Variable-Range Hopping Conduction in LaMnO$_3$ + $\delta$

V. S. Zakhvalinskii$^a$, R. Laiho$^b$, K. G. Lisunov$^c$, E. Lähderanta$^d$, P. A. Petrenko$^e$, Yu. P. Stepanov$^f$, V. N. Stamov$^g$, M. L. Shubnikov$^h$, and A. V. Khokhulin$^a$

$^a$Belgorod State University, Belgorod, 308015 Russia
$^b$Wihuri Physical Laboratory, University of Turku, Turku, FIN-20014 Finland
$^c$Institute of Applied Physics, Academy of Sciences of Moldova, Academiei 5, Chisinau, MD-2028 Moldova
$^d$Department of Physics, Lappeenranta University of Technology, Lappeenranta, FIN-53851 Finland
$^e$Ioffe Physicotechnical Institute, Russian Academy of Sciences, Politekhnicheskaya ul. 26, St. Petersburg, 194021 Russia

Received July 18, 2006; in final form, September 18, 2006

Abstract—The temperature dependence of the electrical resistivity $\rho(T)$ for ceramic samples of LaMnO$_3$ + $\delta$ ($\delta = 0.100–0.154$) are studied in the temperature range $T = 15–350$ K, in magnetic fields of 0–10 T, and under hydrostatic pressures $P$ of up to 11 kbar. It is shown that, above the ferromagnet–paramagnet transition temperature of LaMnO$_3$ + $\delta$, the dependence $\rho(T)$ of this compound obeys the Shklovskii–Efros variable-range hopping conduction: $\rho(T) = \rho_0(T) \exp[(T/T_0)^{2/3}]$, where $\rho_0(T) = AT^{9/2}$ (A is a constant). The density of localized states $g(\varepsilon)$ near the Fermi level is found to have a Coulomb gap $\Delta$ and a rigid gap $\gamma(T)$. The Coulomb gap $\Delta$ assumes values of 0.43, 0.46, and 0.48 eV, and the rigid gap satisfies the relationship $\gamma(T) = \gamma(T_c) = \frac{\gamma(T)}{T/T_c}$, where $T_c$ is the temperature of the onset of variable-range hopping conduction and $\gamma(T_c) = 0.13, 0.16$, and 0.17 eV for $\delta = 0.100, 0.125$, and 0.154, respectively. The carrier localization lengths $a = 1.7, 1.4$, and 1.2 Å are determined for the same values of $\delta$. The effect of hydrostatic pressure on the variable-range hopping conduction in LaMnO$_3$ + $\delta$ with $\delta = 0.154$ is analyzed, and the dependences $\Delta(P)$ and $\gamma(P)$ are obtained.

PACS numbers: 75.47.Lx, 74.25.Fy, 74.62.Dh, 75.47.Gk, 75.30.Et

DOI: 10.1134/S1063783407050198

1. INTRODUCTION

The compound LaMnO$_3$ + $\delta$ belongs to hole-doped mixed-valence (Mn$^{3+}$–Mn$^{4+}$) perovskite manganites exhibiting colossal magnetoresistance [1]. The magnetic phase diagram of these compounds includes the high-temperature paramagnetic, ferromagnetic, and spin glass regions [1, 2].

The hole doping of LaMnO$_3$ + $\delta$ differs from that used for close analogs of this compound, for instance, La$_{1-x}$Ca$_x$MnO$_3$. In the latter materials, holes are created by substituting Ca$^{2+}$ ions for La$^{3+}$ ions in the lattice. Because excess oxygen cannot occupy interstitial sites in the perovskite structure [3, 4], the nonstoichiometry of LaMnO$_3$ + $\delta$ can be associated with the formation of cation vacancies. The concentration of cation vacancies $\delta = (2/3)\delta$ corresponds to the relative hole concentration (or the Mn$^{4+}$/Mn$^{3+}$ ratio) $c = 2\delta$. The absence of Ca ions leads to a decrease in the degree of disorder in the lattice and to a more uniform hole distribution in LaMnO$_3$ + $\delta$ as compared to that in La$_{1-x}$Ca$_x$MnO$_3$ [5].

