

## MAGNETISM AND FERROELECTRICITY

# Variable-Range Hopping Conduction in $\text{LaMnO}_{3+\delta}$

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**Abstract**—The temperature dependence of the electrical resistivity  $\rho(T)$  for ceramic samples of  $\text{LaMnO}_{3+\delta}$  ( $\delta = 0.100\text{--}0.154$ ) are studied in the temperature range  $T = 15\text{--}350$  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  $\text{LaMnO}_{3+\delta}$ , the dependence  $\rho(T)$  of this compound obeys the Shklovskii–Efros variable-range hopping conduction:  $\rho(T) = \rho_0(T)\exp[(T_0/T)^{1/2}]$ , where  $\rho_0(T) = AT^{9/2}$  ( $A$  is a constant). The density of localized states  $g(\epsilon)$  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  $\gamma(T) \approx \gamma(T_v)(T/T_v)^{1/2}$ , where  $T_v$  is the temperature of the onset of variable-range hopping conduction and  $\gamma(T_v) = 0.13, 0.16,$  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  $\text{LaMnO}_{3+\delta}$  with  $\delta = 0.154$  is analyzed, and the dependences  $\Delta(P)$  and  $\gamma_v(P)$  are obtained.

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## 1. INTRODUCTION

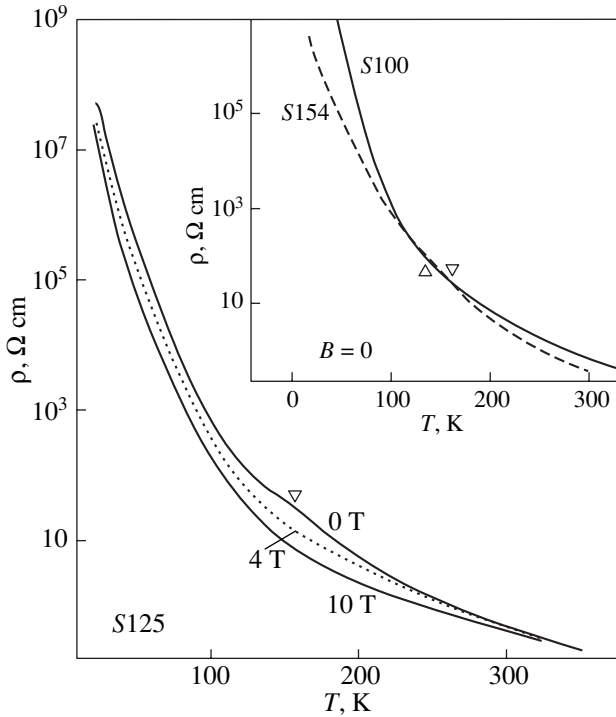
The compound  $\text{LaMnO}_{3+\delta}$  belongs to hole-doped mixed-valence ( $\text{Mn}^{3+}\text{--Mn}^{4+}$ ) perovskite manganites exhibiting colossal magnetoresistance [1]. The magnetic phase diagram of these compounds includes the high-temperature paramagnetic, ferromagnetic, and spin glass regions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

The hole doping of  $\text{LaMnO}_{3+\delta}$  differs from that used for close analogs of this compound, for instance,  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ . In the latter materials, holes are created by substituting  $\text{Ca}^{2+}$  ions for  $\text{La}^{3+}$  ions in the lattice. Because excess oxygen cannot occupy interstitial sites in the perovskite structure [3, 4], the nonstoichiometry of  $\text{LaMnO}_{3+\delta}$  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  $\text{Mn}^{4+}/\text{Mn}^{3+}$  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  $\text{LaMnO}_{3+\delta}$  as compared to that in  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  [5].

In compounds exhibiting colossal magnetoresistance, one observes hopping conduction of small-radius polarons (associated with local Jahn–Teller lat-

tice 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  $g(\epsilon)$  near the Fermi level  $\mu$  [6]. Scanning tunneling spectroscopy of  $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$  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  $g(\epsilon)$  with a width  $\Delta \sim 0.5$  eV (soft gap) and the range with  $g(\epsilon) = 0$  and  $\gamma(T) \sim 0.11$  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]. A



