

# Unusual substitutional properties of Cu in bulk polycrystalline samples of $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Cu}_x\text{O}_{3-\delta}$

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The transport and magnetoresistive properties of bulk polycrystalline samples of the  $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Cu}_x\text{O}_{3-\delta}$  ( $x \leq 0.15$ ) system are studied in the temperature range 77 K–300 K. All the samples investigated exhibit the giant magnetoresistance effect associated with the transition from the ferromagnetic metallic to the paramagnetic insulating state. As a function of copper concentration, the temperature of the resistivity peak,  $T_p$ , first decreases from 193 K ( $x = 0$ ) to 108 K ( $x = 0.10$ ) and then gradually grows, reaching 120 K at  $x = 0.15$ . Significant temperature broadening of the resistive transition as well as anomalous behavior of the peak value of the resistivity are observed near  $x = 0.10$ . The unusual properties of the  $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Cu}_x\text{O}_{3-\delta}$  system are well explained in terms of a mixed valence of the Cu ions.

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## Introduction

An intense research effort has recently been devoted to studying the interplay between the structure, magnetism, and electronic transport in doped manganites  $\text{La}_{1-x}\text{M}_x\text{MnO}_3$  (M = alkaline earth) [1,2]. By tuning the size mismatch of the A- and B-site ions in these  $\text{ABO}_3$ -type perovskites one can control the competition between the double exchange, superexchange, and Coulomb interactions among the Mn ions and, thus, their magnetoresistive properties, which are of crucial importance for applications [3]. It has been shown that both the ferromagnetic ordering,  $T_C$ , and metal-insulator,  $T_p$ , temperatures are very sensitive to the structural distortions induced by changing the average A-site radius  $\langle r_A \rangle$ . A few percent substitution of La by smaller rare-earth cations could result in a significant drop in the Curie temperature  $T_C$  and in a drastic enhancement of the magnetoresistance effect. On the basis of the double exchange model and with the strong electron-phonon interaction, taken into account, the complex lattice effects can be understood, at least qualitatively, in both the paramagnetic and ferromagnetic regions. The introduc-

tion of smaller A-site ions leads to a larger steric buckling of the corner-shared octahedra in the perovskites, to bending of the Mn–O–Mn bonds and, as a result, to weakening of the double exchange between  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  ions and enhancement of the antiferromagnetic superexchange interaction [1].

An interesting way to modify the crucial  $\text{Mn}^{3+}\text{--O--Mn}^{4+}$  network is to dope at the Mn site itself. Co and Ni substitutions for Mn in  $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$  thin films have been shown to lower the magnetic transition temperature because of weakening of the double exchange between two unlike ions [4]. Recently, Sun et al. [5] reported the effects of Fe and Ge doping at the Mn site in bulk polycrystalline  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ . It was shown that Mn-site doping favored a reduced magnetic/resistive transitions and elevated resistivity. No metal-insulator transition occurred when the content of Fe exceeded  $\sim 0.1$ . Similar results were obtained by substitution of  $\text{Mn}^{3+}$  by  $\text{Al}^{3+}$ , although both ferromagnetic and resistive transitions were reported still to occur in  $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Al}_x\text{O}_3$  at  $x \approx 0.1$  [6].

Recently, several studies have been undertaken to clarify the effect of Cu doping at the Mn site of bulk polycrystalline  $\text{La}_{1-x}\text{M}_x\text{MnO}_3$  ( $\text{M} = \text{Ba}, \text{Sr}$ ) [7–10]. The results of a detailed structural investigation of  $\text{La}_{1-z}\text{Sr}_z\text{Mn}_{1-x}\text{Cu}_x\text{O}_3$  ( $z = 0; 0.1; 0.3; 0 \leq x \leq 0.5$ ) polycrystalline samples [9] show that Cu doping favors rhombohedral distortions of the perovskite structure and that copper ions can be found both in  $2^+$  and  $3^+$  valence states in these compounds. The electronic transport, magnetic, and infrared properties of  $\text{La}_{1-z}\text{Ba}_z\text{Mn}_{1-x}\text{Cu}_x\text{O}_{3-\delta}$  and  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{1-x}\text{Cu}_x\text{O}_{3-\delta}$  ( $x = 0; 0.1; \dots$ ) systems were reported in Refs. 7,8. It was found that 20% copper was sufficient to suppress ferromagnetism in the latter system and to lead to the cluster spin glass state at  $0.2 \leq x \leq 0.4$ . A broadened ferromagnetic transition and a double-peaked character of the resistivity vs. temperature curve were observed at  $x = 0.1$ .