In compounds exhibiting colossal magnetoresistance, one observes hopping conduction of small-radius polarons (associated with local Jahn–Teller lattice distortions) over nearest neighbors above room temperature, which obeys an Arrhenius-type equation [1]. Below room temperature, hopping conduction depends strongly on the specific features in the density of localized states $g(\varepsilon)$ near the Fermi level $\mu$ [6]. Scanning tunneling spectroscopy of La$_{0.8}$Ca$_{0.2}$MnO$_3$ films revealed a complex structure of the density of localized states near the Fermi level $\mu$, which includes the range characterized by a quadratic dependence $g(\varepsilon)$ with a width $\Delta < 0.5$ eV (soft gap) and the range with $g(\varepsilon) = 0$ and $\gamma(T) < 0.11$ eV (rigid gap) [7]. The soft gap was explained by the effect of Coulomb interaction of charge carriers (the Coulomb gap [8]), whereas the rigid gap was attributed to the Jahn–Teller effect [7].

As the temperature decreases, it becomes increasingly more favorable energywise for carriers to hop beyond the region of nearest sites, thus giving rise to variable-range hopping conduction [8, 9]. The Mott conduction occurs under the conditions where the density of localized states near the Fermi level $\mu$ is constant and finite [9]. The existence of a Coulomb gap brings about another kind of deviation from the Arrhenius law, namely, the Shklovskii–Efros (SE) variable-range hopping conduction [8]. Moreover, the rigid gap also affects the variable-range hopping conduction [6].
comprehensive analysis of the electrical resistivity [6] and thermopower [10] in La$_{0.7}$Ca$_{0.3}$Mn$_{1-y}$Fe$_y$O$_3$ above the Curie temperature $T_C$ led to $\Delta \approx 0.4$ eV and $\gamma(T) \approx \gamma(T_v)(T/T_v)^{1/2}$, where $\gamma(T_v) = 0.16–0.12$ eV decreases with increasing $y$ and assumes values close to those obtained in [7].

In this work, we studied the electrical conductivity and magnetoresistance of LaMnO$_3 + \delta$ samples with the aim of obtaining information regarding the conduction mechanisms and the carrier energy spectrum, including data on the structure of the density of localized states near the Fermi level.

### 2. PREPARATION OF SAMPLES AND THEIR CHARACTERIZATION

Ceramic samples of LaMnO$_3 + \delta$ with $\delta = 0.100$, 0.125, and 0.154 (referred to as S100, S125, and S154, respectively) were prepared by standard solid-phase technology. The specific features of this technology and subsequent annealing in Ar, O$_2$, and air were described in considerable detail in [5]. X-ray powder diffraction analysis revealed that sample S100 has a cubic structure (space group $Pm3m$) with small rhombohedral distortions, whereas samples S125 and S154 have a rhombohedral structure (space group $R-3c$). The parameter $\delta$, which is related to the La and Mn vacancy concentration $\delta'$ and determines the hole concentration $c$, was determined by iodometric titration [5].

### 3. RESULTS AND DISCUSSION

#### 3.1. Temperature Dependence of the Electrical Resistivity

The electrical resistivity was studied by the four-point probe technique in the transverse magnetic field configuration in the range of magnetic fields $B = 0–10$ T. The samples were contained in a helium gas-exchange Dewar, where their temperature could be varied in the range 4.2–350 K with an accuracy of 0.5%.

The temperature dependences of the electrical resistivity of samples S100, S125, and S154 are shown in Fig. 1 (with magnetic fields applied to one of the samples). Open triangles in Figs. 1 and 2 identify the paramagnetic–ferromagnetic phase transition temperatures $T_C$.

#### 3.2. Analysis and Discussion of the Dependences $\rho(T)$

The electrical resistivity of LaMnO$_3 + \delta$ above $T_C$ was analyzed by fitting it with a universal relationship,

$$\rho(T) = \rho_0(T) \exp\left(\left(T/T_v\right)^p\right).$$

(1)