MAGNETISM
AND FERROELECTRICITY

Preparation and Magnetic Properties of LaMnO$_{3+\delta}$ (0 ≤ δ ≤ 0.154)

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Abstract—The structural, electrical, and magnetic properties of ceramic perovskite manganites LaMnO$_{3+\delta}$ (δ = 0–0.154) are investigated. It is found that, in a weak magnetic field ($B = 2$ G), the LaMnO$_{3+\delta}$ manganite with δ = 0.065 at temperatures below the Curie temperature T_C of the paramagnet–ferromagnet phase transition has a mixed (spin glass + ferromagnet) phase. In LaMnO$_{3+\delta}$ manganites with the parameter δ = 0.100–0.154, this phase transforms into a frustrated ferromagnetic phase. A similar transformation was observed previously in La$_{1-x}$Ca$_x$MnO$_3$ compounds at calcium contents in the range 0 ≤ x ≤ 0.3. This similarity is explained by the fact that, in both materials, the Mn^{4+} concentration and, accordingly, the hole concentration c change equally in the concentration range from ≈0.13 to 0.34 with an increase in x or δ. However, the magnetic irreversibility, the concentration dependences of the Curie temperature $T_C(c)$ and the magnetic susceptibility $\chi(c)$, and the critical behavior of the temperature dependence of the susceptibility $\chi(T)$ in the vicinity of the Curie temperature T_C differ substantially for these two materials. The observed differences are associated with the distortion of the cubic perovskite structure, the decrease in the degree of lattice disorder, and a more uniform distribution of holes in the LaMnO$_{3+\delta}$ manganites as compared to the La$_{1-x}$Ca$_x$MnO$_3$ compounds.

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1. INTRODUCTION

Mixed-valence perovskite manganites doped with holes have a complex magnetic phase diagram. The phase diagram involves the following phases: high-temperature paramagnetic, ferromagnetic, and antiferromagnetic phases; a phase with noncollinear spin ordering [1, 2]; and spin-glass phases [3, 4]. A number of interesting physical properties of manganites, such as the colossal magnetoresistance [2], phase separation [5], and charge ordering [6], are closely related to their magnetic properties and manifest themselves in different ranges of hole concentrations c. It is known that the electronic properties of perovskite manganites are governed by the competition between the Mn^{3+}–Mn^{3+} superexchange and the Mn^{3+}–Mn^{4+} double exchange [7], which are accompanied by local Jahn–Teller distortions and the formation of states with mobile small polarons [8].

Doping of the LaMnO$_3$ compound with holes gives rise to mixed-valence (charge) states of manganese ions (Mn^{3+} and Mn^{4+}) and can be accomplished in two ways. The first way is to substitute Ca$^+$ ions or other *AE* divalent ions (*AE* = Sr, Ba) for La^{3+} ions with the formation of La$_{1-x}$Ca$_x$MnO$_3$-type alloys [9]. The second way involves the formation of LaMnO$_{3+\delta}$ compounds in which the nonstoichiometry with a considerably higher probability is determined by cation vacancies rather than by excess oxygen ions at interstices. In this case, the concentration of cation vacancies can be defined as δ' = (2/3)δ for a relative hole concentration $c = 2\delta$. The formation of cation vacancies is confirmed by the fact that interstices in the perovskite structure cannot be occupied by excess oxygen ions [10]. It should be noted that, in the case of oxygen nonstoichiometry, La$_{1-x}$Ca$_x$MnO$_{3+\delta}$ ceramics at a calcium content $x = 0$–0.4 also contain cation vacancies [4, 11]. The difference between these two materials lies in the following: the hole concentration c in the La$_{1-x}$Ca$_x$MnO$_3$ compounds is controlled by varying the cation composition at a constant coefficient δ (δ = 0), whereas the hole concentration c in the LaMnO$_{3+\delta}$ compounds is governed by varying the coefficient δ at a constant cation composition.

Preparation conditions, coefficients δ, space groups, and lattice parameters a and c for the LaMnO$_{3+\delta}$ ($0 \leq \delta \leq 0.154$) samples under investigation

Sample	Preparation conditions	δ	Space group	Lattice parameters	
				a, Å	c, Å
S000	40 h, Ar, 1114°C	0.000	Orthorhombic Pbnm*	5.531(1)	7.689(2)
S065	38 h, Ar, 1100°C	0.065	Cubic Pm3m**	7.813(2)	
	48 h, air, 1100°C				
S100	32 h, Ar, 1114°C	0.100	Cubic Pm3m**	7.795(1)	
	45 h, O$_2$, 800°C				
	40 h, air, 900°C				
S112	40 h, Ar, 1114°C	0.112	Cubic Pm3m**	7.791(1)	
	45 h, O$_2$, 800°C				
	42 h, air, 850°C				
S125	25 h, Ar, 1100°C	0.125	Rhombohedral R–3c	5.530(2)	13.333(5)
	54 h, air, 800°C				
S133	30 h, Ar, 1125°C	0.133	Rhombohedral R–3c	5.523(2)	13.329(6)
	30 h, O$_2$, 800°C				
	30 h, O$_2$, 850°C				
S140	35 h, Ar, 1100°C	0.140	Rhombohedral R–3c	5.521(1)	13.322(4)
	36 h, O$_2$, 800°C				
S154	40 h, Ar, 1114°C	0.154	Rhombohedral R–3c	5.516(1)	13.311(4)
	45 h, O$_2$, 800°C				
	100 h, O$_2$, 700°C				

* $b = 5.536(1)$ Å.

** Weak rhombohedral distortions of the cubic structure are observed.

At present, the properties of La$_{1-x}$Ca$_x$MnO$_3$ compounds are better understood than the properties of LaMnO$_{3+\delta}$ manganites. In this work, we investigated the low-field magnetization and the electrical resistivity of LaMnO$_{3+\delta}$ manganites and compared the properties of these two materials in order to elucidate the differences associated with the procedures used for their syntheses.