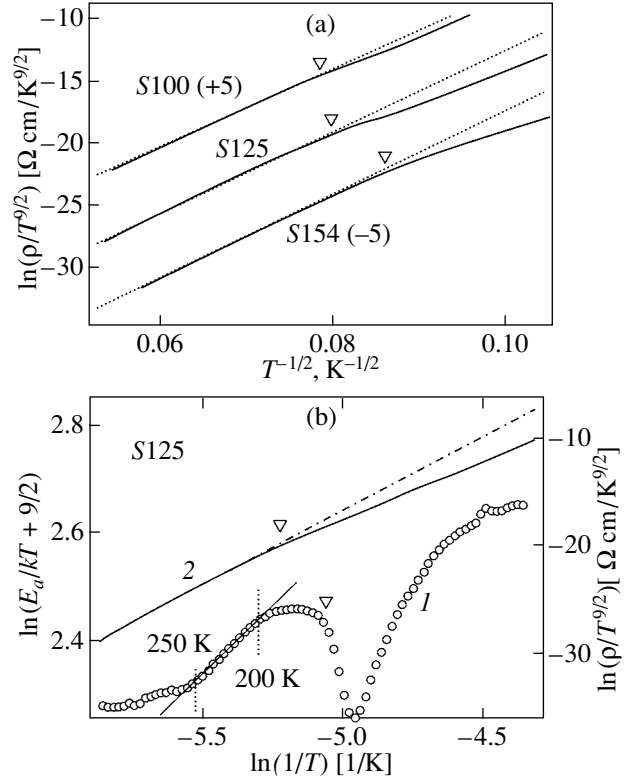
**Fig. 1.** Temperature dependences of the electrical resistivity measured for the  $\text{LaMnO}_{3+\delta}$  sample (S125) in magnetic fields  $B = 0, 4,$  and  $10$  T and for samples S100 and S154 in a zero field (inset).

comprehensive analysis of the electrical resistivity [6] and thermopower [10] in  $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-y}\text{Fe}_y\text{O}_3$  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  $\gamma(T_v) = 0.16\text{--}0.12$  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  $\text{LaMnO}_{3+\delta}$  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  $\text{LaMnO}_{3+\delta}$  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,  $\text{O}_2$ , and air were described in considerable detail in [5]. X-ray powder diffraction analysis revealed that sample S100 has a cubic structure (space group  $Pm\bar{3}m$ ) with small rhombohedral distortions, whereas samples S125 and S154 have a rhombohedral structure (space group  $R\bar{3}c$ ). The parameter  $\delta$ , which is related to the La and Mn vacancy concentration



**Fig. 2.** (a) Dependences of  $\ln(\rho/T^{9/2})$  on  $T^{-1/2}$  for  $\text{LaMnO}_{3+\delta}$  samples (S100, S125, and S154). Two curves are shifted along the y axis by  $\pm 5$  units. (b) Dependences of (1)  $\ln(E_a/kT + 9/2)$  on  $\ln(1/T)$  and (2)  $\ln(\rho/T^{9/2})$  on  $T^{-1/2}$  for the  $\text{LaMnO}_{3+\delta}$  sample (S125).

$\delta'$  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  $B = 0\text{--}10$  T. The samples were contained in a helium gas-exchange Dewar, where their temperature could be varied in the range  $4.2\text{--}350$  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  $\text{LaMnO}_{3+\delta}$  above  $T_C$  was analyzed by fitting it with a universal relationship,

$$\rho(T) = \rho_0(T) \exp[(T_0/T)^p], \quad (1)$$

where  $T_0$  is the characteristic temperature; and  $p = 1$  for conduction over the nearest sites (in this case,  $T_0$  is usually replaced by the activation energy  $E_0 \equiv kT_0$ ),  $p = 1/4$  for the Mott-type variable-range hopping conduction [9], and  $p = 1/2$  for the Shklovskii–Efros variable-range hopping conduction [8]. If the condition  $\Gamma \equiv [kT(T_0/T)^p a / (2\hbar s)]^2 \gg 1$  is met, the preexponential factor in Eq. (1) can be written in the form

$$\rho_0(T) = AT^m. \quad (2)$$

Here,

$$A = Ca^{11} T_0^{(7+q)p}, \quad (3)$$

$a$  is the carrier localization length,  $s$  is the velocity of sound, and  $C$  is a constant [6]. For the Shklovskii–Efros variable-range hopping conduction, we have  $m = 9/2$  or  $5/2$ , while for the Mott variable-range hopping conduction,  $m = 25/4$  or  $21/4$ , if the localized-carrier wave function has the form  $\psi_1(r) \sim \exp(-r/a)$  for  $q = 0$  or  $\psi_2(r) \sim r^{-1} \exp(-r/a)$  for  $q = 4$  in Eq. (3), respectively. The wave function  $\psi_2$  is used in the case where the fluctuating short-range potential associated with lattice disorder strongly affects the carrier localization [8]. For (adiabatic) conduction over the nearest centers, we have  $m = 1$  for any values of  $\psi$ ,  $q$ , and  $\Gamma$  [9]. In Eq. (1),  $T_0 = T_{OM}$  or  $T_{OSE}$  for  $p = 1/4$  or  $1/2$ , respectively, where

$$T_{OM} = \beta_M / [kg(\mu)a^3], \quad T_{OSE} = \beta_{SE} e^2 / (\kappa ka), \quad (4)$$

