing the characteristic temperature from $T_{0SE}$ to $T_0$ [8] given by the equation
\[
T_0 = \left(\frac{\gamma}{2k} + \sqrt{\frac{\gamma^2}{4k^2} + T_{0SE}}\right)^2.
\] (2)

The best fit of the data with Eq. (1) is obtained for $p = 1/2$ and $m = 9/2$ (see Fig. 3). This corresponds to the high-temperature SE-like VRH mechanism [8]. In the table below there are collected the values of $A$ and those of $T_0$ and $T_v$ (the VRH onset temperature), obtained by fitting of the plots in Fig. 3. Using the temperature parameters, the values of the Coulomb gap were evaluated with the equation $\Delta \approx k (T_0 T_v)^{1/2}$ (valid in the high-$T$ one-electron approximation) [8] and are displayed in the table below. In addition, the analysis of the magnetoresistance (which is completely the same as in Ref. 8) allowed us to establish the existence of a non-zero rigid gap, depending on $T$ as $\gamma(T) \approx \gamma(T_v) (T / T_v)^{1/2}$, and to obtain the values of $\delta$, which with the values of $\gamma(T_v)$ are given in the table below.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$A$ ($10^{-20}$ Ω cm K$^{-9/2}$)</th>
<th>$T_0$ (10$^4$ K)</th>
<th>$T_v$ (K)</th>
<th>$\Delta$ (eV)</th>
<th>$\gamma(T_v)$ (eV)</th>
<th>$\alpha$ (E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S100</td>
<td>7.3</td>
<td>9.8</td>
<td>250</td>
<td>0.43</td>
<td>0.13</td>
<td>1.7</td>
</tr>
<tr>
<td>S125</td>
<td>2.1</td>
<td>10.8</td>
<td>250</td>
<td>0.46</td>
<td>0.16</td>
<td>1.4</td>
</tr>
<tr>
<td>S154</td>
<td>1.0</td>
<td>11.3</td>
<td>270</td>
<td>0.48</td>
<td>0.17</td>
<td>1.2</td>
</tr>
</tbody>
</table>
3. Discussion and conclusions

The temperature dependence of the pre-exponent $\rho_0(T) = AT^m$ in Eq. (1) given by $m = 9/2$ in the investigated samples means that the fluctuating short-range potential, connected to the lattice disorder, is not important for the carrier localization in LaMnO$_3$+$\delta$ [6, 8].

The values of the width of the soft gap, $\Delta$, in LaMnO$_3$+$\delta$ are close to those in La$_{0.8}$Ca$_{0.2}$MnO$_3$ [7] and La$_{0.7}$Ca$_{0.3}$Mn$_{1-y}$Fe$_y$O$_3$ [8]. On the other hand, $\Delta$ should be comparable with the energy of the Coulomb interaction $U \approx e^2/(\kappa R)$ where $R = 2(4\pi N_h/3)^{1/3}$ is the mean distance between the holes and $N_h = cN_0 = 2\delta N_0$ is the concentration of the holes [7]. The values of $U \approx 0.51, 0.55$ and $0.59$ eV for S100, S125 and S154 are found to be similar to those of $\Delta$, increasing with $\delta$ in agreement with the corresponding increase of $\Delta$ in the table above.

The values of $\alpha$ are consistent with small-polaron nature of the charge carriers in LaMnO$_3$+$\delta$ [5]. They decrease with $\delta$ as may be expected from the corresponding increase of the degree of the localization due to progressive distortions of the perovskite structure.

Finally, the values of $\gamma$ ($T_v$) are similar to those in La$_{0.8}$Ca$_{0.2}$MnO$_3$ [7] and La$_{0.7}$Ca$_{0.3}$Mn$_{1-y}$Fe$_y$O$_3$ [8]. On the other hand, they are comparable with the typical values of the activation energy of the adiabatic nearest-neighbor hopping of small polarons in CMR compounds [2-3], $E_0 \approx E_b / 2$, where $E_b$ is the polaron binding energy [5]. Therefore, the origin of the rigid gap in the manganite perovskites can be attributed to the polaron formation.

To conclude, the resistivity and the magnetoresistance of LaMnO$_3$+$\delta$ are investigated. The analysis of $\rho(T)$ above $T_C$ established the SE-like VRH conductivity regime, governed by existence of the soft Coulomb gap and the rigid gap in the DOS spectrum.

Acknowledgments

This work is supported by the Wihuri Foundation, Finland, and by INTAS (Project No. INTAS 00-00728).

References