2. SAMPLE PREPARATION AND CHARACTERIZATION

Ceramic samples of LaMnO$_{3+\delta}$ manganites were synthesized in three stages. The first stage involved a conventional solid-phase reaction similar to that used for preparing La$_{1-x}$Ca$_x$MnO$_3$ compounds [4, 11]. Since the La$_2$O$_3$ powder used in our case is hygroscopic, it was subjected to preliminary annealing. Mixtures of La$_2$O$_3$ and MnO$_2$ oxide powders were annealed in air at a temperature of 1320°C for 40 h with intermediate milling. The powders thus prepared were pressed in the form of pellets under a pressure of 2000 kg/cm^2. Then, the pellets were annealed in air at a temperature of 1370°C for 22 h. According to the x-ray powder diffraction data, the samples have a cubic structure with the

lattice parameter $a = 7.813(2)$ Å and exhibit an insignificant rhombohedral distortion. The oxygen content in the samples was examined using gravimetry and iodometric titration. It was found that these samples are LaMnO$_{3+\delta}$ nonstoichiometric manganites with $\delta \approx 0.065$.

At the second stage, the synthesized material was annealed for a long time in a pure argon flow [10] in order to prepare the stoichiometric compound LaMnO$_{3.00}$. At the last (third) stage of the synthesis, the LaMnO$_{3+\delta}$ samples with $\delta = 0.065$, 0.100, 0.112, 0.125, 0.133, 0.140, and 0.154 (in what follows, these samples will be designated as S065, S100, S112, S125, S133, S140, and S154, respectively) were prepared through combined annealing in argon, oxygen, and air with variations in the temperature and time of annealing (see table). The contents of oxygen and manganese ion species Mn^{2+}, Mn^{3+}, and Mn^{4+} in the LaMnO$_{3+\delta}$ samples prepared under conditions with excess oxygen and an oxygen deficiency were determined by gravimetry and iodometric titration [12]. Since the characterization of the composition of the synthesized samples is of considerable importance, the latter method used for determining the oxygen content in the manganites should be considered in more detail.
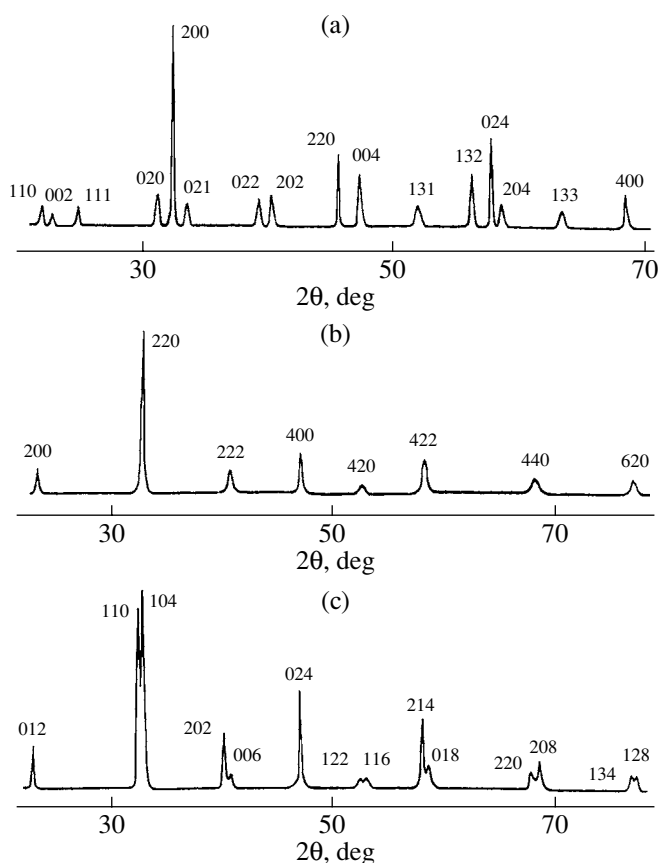
Fig. 1. X-ray powder diffraction patterns of the (a) $S000$, (b) $S100$, and (c) $S140$ samples of the LaMnO$_{3+\delta}$ manganites.

According to the chemistry of defects in lanthanum manganites [13], the following assumptions are valid for the LaMnO$_{3+\delta}$ perovskite: (i) lanthanum and manganese are in a stoichiometric ratio of 1 : 1; (ii) lanthanum is in the La^{3+} oxidation state; and (iii) manganese can be in the Mn^{2+}, Mn^{3+}, and Mn^{4+} oxidation states. Consequently, the chemical formula of the LaMnO$_{3+\delta}$ compound can be written as

$$\text{La}^{3+}\text{Mn}^{3+}_{1-\alpha-\beta}\text{Mn}^{4+}_{\alpha}\text{Mn}^{2+}_{\beta}\text{O}_{3+\delta}. \tag{1}$$

In order to ensure lattice neutrality, the stoichiometric coefficients α, β, and δ must satisfy the relationship
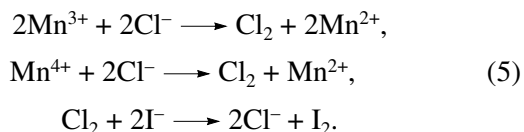
$$\delta = (\alpha - \beta)/2. \tag{2}$$

The concentrations of the manganese ion species Mn^{2+}, Mn^{3+}, and Mn^{4+} in chemical formula (1) are determined by the disproportionation reaction

$$2\text{Mn}^{3+} \rightleftharpoons \text{Mn}^{2+} + \text{Mn}^{4+}. \tag{3}$$

The equilibrium constant of disproportionation reaction (3) for the LaMnO$_{3+\delta}$ compound at a temperature of 1273 K can be represented in the form [13]

$$K_i = \alpha\beta/(1-\alpha-\beta)^2 \cong 10^{-4}. \tag{4}$$

In the experiment, the oxygen content in the LaMnO$_{3+\delta}$ samples was determined by iodometric titration. For this purpose, a weighed portion (approximately 50 mg) of the LaMnO$_{3+\delta}$ compound in the form of a powder was dissolved in a mixture of a 1 M KI solution (7.2 ml) with a 1 M HCl solution (5.5 ml). In the stirred acid solution, the dissolution of the sample is accompanied by the sequential reduction of Mn^{3+} and Mn^{4+} ions to the divalent state and by the formation of free iodine:

$$2\text{Mn}^{3+} + 2\text{Cl}^- \longrightarrow \text{Cl}_2 + 2\text{Mn}^{2+},$$
$$\text{Mn}^{4+} + 2\text{Cl}^- \longrightarrow \text{Cl}_2 + \text{Mn}^{2+}, \tag{5}$$
$$\text{Cl}_2 + 2\text{I}^- \longrightarrow 2\text{Cl}^- + \text{I}_2.$$