$\kappa$  is the dielectric constant,  $\beta_M = 21$ , and  $\beta_{SE} = 2.8$  [8]. If the rigid gap is present, i.e.,  $\gamma < \Delta$ , the variable-range hopping conduction satisfies Eq. (1) with  $p = 1/2$ , in which  $T_0$  [6] is given by the relationship

$$T_0 = \left( \frac{\gamma}{2k\sqrt{T}} + \sqrt{\frac{\gamma^2}{4k^2 T} + T_{OSE}} \right)^2. \quad (5)$$

As can be seen from Eq. (4),  $T_{OSE}$  and  $T_{OM}$  do not depend on  $T$  for constant  $a$  or  $g(\mu)a^3$ , respectively. As follows from Eq. (5),  $T_0$  does not depend on  $T$  if, in addition, one of the following conditions is met: (1)  $\gamma/(2kT) \ll (T_{OSE}/T)^{1/2}$  and  $\gamma \sim T$  or (2)  $\gamma \sim T^{1/2}$ . For case 1, we have  $T_0 = T_{OSE}$  because  $(T_0/T)^{1/2} \approx (T_{OSE}/T)^{1/2} + \gamma/(2kT)$  and, if  $\gamma \sim T$ , the second term does not depend on  $T$  and can be included in the preexponential factor, whereas the relationship  $T_0 \neq T_{OSE}$  holds for case 2.

Equation (1) allows a better fit to the temperature dependences of the electrical resistivity for constant  $T_0$  if we set  $p = 1/2$  and  $m = 9/2$  in the range limited by a temperature close to  $T_C$  (Fig. 2a). The fact that  $\rho(T)$  of the samples studied is consistent with the Shklovskii–Efros variable-range hopping conduction mechanism, which satisfies the  $\Gamma \gg 1$  and  $\psi = \psi_1$  conditions for the above values of  $p$  and  $m$ , is borne out by an analysis of the local activation energy  $E_a(T) \equiv \delta \ln \rho(T) / d(kT)^{-1}$  [8]. As can be seen from Eq. (1), if  $T_0$  does not depend on

$T$ , the dependence  $E_a(T)$  can be written in the form  $\ln[E_a/(kT) + m] = \ln p + p \ln T_0 + p \ln(1/T)$ . Figure 2b suggests that the dependence of  $\ln[E_a/kT + 9/2]$  on  $\ln(1/T)$  is linear in the same temperature range as in Fig. 2a, with the slope corresponding to  $p = 1/2$ . The linear parts of the graphs in Fig. 2 were used to find the values  $T_0 = 9.8 \times 10^4$ ,  $10.8 \times 10^4$ , and  $11.3 \times 10^4$  K and the temperatures of the onset of the variable-range hopping conduction  $T_v = 250$ ,  $250$ , and  $270$  K for samples S100, S125, and S154, respectively. By substituting these parameters into the equation [6]

$$\Delta \approx k(T_0 T_v)^{1/2}, \quad (6)$$

we obtained the following values of the Coulomb gap:  $\Delta = 0.43$ ,  $0.46$ , and  $0.48$  eV for the same samples.

The existence of a temperature range within which  $T_0$  is constant (Fig. 2) implies that we are considering one of the cases commented on when we discussed Eq. (5). To pinpoint this case, we studied the temperature dependence of the electrical resistivity in a magnetic field. The localization length of small-radius polarons in the paramagnetic phase varies in a field as  $a(B) = a(0)(1 + b_1 B^2)$ , where  $b_1 \sim \chi(T)$  [11]. As follows from Eqs. (4)–(6), for  $b_1 B^2 \ll 1$ , we have  $T_0(B) = T_0(0)(1 - b_2 B^2)$ , where  $b_2 = b_1 T_{OSE}(0) \{T_0(0) - [T_0(0)/T]^{1/2} \gamma/(2k)\}^{-1}$ , provided  $\gamma$  does not depend on  $B$ . Hence, we arrive at the relationship