Throughout the course of titrimetric determination, argon free of oxygen was passed over the solution. The liberated iodine was titrated with a 0.1 N sodium thiosulfate solution. The amount of iodine [I$_2$] (in mol) formed in reactions (5) can be written as

$$\begin{aligned}[\text{I}_2] &= 0.5[\text{Mn}^{3+}] + [\text{Mn}^{4+}] \\ &= 0.5(1 - \alpha - \beta)m/M + \alpha m/M,\end{aligned} \tag{6}$$

where [Mn^{3+}] and [Mn^{4+}] are the molar concentrations of manganese ion species in the sample, M (g/mol) is the molar weight of the sample material, and m (g) is the weight of the sample. The molar weight of the LaMnO$_{3+\delta}$ compounds depends on the oxygen content and can be represented in the form

$$M = M_0 + m_1\delta, \tag{7}$$

where $M_0 = 241.8417$ g/mol is the molar weight of the LaMnO$_3$ compound and $m_1 = 15.9994$ g/mol is the atomic weight of oxygen. The amount of titrated iodine was determined from the relationship

$$[\text{I}_2] = CV/2, \tag{8}$$

where C (mol/ml) is the concentration of the sodium thiosulfate solution and V (ml) is the sodium thiosulfate solution volume expended for titration. Substituting expressions (7) and (8) into relationship (6) gives the following formula for calculating the oxygen content in the sample:

$$\delta = (m - CVM_0)/(CVm_1 - 2m). \tag{9}$$

The Mn^{2+}, Mn^{3+}, and Mn^{4+} concentrations in the LaMnO$_{3+\delta}$ samples were calculated from relationships (2) and (4). The total error in the determination of the oxygen content δ by the iodometric method did not exceed ±0.02.

Figure 1 shows the x-ray powder diffraction patterns of the $S000$ (Fig. 1a), $S100$ (Fig. 1b), and $S140$ (Fig. 1c) samples. The samples of the stoichiometric composition LaMnO$_{3.00}$ have an orthorhombic structure (space group *Pbnm*) (Fig. 1a). The LaMnO$_{3+\delta}$ samples with the parameter δ in the range $0.065 \le \delta \le 0.112$ have a
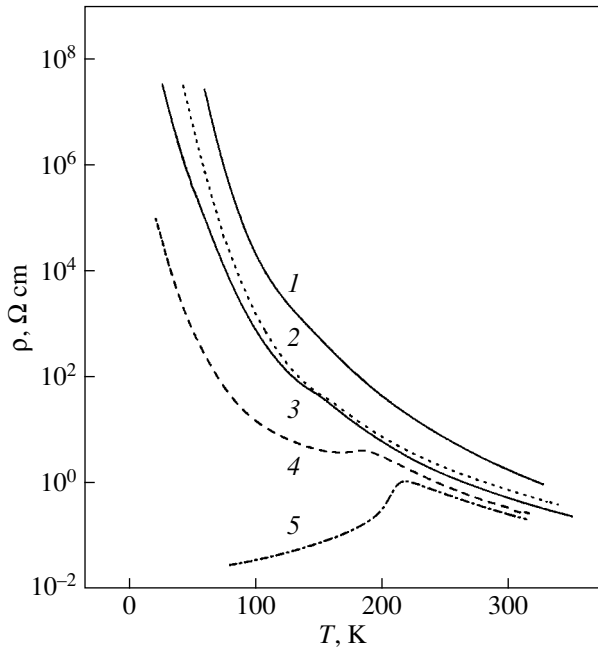
Fig. 2. Temperature dependences of the electrical resistivity for the (*1*) *S*065 ($\delta = 0.065$, $c = 0.13$), (2) *S*100 ($\delta = 0.10$, $c = 0.20$), and (3) *S*125 ($\delta = 0.125$, $c = 0.25$) samples of the LaMnO$_{3+\delta}$ manganites and La$_{1-x}$Ca$_x$MnO$_3$ compounds at calcium contents $x = $ (*4*) 0.15 ($c = 0.22$) and (5) 0.20 ($c = 0.26$) [25] in a zero magnetic field ($B = 0$ T).
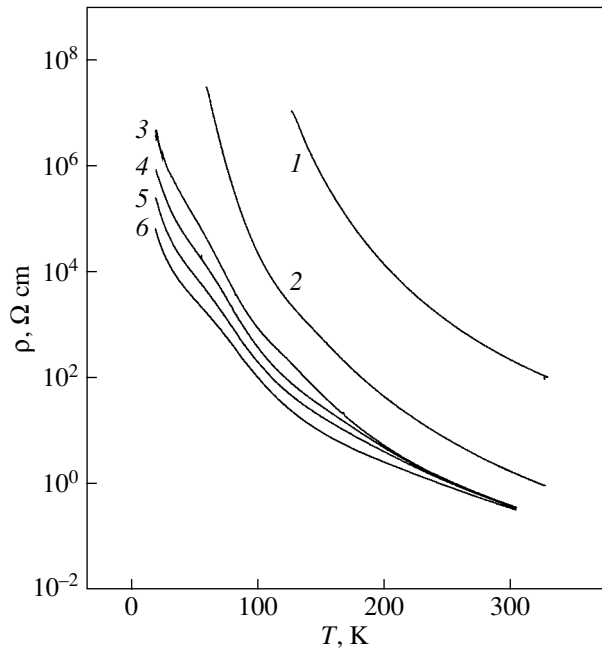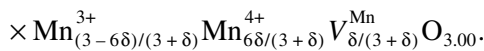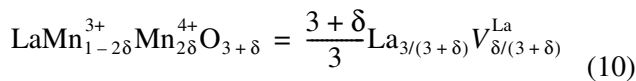

Fig. 3. Temperature dependences of the electrical resistivity for the (*1*) *S*000, (2) *S*065, and (*3–6*) *S*154 samples of the LaMnO$_{3+\delta}$ manganites in magnetic fields $B = $ (*1*) 0–10, (*2*, *3*) 0, (*4*) 2, (*5*) 4, and (*6*) 8 T.

cubic unit cell (space group *Pm3m*). The analysis of the profiles of the 220, 440, and 222 reflections revealed that the cubic unit cell has weak rhombohedral distortions (Fig. 1b) [14]. The other samples with $\delta = 0.125$–0.154 have a rhombohedral structure (space group *R–3c*), and their diffraction patterns are similar to the x-ray powder diffraction pattern shown in Fig. 1c. The space groups, the lattice parameters *a* and *c*, and the coefficients δ are presented in the table.