$$\gamma(T) = 2[(b_1/b_2 - 1)/(2b_1/b_2 - 1)]k[T_0(0)T]^{1/2}. \quad (7)$$

Close to  $T_v \gg T_C$ , the magnetic susceptibility  $\chi$  varies very little with temperature [5]. Hence, the dependences of  $T_0$  and  $A$  on  $B$  in the temperature range near  $T_v$  can be derived from a linear approximation of the  $\ln(\rho/T^{9/2})$  versus  $T^{-1/2}$  graphs obtained in a magnetic field. The  $a(B)/a(0)$  ratio can be found from Eq. (3). It was established that the dependences of  $a(B)/a(0)$  on  $B^2$  and  $T_0(B)/T_0(0)$  on  $B^2$  are linear functions up to  $B = 10$  T for samples S100 and S125 and almost up to 8 T for sample S154 (these dependences are illustrated for sample S125 in Fig. 3). The ratios  $b_1/b_2 = 1.24 \pm 0.04$ ,  $1.26 \pm 0.06$ , and  $1.28 \pm 0.05$  for samples S100, S125, and S154, respectively, are above unity and outside the error limits. According to Eq. (7), this implies the existence of a nonzero rigid gap that depends on  $T$  as

$$\gamma(T) \approx \gamma(T_v)(T/T_v)^{1/2}, \quad (8)$$

where  $\gamma(T_v) = 0.13$ ,  $0.16$ , and  $0.17$  eV for samples S100, S125, and S154, respectively.

The carrier localization length was found using the expression for the density of localized states outside the Coulomb gap:  $g_0 \approx N_0 \phi \sigma \eta / W$  [12], where  $N_0 = 1.74 \times 10^{22} \text{ cm}^{-3}$  is the Mn site concentration,  $W$  is the width of the localized-state band,  $\eta \approx c$ ,  $\phi \approx 0.5$  is the geometric factor, and  $\sigma \approx 1 - c$  [12]. The values of  $W$  were calculated from the expression  $kT_C \approx 0.05 Wc(1 - c)$  [11],

where the temperatures  $T_C$  were derived from magnetization measurements [5]. Next, the relationship  $g_0 = (3/\pi)(\kappa^3/e^6)[\Delta - \gamma(T_v)]^2$  [6] was used to obtain  $\kappa \approx 3.5$ . The values  $a = 1.7, 1.4,$  and  $1.2 \text{ \AA}$  were found from Eqs. (4) and (6). The values of  $a$  and  $T_0$  obtained by us here show directly that the condition  $\Gamma \gg 1$  is met for all the  $\text{LaMnO}_{3+\delta}$  samples studied.

The value  $\kappa \approx 3.5$  is close to the values found earlier for  $\text{La}_{1-x}\text{Ba}_x\text{MnO}_3$  [13],  $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-y}\text{Fe}_y\text{O}_3$  [6], and  $\text{LaMnO}_{3+\delta}$  [14]. The values of  $\kappa$  in these cases are substantially smaller than the static dielectric constant  $\kappa_0 = 16$  [15]. On the other hand,  $\kappa$  is much closer to  $\kappa_p$  than to  $\kappa_0$ , whereas we have  $\kappa = \kappa_0$  for doped semiconductors [16]. The point is that, in the perovskite manganites, the concentration of carriers (which is equal to that of holes) is much higher than that in doped semiconductors. Moreover, carriers in the perovskite manganites are polarons of small radius and, in nonmagnetic semiconductors, the contribution from polarons of small radius is very small [8]. As a result of the high concentration of polarons, their average separation is comparable to the lattice parameters. On the other hand, the major contribution to  $\Delta$  comes from interaction among the nearest carriers. The space around a polaron is characterized, however, not by the parameter  $\kappa_0$  but by the quantity  $\kappa_p = (\kappa_\infty^{-1} - \kappa_0^{-1})^{-1}$ , where  $\kappa_\infty$  is the high-frequency permittivity [9, 17]. The electrostatic interaction between polarons at a distance  $R$  does not obey the conventional Coulomb relationship and can be written in the form  $U \approx e^2/(\kappa_p R)$ , i.e., assuming  $\kappa \approx \kappa_p$ . The Coulomb gap widths  $\Delta$  in  $\text{LaMnO}_{3+\delta}$  obtained by us are close to those found for  $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$  [7] and  $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-y}\text{Fe}_y\text{O}_3$  [6].

The values of  $a$  are consistent with the assumption that small-radius polarons are formed in perovskite manganites [9]. Moreover,  $a$  decreases with increasing  $\delta$ , as should be expected in accordance with the increase in the degree of localization with increasing perovskite structure distortions. The values of  $\gamma(T_v)$  are similar to those obtained for  $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$  [7] and  $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-y}\text{Fe}_y\text{O}_3$  [6]. On the other hand, they are comparable to the activation energy of adiabatic hopping of small-radius polarons over nearest neighbors,  $E_0 \approx E_b/2$ , where  $E_b$  is the polaron binding energy [1]. Hence, the origin of the rigid gap in the perovskite manganites can be associated with the polaron nature of the carriers. In performing a hop, the electron has to annihilate polarization in the initial position and create it in the final position. It is the existence of a minimum energy required for a hop to be realized that gives rise to a rigid gap in the density of localized states near the Fermi level  $\mu$ , provided local lattice distortions account primarily for carrier localization. It is the case of reduced lattice disorder [5] and of lattice distortions increasing with increasing  $\delta$  that is realized in

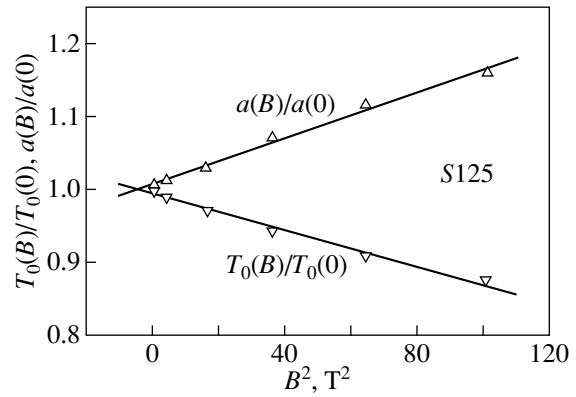


Fig. 3. Dependences of  $a(B)/a(0)$  and  $T_0(B)/T_0(0)$  on  $B^2$  for the  $\text{LaMnO}_{3+\delta}$  sample (S125).

$\text{LaMnO}_{3+\delta}$ , and this can account primarily for the increase in  $\gamma$  with increasing  $\delta$ .

### 3.3. Study of the Electrical Resistivity under Pressure

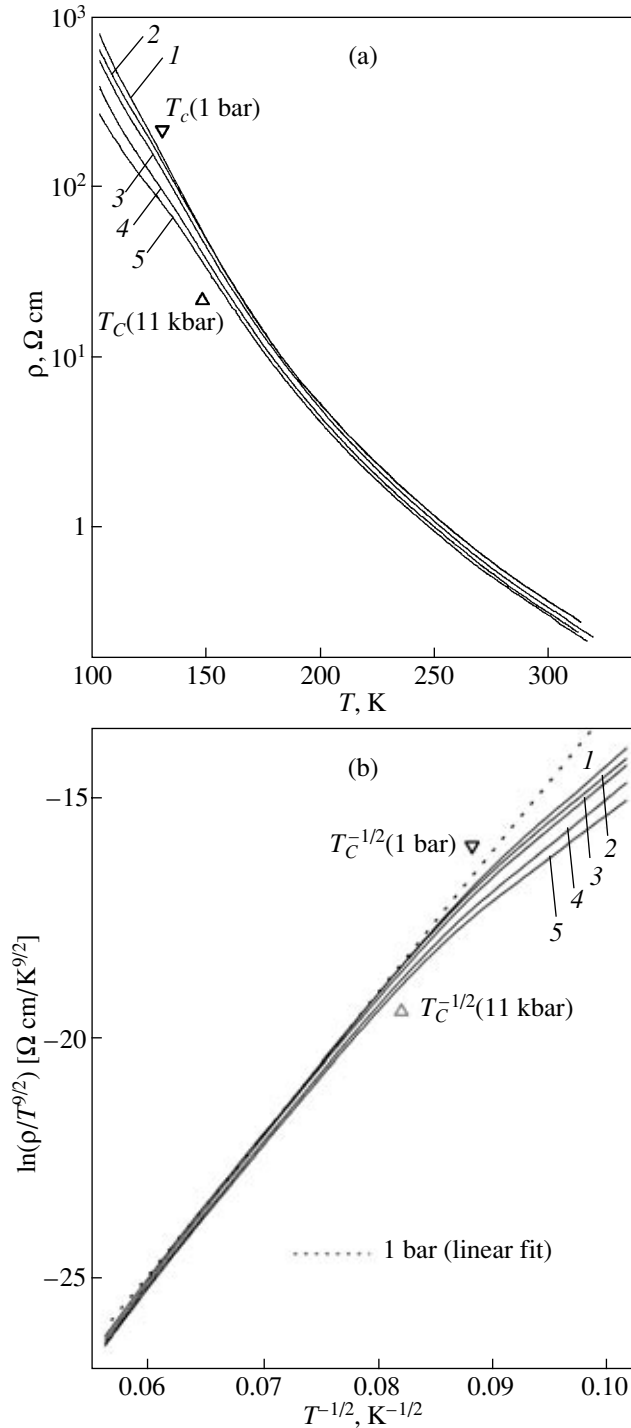
The measurements of the dependences  $\rho(T)$  were performed by the four-point probe technique under hydrostatic pressures of up to 11 kbar. The pressure was generated in a Be–Cu cell with a gasoline–oil mixture serving as a pressure-transmitting liquid.