Let us consider a LaMnO$_{3+\delta}$ manganite containing cation vacancies V^{La} and V^{Mn}. The chemical formula of this compound can be written in the following form equivalent to the formula La$_{1-\varepsilon}$Mn$_{1-\varepsilon}$O$_3$ with $\varepsilon = \delta/(3 + \delta)$ [10]:

$$\text{LaMn}^{3+}_{1-2\delta}\text{Mn}^{4+}_{2\delta}\text{O}_{3+\delta} = \frac{3+\delta}{3}\text{La}_{3/(3+\delta)}V^{La}_{\delta/(3+\delta)}$$
$$\times \text{Mn}^{3+}_{(3-6\delta)/(3+\delta)}\text{Mn}^{4+}_{6\delta/(3+\delta)}V^{Mn}_{\delta/(3+\delta)}\text{O}_{3.00}. \quad (10)$$

It is known [10, 15] that, in $ABO_{3+\delta}$ perovskite oxides, oxygen ions occupy only anion positions. We found that the coefficient δ in the formula LaMnO$_{3+\delta}$ varies in the course of treatment at a high temperature in pure argon, air, and oxygen atmospheres (see table). Previously, it was revealed [10, 12–14] that, upon this treatment, oxygen reacts with lanthanum and manganese in the bulk of the sample. This results in the formation of new unit cells and additional La and Mn defects as can be judged from the increase in the size of the

sample. The number of unit cells in the $ABO_{3+\delta}$ perovskite with $\delta = 0.06$ increases by 2% as compared to the stoichiometric compound with $\delta = 0.00$. The positive deviations of the coefficient δ for perovskite oxides cannot be explained by the presence of excess oxygen in the structure [16]. In the present work, we prepared the LaMnO$_{3.00}$ stoichiometric compound by annealing of the samples in a pure argon flow at a temperature of 1100°C according to the procedure described in [10]. As follows from Eq. (10), the coefficient δ is related to the number of lanthanum and manganese defects and the oxygen content is always stoichiometric. The hole concentration c ($c = 2\delta$) in the LaMnO$_{3+\delta}$ samples in the range $0.065 \leq \delta \leq 0.154$ varies from 0.130 to 0.308. The same variations in the hole concentration c were previously observed in two series of La$_{1-x}$Ca$_x$MnO$_3$ ceramic samples at calcium contents $x = 0$–0.3 ($c \approx$ 0.15–0.33 [4] and $c \approx$ 0.18–0.34 [11]).

3. RESULTS AND DISCUSSION

3.1. Investigation of the Electrical Resistivity

The electrical resistivity of the samples was measured by the four-point probe method in the transverse magnetic field ($\mathbf{B} \perp \mathbf{j}$) at $B = 0$–10 T. As can be seen from Figs. 2 and 3, the electrical resistivity of the LaMnO$_{3+\delta}$ compounds at $B = 0$ T decreases monotonically with an increase in the coefficient δ. In the temperature range 4.2–350 K under investigation, the electrical resistivity of all the compounds ($\delta = 0$–0.154)
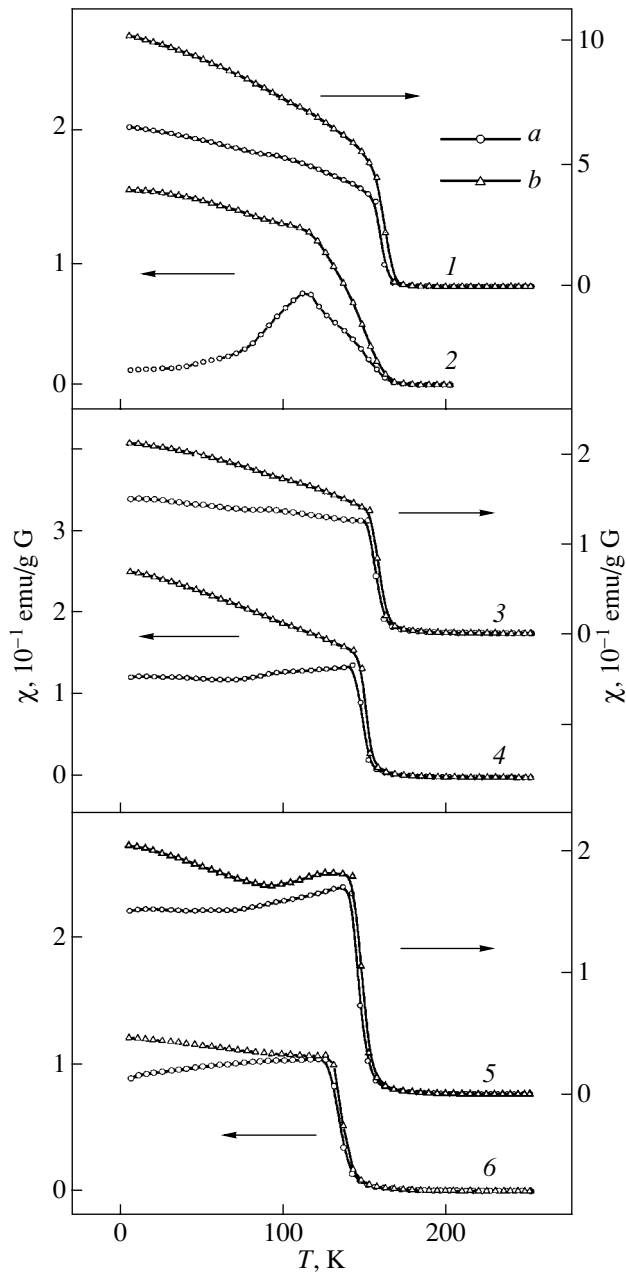
Fig. 4. Temperature dependences of the magnetic suscepti-bilities (*a*) $\chi_{ZFC}(T)$ and (*b*) $\chi_{FC}(T)$ in the magnetic field $B = 2$ G for the (*1*) *S*100, (*2*) *S*065, (*3*) *S*125, (*4*) *S*133, (*5*) *S*140, and (*6*) *S*154 samples of the LaMnO$_{3+\delta}$ manga-nites.