As can be seen from Fig. 4a, the electrical resistivity of sample S154 exhibits activation behavior. The  $\rho(T)$  curve has slight bends near  $T_C$ , which are identified for  $P = 1$  bar and 11 kbar by open triangles. The value  $T_C(1 \text{ bar}) = 129 \text{ K}$  is close to  $T_C = 135 \pm 1 \text{ K}$ , which is derived from magnetization measurements in the absence of excess pressure [5]. The dependence  $T_C(P)$  shown in Fig. 5 is nearly linear with  $dT_C/dP = 1.6 \pm 0.2 \text{ K/kbar}$ ,  $d \ln T_C/dP = 0.012 \pm 0.002 \text{ kbar}^{-1}$ , and a maximum change of  $\sim 14\%$  (at 11 kbar). This dependence  $T_C(P)$  and the values of  $dT_C/dP$  are typical of perovskite manganites [18, 19]. As can be seen from Fig. 4a,  $\rho(T)$  decreases with increasing  $P$  for all temperatures.

As was already shown before, in  $\text{LaMnO}_{3+\delta}$  at atmospheric pressure and for  $T > T_C$ , the dependence  $\rho(T)$  follows the Shklovskii–Efros variable-range hopping conduction law (Eq. (1) for  $p = 1/2$ ,  $m = 9/2$ , and  $A \sim T_0^{7/2}$ ). Expression (5) for the characteristic temperature  $T_0$  can be recast for  $\gamma_v \equiv \gamma(T_v)$  in the form

$$T_0 = \left( \frac{\gamma_v}{2k\sqrt{T_v}} + \sqrt{\frac{\gamma_v^2}{4k^2 T_v} + T_{0SE}} \right)^2. \quad (9)$$

The quantities  $\Delta$  and  $\gamma_v$  are related to  $T_0$  and  $T_v$  and the density of localized states  $g_0$  outside the Coulomb

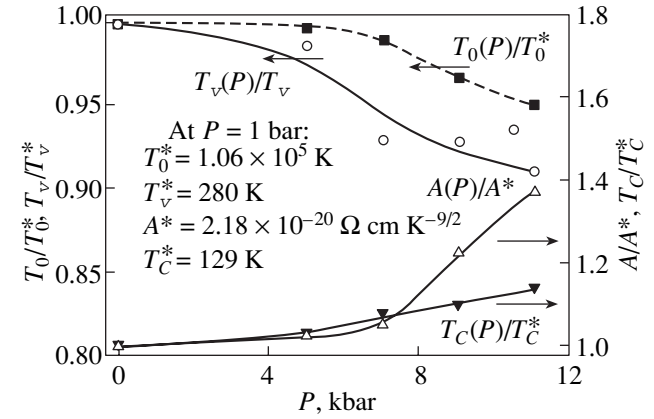


**Fig. 4.** Dependences of (a)  $\rho$  on  $T$  and (b)  $\ln(\rho/T^{9/2})$  on  $T^{-1/2}$  at different pressures  $P = (1) 0.001, (2) 5, (3) 7, (4) 9,$  and  $(5) 11$  kbar.

gap through Eq. (6) and the expression [6]

$$g_0 \approx (3/\pi)(\kappa^3/e^6)(\Delta - \gamma_v)^2. \quad (10)$$

As can be seen from Fig. 4b, the dependence of  $\ln[\rho(T)/T^{9/2}]$  on  $T^{-1/2}$  obtained under pressure contains



**Fig. 5.** Dependences of  $T_C/T_C^*$ ,  $T_0/T_0^*$ ,  $T_v/T_v^*$ , and  $A/A^*$  on the pressure. The solid and dashed lines are drawn to aid the eye.

a linear portion below  $T_v$ . Deviations from linearity are observed for  $T \rightarrow T_C$  (the values of  $T_C^{-1/2}$  are identified by open triangles for  $P = 1$  bar and 11 kbar). These dependences were used to derive the values of  $T_v(P)$ ,  $T_0(P)$ , and  $A(P)$  presented in Fig. 5. The values of  $\Delta(P)$  derived from Eq. (6) are given in Fig. 6a. The relative variation in the localization length  $a(P)/a^*$  (all symbols with an asterisk refer to  $P = 1$  kbar) was obtained using Eq. (3) and is shown in Fig. 6b.