Fig. 5. (a) Dependence of the Curie temperature T_C on the coefficient δ and the hole concentration c for the LaMnO$_{3+\delta}$ manganites. The Curie temperatures T_C were determined from the points of inflection in the dependences (*1*) $\chi_{ZFC}(T)$ and (*2*) $\chi_{FC}(T)$ and the critical behavior of the dependences (*3*) $\chi_{ZFC}(T)$ and (*4*) $\chi_{FC}(T)$. The inset shows the dependence of the Curie temperature T_C on the hole concentration c for the La$_{1-x}$Ca$_x$MnO$_3$ compounds [4]. (b) Dependences of the susceptibilities (*1*) χ_{FC} and (*2*) χ_{ZFC} on the coefficient δ and the hole concentration c for the LaMnO$_{3+\delta}$ manganites and the dependences of the suscep-tibilities (*3*) χ_{FC} and (*4*) χ_{ZFC} on the hole concentration c for the La$_{1-x}$Ca$_x$MnO$_3$ compounds at $T = 5$ K [4].

exhibits an activation nature. The dependences $\rho(T)$ for all samples, except for the *S*000 sample, have weakly pronounced inflections in the vicinity of the tempera-tures T_C of the paramagnet–ferromagnet phase transi-tions (the temperatures T_C are presented in Fig. 5a). As the magnetic field strength increases, the maximum of the magnetoresistance in the vicinity of the temperature T_C shifts toward the low-temperature range. The electri-cal resistivity of the *S*000 sample is insensitive to the
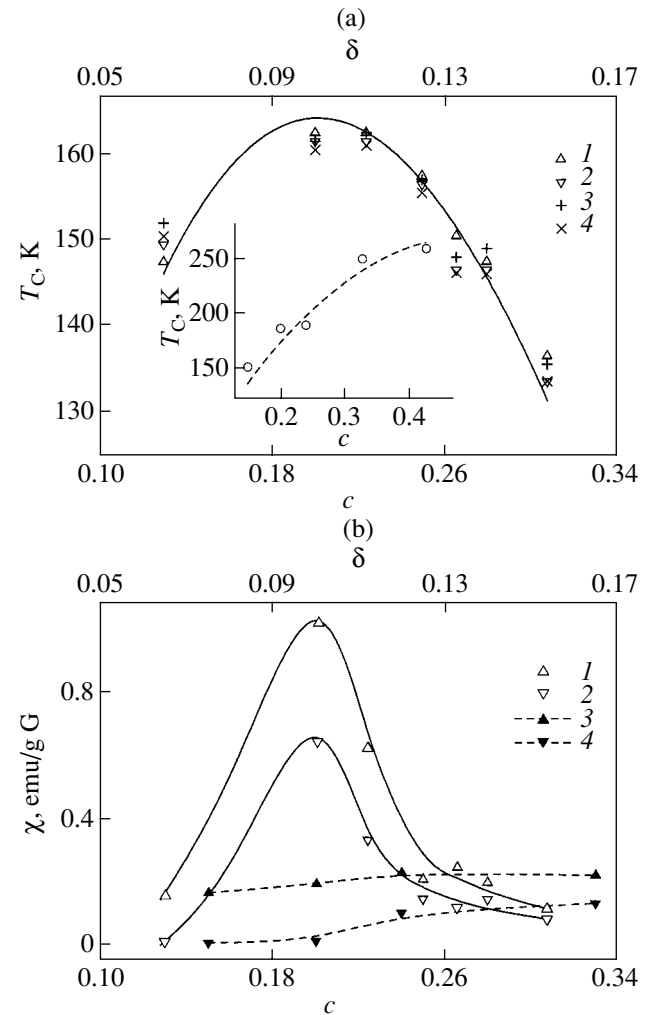
magnetic field B in the range from 0 to 10 T. The possi-ble concentration of Mn^{4+} ions in the *S*000 sample (with an accuracy of determination $\delta = \pm0.002$) amounts to ≤1%. The negligible magnetoresistance of the LaMnO$_{3.00}$ compound is in agreement with the notion that the Mn^{3+}–Mn^{4+} double exchange mechanism plays an important role in the colossal magnetoresis-tance effect. The curves $\rho(T)$ for the *S*154 sample (Fig. 3), in which the concentration of Mn^{4+} ions is

equal to 31%, depend substantially on the magnetic field B (in the magnetic field range B = 0–8 T).

3.2. Magnetic Irreversibility and Dependences of the Susceptibility χ and the Curie Temperature T_C on δ

The temperature dependences of the magnetization $M(T)$ were measured on a SQUID magnetometer. The sample was cooled from room temperature to 5 K in either a zero magnetic field (ZFC) or a static magnetic field B = 2 G (FC). Before measurements, the superconducting solenoid was heated to the transition to the normal state in order to eliminate residual fields. External magnetic fields were reduced to a strength of less than 0.05 G with the use of a μ-metal screen. It can be seen from Fig. 4 that the magnetic susceptibility $\chi(T)$ = $M(T)/B$ for the LaMnO$_{3+\delta}$ manganites increases drastically with a decrease in the temperature. This indicates that the paramagnet–ferromagnet phase transition occurs at the Curie temperature T_C.

Below the Curie temperature T_C, the magnetic irreversibility manifests itself in a deviation of the dependence $\chi_{ZFC}(T)$ from the dependence $\chi_{FC}(T)$. The susceptibility curves for the $S065$ sample differ from those for the other samples. The phase transition range in the vicinity of the Curie temperature T_C in the dependence $\chi_{FC}(T)$ is widened, and the dependence $\chi_{ZFC}(T)$ exhibits a clear maximum at a temperature below the Curie point T_C. In general, the dependences $\chi_{ZFC}(T)$ and $\chi_{FC}(T)$ for the LaMnO$_{3+\delta}$ manganites with δ = 0.100–0.154 (c = 0.200–0.308) are similar to those for the La$_{1-x}$Ca$_x$MnO$_3$ ceramic samples at calcium contents x = 0–0.3 and hole concentrations $c \approx$ 0.20–0.33 [4]. However, the dependences of the magnetic susceptibilities $\chi_{ZFC}(T)$ and $\chi_{FC}(T)$ for the LaMnO$_{3+\delta}$ manganites differ from each other to a considerably lesser extent. This is typical of a frustrated ferromagnet. The specific features of the dependences $\chi_{ZFC}(T)$ and $\chi_{FC}(T)$ for the $S065$ sample (c = 0.130) are similar to those for the La$_{1-x}$Ca$_x$MnO$_3$ compounds at x = 0 ($c \approx$ 0.19) and 0.05 ($c \approx$ 0.15) [4]. In particular, the dependences exhibit features characteristic of both the ferromagnetic transition (an abrupt increase in the susceptibility $\chi_{FC}(T)$ with a decrease in the temperature) and the spin-glass phase (a strong irreversibility and a peak in the dependence $\chi_{ZFC}(T)$). These findings suggest that there exists a mixed ferromagnet + spin-glass phase or a phase intermediate between the frustrated ferromagnetic phase and the pure spin-glass phase. According to the Almeida model [17], the frustrations in magnetic perovskites originate from the competition between the superexchange and double exchange mechanisms attended by the appearance of disorder in the lattice. The Almeida model predicted the existence of all the main components of the magnetic phase diagram, including the frustrated ferromagnetic phase, the pure spin-glass phase, and mixed ferromagnet + spin-glass states [17]. Investigations of the ac susceptibility [18]

and long-term magnetic relaxation in La$_{1-x}$Ca$_x$MnO$_3$ samples with close values of the hole concentration c [4, 18] have confirmed the validity of the Almeida model (in particular, the existence of the mixed ferromagnet + spin-glass state). Moreover, the existence of two spatially separated phases with different dynamics of manganese ion spins was revealed in the muon spin relaxation and neutron spin echo experiments performed with La$_{1-x}$Ca$_x$MnO$_3$ compounds in the temperature range $0.7T_C \leq T \leq T_C$ [17]. The role of the lattice disorder was determined by Mira et al. [19] in the study of the magnetic relaxation and irreversibility in La$_{1-x}$Ca$_x$Mn$_{1-y}$Fe$_y$O$_3$ compounds. These authors established that the frustration is enhanced with an increase in the degree of disorder upon doping with iron. Consequently, the similarity of the magnetic properties of the LaMnO$_{3+\delta}$ and La$_{1-x}$Ca$_x$MnO$_3$ manganites is governed by the similarity of the change in the hole concentration c in both materials. The observed decrease in the magnetic irreversibility of the LaMnO$_{3+\delta}$ compounds can be explained by the lower degree of disorder, which is responsible for the more uniform distribution of holes at a fixed chemical composition.

As can be seen from Fig. 4, the dependence of the magnetic susceptibility χ on the hole concentration c or the coefficient δ is nonmonotonic at temperatures below the Curie point T_C. This is even more clearly seen from Fig. 5b, in which both dependences $\chi_{ZFC}(T)$ and $\chi_{FC}(T)$ for the LaMnO$_{3+\delta}$ manganites (open triangles) exhibit a maximum at δ = 0.1 or c = 0.2. However, the corresponding maxima are absent in the susceptibility curves for the La$_{1-x}$Ca$_x$MnO$_3$ compounds (closed triangles): the susceptibility increases monotonically with an increase in the hole concentration c [4]. It should be noted that the magnetic susceptibility of both materials was measured in the same magnetic field B = 2 G. Another interesting feature (Fig. 5a) is the maximum in the concentration dependence of the Curie temperature T_C (open triangles) for the LaMnO$_{3+\delta}$ manganites in the vicinity of the same values δ = 0.1 and c = 0.2 (the Curie temperatures T_C were determined from the points of inflection in the dependences $\chi_{ZFC}(T)$ and $\chi_{FC}(T)$). The dependence $T_C(c)$ for the La$_{1-x}$Ca$_x$MnO$_3$ compounds [4] (which is shown by open circles in the inset to Fig. 5a) does not exhibit a maximum. The electrical resistivity of the LaMnO$_{3+\delta}$ manganites (Fig. 2) decreases monotonically with an increase in the coefficient δ without anomalies in the vicinity of the coefficient δ = 0.1, at which the susceptibility has a maximum.

The dependence of the Curie temperature T_C on the hole concentration c or the coefficient δ will be discussed in the framework of the Varma model [20], which accounts for the paramagnet–ferromagnet phase transition in lanthanum-containing manganites by assuming that charge carriers are localized below the mobility threshold within a band of width W and that
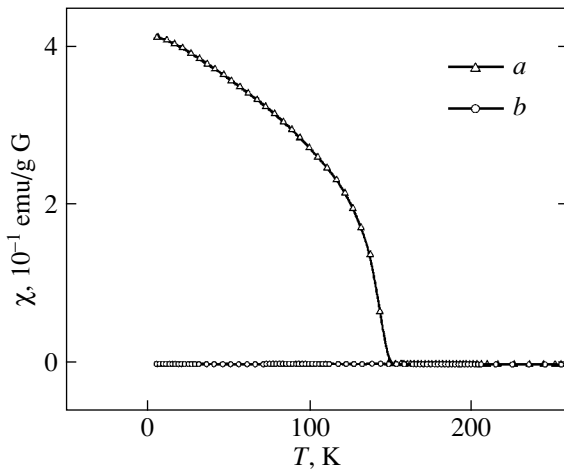
Fig. 6. Temperature dependences of the susceptibilities (*a*) χ_{FC} and (*b*) χ_{ZFC} in the magnetic field $B = 2$ G for the $S000$ sample of the LaMnO$_{3 + \delta}$ manganite.

the density of states is characterized by a rectangular distribution. The localization of charge carriers is caused by the magnetic disorder and spin fluctuations. Within the Varma model, the Curie temperature T_C can be determined from the relationship

$$kT_C \approx 0.05 Wc(1 - c). \quad (11)$$

The dashed line in the inset to Fig. 5a is obtained with the use of relationship (11) for the La$_{1-x}$Ca$_x$MnO$_3$ compound studied in [4]. The experimental data on the concentration dependence of the Curie temperature $T_C(x)$ for two series of La$_{1-x}$Ca$_x$MnO$_3$ ceramic samples with $W = 1.88$ eV, $\delta' = 0.062$ [4] and $W = 1.90$ eV, $\delta' = 0.070$ [11] are in good agreement. Moreover, these data on the concentration dependence of the Curie temperature are in complete agreement with the experimental data on the dependence $T_C(x)$ for La$_{1-x}$Sr$_x$MnO$_3$ compounds [19] with the bandwidth $W \approx 2.5$ eV, which is very close to the corresponding bandwidths obtained for the La$_{1-x}$Ca$_x$MnO$_3$ ceramic samples in [4, 11]. However, relationship (11) predicts a maximum in the Curie temperature T_C at the hole concentration $c = 0.5$, which is considerably higher than the hole concentration $c = 0.2$ (Fig. 5a). It is well known that the bandwidth W in manganese perovskites is very sensitive to the Mn–O–Mn bond angle [21]. It follows from the table that, as the coefficient δ increases, the orthorhombic structure of the LaMnO$_{3 + \delta}$ manganite transforms into a cubic structure with small rhombohedral distortions and then into a rhombohedral structure. The lattice disorder also affects the bandwidth W in such a way that the electron localization is enhanced and the band of localized states narrows [19]. The hole doping of the LaMnO$_{3 + \delta}$ manganites occurs without introducing impurity atoms. Consequently, it can be expected that an increase in the coefficient δ does not lead to an increase in the degree of disorder in the material under