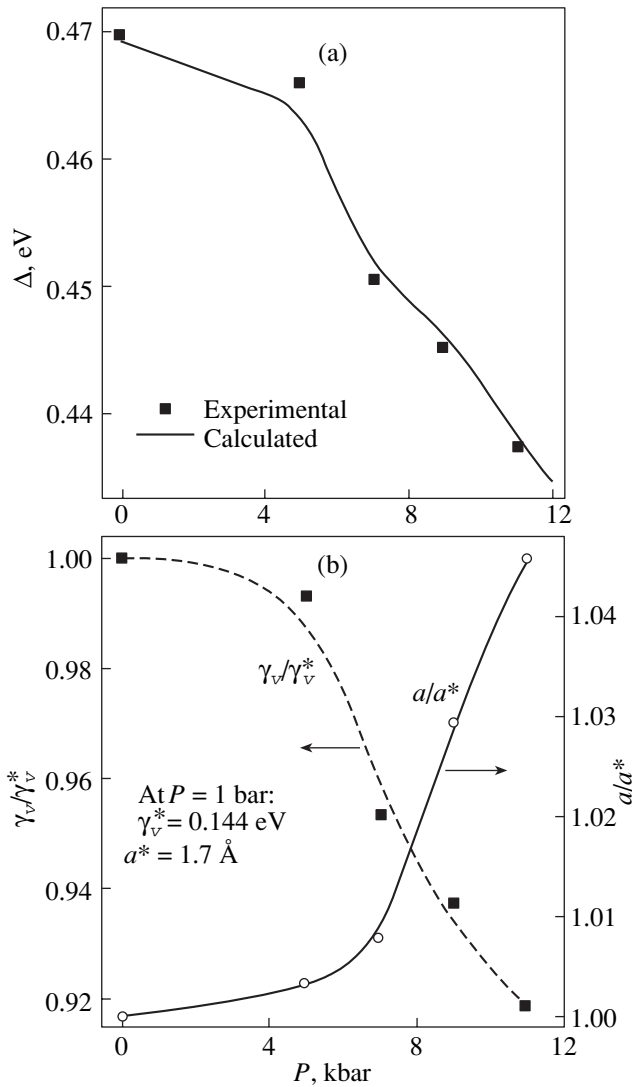
The macroscopic ( $T_0$ ,  $T_v$ , and  $A$ ) and microscopic ( $\Delta$ ,  $\gamma_v$ ,  $g_0$ , and  $a$ ) parameters are interrelated. This interrelation is given by Eqs. (3)–(10). Therefore, we present below a quantitative analysis of the dependence  $\Delta(P)$  only. Equation (8) can be used to obtain

$$\Delta(P) \approx \gamma_v(P) + (\pi/3)^{1/2} e^3 g_0^{1/2}(P)/(\kappa^{3/2}); \quad (11)$$

and from Eq. (7), we have

$$\gamma_v(P) = k[T_v(P)/T_0(P)]^{1/2} \times \{T_0(P) - \beta e^2/[\kappa k a^* a(P)/a^*]\}. \quad (12)$$

On the other hand,  $g_0(P) = \phi\sigma\eta N(P)/W(P)$  [12], where  $\phi \approx 0.5$ ,  $\sigma = 1 - c$ , and  $\eta = c$  are numerical parameters which are constant for  $c = 2\delta = 0.308$  (see above);  $N(P) = N^*(1 + 3P/G)$ ;  $N^* \approx 1.7 \times 10^{22} \text{ cm}^{-3}$  is the Mn concentration in  $\text{LaMnO}_{3+\delta}$  at  $P = 1$  bar;  $G = 5 \times 10^{11} \text{ N/m}^2$  is Young's modulus [20]; and  $W(P) \approx 20kT_C(P)/[c(1 - c)]$  is the localized-carrier band width [11]. Hence, the dependence  $\Delta(P)$  can be found from Eqs. (6)–(9) using the dependences  $T_0(P)$ ,  $T_v(P)$ , and  $T_C(P)$  in Fig. 5a and  $a(P)/a^*$  in Fig. 6 and two fitting parameters ( $a^*$  and  $\kappa$ ). The dependence  $\Delta(P)$  thus calculated is shown in Fig. 6a. The best fit of the  $\Delta(P)$  function to experimental data is reached for  $a^* \approx 1.7 \text{ \AA}$  and  $\kappa \approx 3.75$ ; these values are consistent with the values  $a^* \approx 1.2\text{--}1.7 \text{ \AA}$  and  $\kappa \approx 3.5$  obtained for  $\text{LaMnO}_{3+\delta}$  (see