investigation. This assumption agrees with the results described above. Therefore, a gradual systematic decrease in the bandwidth W with an increase in the coefficient δ can be attributed to the increase in distortions of the cubic structure and the bandwidth W can be approximated by the relationship $W(\delta) = W_0 - W_1\delta$. The fitting of relationship (11) to the experimental data (Fig. 5a, solid line) reproduces well the dependence of the Curie temperature T_C on the coefficient δ at $W_0 = 3.05 \pm 0.05$ eV and $W_1 = 12.9 \pm 0.4$ eV.

In order to assess the correctness of these results and the applicability of the linear approximation to the dependence $W(\delta)$, we used the quantities W_0 and W_1 obtained in the present work. In order to evaluate the bandwidth W for two series of the La$_{1-x}$Ca$_x$MnO$_3$ ceramic samples studied in [4, 11], we used the aforementioned quantities $\delta' = (2/3)\delta$. As a result, we obtained the bandwidths $W \approx 1.9$ and 1.7 eV, which are in good agreement with those determined in [4, 11]. Consequently, the maximum in the concentration dependence of the Curie temperature $T_C(\delta)$ for the LaMnO$_{3 + \delta}$ manganites reflects the competition between two tendencies: an increase in the hole concentration c and a decrease in the bandwidth W with an increase in the coefficient δ. Both tendencies are also responsible for the maximum in the concentration dependence of the susceptibility. The former tendency leads to an additional ferromagnetic interaction, whereas the latter tendency results in a decrease in the ferromagnetic contribution due to the decrease in the exchange integral in the double exchange mechanism, which is also sensitive to lattice distortions [7]. Nonetheless, the drastic increase in the susceptibility $\chi(\delta)$ of the LaMnO$_{3 + \delta}$ manganites at $\delta = 0.065–0.100$ is predominantly determined by the transition from a strongly frustrated spin-disordered mixed ferromagnet + spinglass phase to a weakly frustrated spin-ordered ferromagnetic phase. It should be emphasized that the changes in the hole concentration c in both materials, LaMnO$_{3 + \delta}$ and La$_{1-x}$Ca$_x$MnO$_3$, are similar to each other, but the magnetic irreversibility in the latter material is considerably stronger than the magnetic irreversibility in the former material and does not substantially change in the corresponding range of hole concentrations c [4]. Furthermore, the susceptibility χ of the La$_{1-x}$Ca$_x$MnO$_3$ compounds in the range $0.05 \le x \le 0.30$ increases only slightly with a change in the hole concentration from 0.13 to 0.34. As compared to the La$_{1-x}$Ca$_x$MnO$_3$ compounds, the maximum of the susceptibility for the LaMnO$_{3 + \delta}$ manganites results from the competition of a decrease in the spin disorder and an enhancement of the lattice distortions (Fig. 5b). Therefore, it is necessary to take into account the decrease in the degree of lattice disorder (and, as a consequence, the decrease in the degree of magnetic frustration), on the one hand, and the enhancement of the distortions of the cubic structure (this is confirmed by
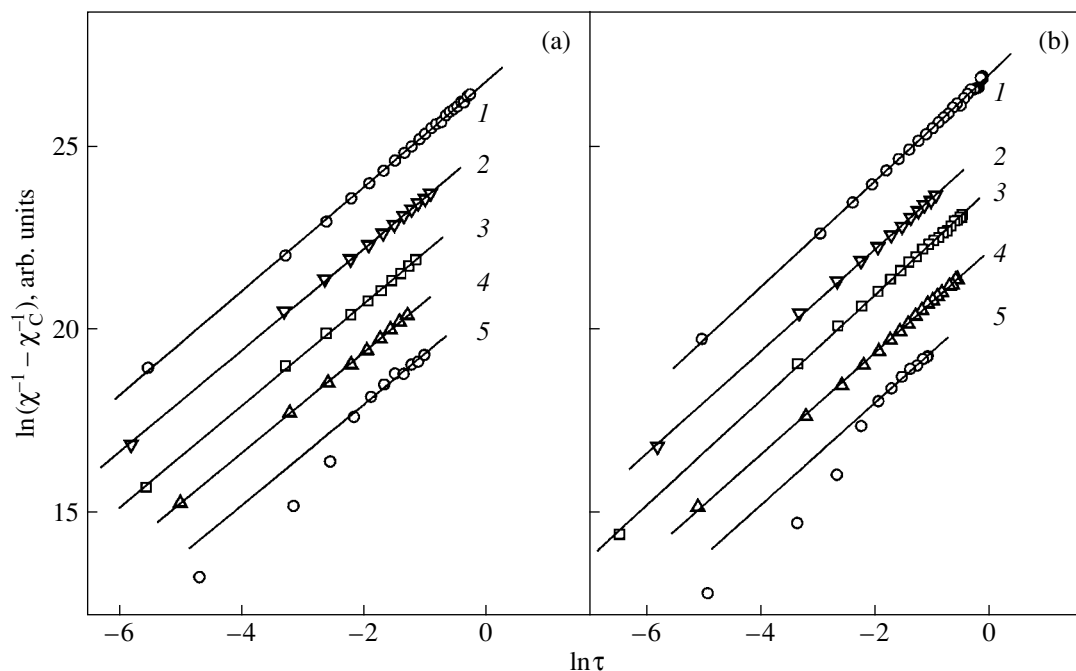
Fig. 7. Critical behavior of the magnetic susceptibilities (a) χ_{ZFC} and (b) χ_{FC} for the curves $\chi(T)$ depicted in Fig. 4 for the (a) (*1*) *S*140, (*2*) *S*133, (*3*) *S*125, (*4*) *S*100, (*5*) *S*065, (b) (*1*) *S*154, (*2*) *S*133, (*3*) *S*125, (*4*) *S*100, and (*5*) *S*065 samples of the LaMnO$_{3+\delta}$ manganite. Solid lines represent the approximation of the experimental data (for explanation, see the text).

the results presented in the table and by the above analysis of the dependence $W(\delta)$), on the other hand.

Figure 6 shows the temperature dependences of the susceptibilities $\chi_{ZFC}(T)$ and $\chi_{FC}(T)$ for the *S*000 sample. At temperatures below the Curie point T_C, the magnetic irreversibility manifests itself in a deviation of the dependence $\chi_{ZFC}(T)$ from the dependence $\chi_{FC}(T)$. Judging from the phase diagram [22], the paramagnet–antiferromagnet phase transition can occur in the *S*000 sample. The susceptibility $\chi_{FC}(T)$ increases progressively as the temperature decreases below a particular value. Unlike the other samples, the dependence $\chi_{ZFC}(T)$ for the *S*000 sample is virtually absent. This behavior does not correspond to a simple antiferromagnet, a noncollinear antiferromagnet, or a weak ferromagnet, as could be expected for the undoped LaMnO$_3$ compound [22].

Therefore, the transition from the ordered structure (the *S*000 sample) to the disordered structure (the *S*065–*S*154 samples) affects not only the electrical conductivity and the magnetoresistance (Fig. 3) but also the magnetic properties of the LaMnO$_{3+\delta}$ manganites (Figs. 4, 6).

4. CRITICAL BEHAVIOR OF THE SUSCEPTIBILITY $\chi(T)$

When the temperature T approaches the Curie point T_C from the side of the paramagnetic phase, it can be expected that the critical behavior of the susceptibility

$\chi(T)$ will manifest itself in accordance with the scaling law $\chi(T) \sim (T/T_C - 1)^{-\gamma}$ due to the enhancement of short-range ferromagnetic fluctuations [23]. The experimental data are conveniently analyzed in terms of the relationship

$$\chi^{-1} - \chi_C^{-1} \sim \tau^{\gamma}, \qquad (12)$$

where $\chi_C = \chi(T_C)$ and $\tau = T/T_C - 1$.

The dependences of $\ln(\chi^{-1} - \chi_C^{-1})$ on $\ln\tau$ were constructed by interpolating the temperature dependence of the susceptibility $\chi(T)$ (the Curie temperature T_C was varied in steps of 0.5 K) in such a way as to minimize the standard deviations of the linear extrapolations from the experimental data. The Curie temperatures T_C (Fig. 5a, crosses) thus determined are close to those obtained from the points of inflection in the temperature dependences of the susceptibility $\chi(T)$ (Fig. 5, triangles). As can be seen from Fig. 7, excellent linear extrapolations with the same slope are obtained for all the LaMnO$_{3+\delta}$ samples ($0.065 \le \delta \le 0.154$). The extrapolations are linear for the samples cooled in a zero magnetic field (Fig. 7a) and in the magnetic field $B = 2$ G (Fig. 7b) over a wide range of quantities τ. An exception is provided by the data obtained for the *S*065 sample, for which the extrapolation is linear only to $\ln\tau \approx -2$. This is consistent with the mixed nature of the ferromagnet + spin-glass phase, which, as was noted above, is observed in this sample with a decrease in the temperature. The critical exponent $\gamma = 1.42 \pm 0.03$

obtained from the dependences shown in Fig. 7 is close to the critical exponents $\gamma = 1.39–1.43$ for $La_{1-x}Sr_xCoO_3$ compounds [19] and $\gamma = 1.45$ for the $La_{0.8}Ca_{0.2}MnO_3$ single crystal [24] and corresponds to a three-dimensional Heisenberg spin system [23].

A more complex critical behavior of the susceptibility was revealed for untreated ceramic materials [4, 11], $La_{1-x}Ca_xMnO_3$ films [25], and $La_{1-x}Ca_xMn_{1-y}Fe_yO_3$ ceramic samples [26]. In these cases, the scaling law (12) leads to two critical exponents that correspond to two universal systems, namely, the Heisenberg spin system and the percolation system. The percolation system is characterized by the phase separation [5, 27] due to the presence of hole-rich ferromagnetic metallic droplets in an insulating paramagnetic matrix. The droplets are joined together into a percolation cluster when the volume of their fractions increases as the Curie temperature T_C is approached [25, 28]. The presence of one critical exponent γ (the graphs with one slope in Fig. 7) implies that the content of the second phase (enriched with holes) in the $LaMnO_{3+\delta}$ manganite is low and insufficient to compete with the main phase in the effect on the formation of the critical magnetic behavior in weak magnetic fields. This is also supported by the dependences $\rho(T)$ that, for the $LaMnO_{3+\delta}$ manganites, exhibit a more pronounced semiconductor behavior as compared to the $La_{1-x}Ca_xMnO_3$ compounds [29] with a close hole concentration (Fig. 2). All the foregoing confirms that the homogeneity of the $LaMnO_{3+\delta}$ manganites is higher than the homogeneity of the $La_{1-x}Ca_xMnO_3$ compounds [26]. This is in complete agreement with the decrease in the degree of disorder of the $LaMnO_{3+\delta}$ lattice as follows from the analysis of the magnetic irreversibility and the dependences of the susceptibility χ and the Curie temperature T_C on the coefficient δ.

5. CONCLUSIONS

Thus, it has been found that the cation-deficient compounds $LaMnO_{3+\delta}$ and solid solutions $La_{1-x}Ca_xMnO_3$ possess a similar sequence of magnetic phases when the hole concentration varies in the same ranges. However, detailed investigations of the magnetic properties of these compounds in weak magnetic fields have revealed substantial differences. In particular, the $LaMnO_{3+\delta}$ manganites are characterized by a smaller degree of magnetic irreversibility and exhibit nonmonotonic dependences of the Curie temperature T_C and the susceptibility χ on the hole concentration. The critical behavior of the temperature dependence of the susceptibility $\chi(T)$ in the $LaMnO_{3+\delta}$ manganites is described by one critical exponent $\gamma \approx 1.42$, which corresponds to a universal three-dimensional Heisenberg spin system. The critical behavior of the susceptibility in the $La_{1-x}Ca_xMnO_3$ compounds is described by an additional critical component associated with the per-

colation behavior at temperatures above the Curie point T_C. These specific features can be explained by the more uniform distribution of holes and by the progressive increase in distortions of the cubic perovskite structure of the $LaMnO_{3+\delta}$ manganites with an increase in the coefficient δ in the range $0.065 \leq \delta \leq 0.154$.

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