**Fig. 6.** Dependences of (a) the Coulomb gap  $\Delta$  and (b) the ratios  $\gamma_v/\gamma_v^*$  and  $ala^*$  on the pressure. The solid and dashed lines in panel (b) are drawn to aid the eye.

Section 3.2) in a different way, i.e., from magnetization measurements performed with no pressure applied. The method described above was also employed to calculate  $\gamma_v^* \approx 0.144$  eV (cf.  $\gamma_v \approx 0.13$ – $0.17$  eV, the values derived above from Eq. (8)) and the  $\gamma_v(P)$  function plotted in Fig. 6b.

Because  $T_C(P) \sim W(P)$ , the observed effect of pressure on  $T_C$  should be assigned to the increasing width of the localized-carrier band. On the other hand, it is known that the pressure-induced variation in  $W$  in perovskite manganites is actually driven by two factors, namely, (1) spatial effects or an increase in the Mn–O–Mn bond angles and a decrease in the corresponding bond lengths, which increases the electron transfer integral and enhances double exchange interaction; and (2) the polaron nature of carriers associated with the effect

of pressure on the electron–phonon coupling and the corresponding Jahn–Teller distortions [18, 19]. In addition, in accordance with the assumed origin of the rigid gap (see Section 3.2), we can write  $\gamma_v = E_p/2 - E_d/2$ , where  $E_p$  is the depth of the polaron potential well associated with the polarization of the medium and  $E_d$  is the width of the electron potential energy distribution governed by disorder. Because the degree of disorder in  $\text{LaMnO}_{3+\delta}$  is small [5], the observed decrease in  $\gamma_v$  with pressure should be connected primarily with suppression of the polaron effect by a pressure that decreases  $E_p$ . The decrease in  $E_p$  implies a decrease in the degree of localization, which brings about an increase in  $a(P)$ , as is seen in Fig. 6b. On the other hand, the effect of pressure on  $\gamma_v$  is weaker (up to  $\sim 8\%$ ) than that on  $T_C$  (up to  $\sim 14\%$ ), which can be explained by the absence of an effect of factor 1 on  $\gamma_v(P)$  or by this effect being smaller than that on  $T_C(P)$ .

#### 4. CONCLUSIONS

Thus, we studied the temperature dependences of the electrical conductivity and magnetoresistance of ceramic  $\text{LaMnO}_{3+\delta}$  samples ( $\delta = 0.100, 0.125,$  and  $0.154$ ). An analysis of these dependences suggests that the behavior of the resistivity of  $\text{LaMnO}_{3+\delta}$  in the paramagnetic phase in the temperature range between  $T_C$  and  $T_v$ , which is  $\sim 250$ – $270$  K, is governed by the complex structure of the density of localized states near the Fermi level. We established the presence of a soft Coulomb gap  $\Delta$  and a rigid gap  $\gamma$ , whose widths increase with increasing  $\delta$ . The increase in the gap width  $\delta$  is accounted for by the increasing hole concentration  $c = 2\delta$  and the corresponding enhancement of the carrier Coulomb interaction. The existence of the rigid gap  $\gamma$  should possibly be attributed to the formation of small-radius polarons, and its increase with increasing  $\delta$ , to the enhancement of lattice distortions under conditions of reduced disorder. The observed dependence of the localization length  $a$  on  $\delta$  is accounted for by the increasing hole localization as a result of increasing lattice distortions.

The pressure dependences of the macroscopic parameters  $\Delta(P)$ ,  $\gamma_v(P)$ , and  $a(P)$  obtained in the studies of the effect of hydrostatic pressure on the variable-range hopping conduction in  $\text{LaMnO}_{3+\delta}$  can be explained by the increase in the electron band width and the decrease in the polaron effect with increasing pressure.

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