During the past few years, rather controversial results have been reported concerning the influence of Cu doping on the transport properties of  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  [11–13]. Sergeenkov et al. [12] examined a 4% Cu-doped  $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$  compound and found both a sharp drop ( $\sim 50\%$ ) in resistivity and a slight decrease ( $\sim 15$  K) in  $T_p$ , with regard to the original Cu-free sample. Similar effects were observed in  $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.95}\text{Cu}_{0.05}\text{O}_3$  by Ghosh et al. [11]. By contrast, unusual temperature and concentration behavior of the resistivity in  $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Cu}_x\text{O}_3$  was reported in Ref. 13. Introduction of a small amount of copper ( $x \leq 0.05$ ) was found to result in a splitting of the resistivity maximum around the metal–insulator transition temperature into two peaks, differently evolving with copper concentration. Although the experimental data were well fitted assuming a nonthermal tunnel conductivity theory with randomly distributed hopping sites, it is not easy to correlate these data with those described in Refs. 11,12.

In view of such ambiguous results, there appears to be a need to explore in more detail the effect of Cu doping on the behavior of the  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  compound. It seems that at least some of the controversies resulting from Refs. 11–13 would have been avoided if the authors had comprehensively characterized the chemical composition as well as the quality of the resulting samples by means of a set of various measurement techniques. The work reported here is intended to be a step in this direction. We present the results of a study of transport and magnetoresistive properties of a series of  $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Cu}_x\text{O}_{3-\delta}$  samples with  $0 \leq x \leq 0.15$ . In addition to conventional electrical

and magnetic measurements, we have characterized the composition and quality of representative samples using x-ray fluorescence and electron paramagnetic resonance (EPR) techniques.

## Experimental procedure

Polycrystalline  $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Cu}_x\text{O}_{3-\delta}$  (LCMC) with  $x = 0; 0.05; 0.075; 0.10; 0.125$ , and  $0.15$  were prepared through two-stage solid-state reaction in air [14]. The starting mixture of  $\text{La}_2\text{O}_3$ ,  $\text{Mn}_2\text{O}_3$ ,  $\text{CuO}$ , and  $\text{CaCO}_3$  was first calcined for 2 h at a temperature of  $1100$  °C. After subsequent ball milling and uniaxial pressing into pellets, the resulting products were sintered for 2 h at  $T_s = 1300$  °C and then furnace cooled down to room temperature. Lattice parameters of the samples were obtained from a least-squares fitting to the relevant diffraction lines in x-ray powder diffraction experiments carried out on a DRON diffractometer in  $\text{Cu } K_\alpha$  radiation. DC resistance measurements were performed in the temperature range  $77$ – $300$  K using the standard four-probe method. Samples for resistance measurements were cut into rectangular bars, with typical dimensions of  $2 \times 3 \times 10$  mm. The magnetoresistance was measured in fields up to  $1.5$  T and is defined as  $(\rho - \rho_H)/\rho$ , where  $\rho$  and  $\rho_H$  are the resistivity in zero field and applied field, respectively. We note that the magnetoresistance ratio defined in such a way cannot exceed 100%. AC magnetic susceptibility ( $\chi$ ) measurements were performed at a frequency of  $1000$  Hz by a mutual inductance bridge. DC magnetization was measured by means of a SQUID magnetometer (Quantum Design MPMS-5S). EPR measurements on powder samples were performed in the temperature range  $77$ – $300$  K using a RADIOPAN spectrometer operating at  $9.2$  GHz.

## Results and discussion

To begin with, let us present the results of a set of measurements, which allow one to achieve rather complete characterization of the parent, i.e.,  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{3-\delta}$  sample. Figure 1 shows the temperature dependence of the magnetization  $M$  measured in a field of  $1$  T. At high temperatures,  $M(T)$  obeys the Curie–Weiss law, and its behavior is characteristic of a paramagnetic state. As the temperature decreases, a sharp rise in magnetization occurs slightly below  $200$  K, after which  $M$  grows more slowly and, finally, reaches a value of  $84.7$  emu/g at  $T = 5$  K. From the hysteresis loop  $M(H)$  at this temperature (see Fig. 1, inset) one can estimate the saturation magnetization  $M_s$  and coer-

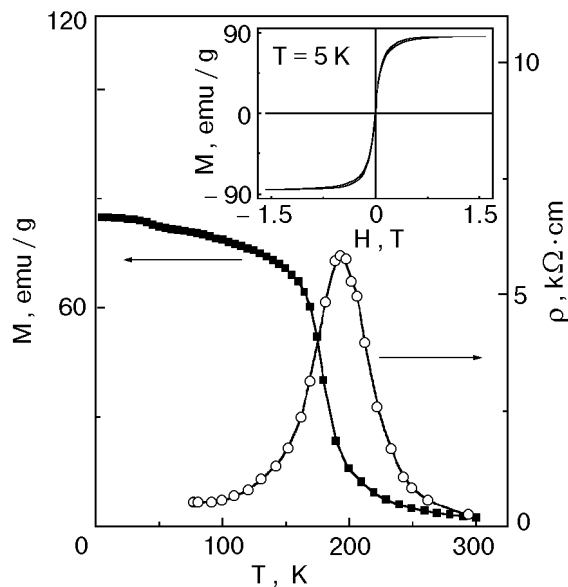


Fig. 1. Temperature dependence of the magnetization in a field  $H = 1$  T and of the electrical resistivity for a  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{3-\delta}$  sample. The inset shows the hysteresis loop  $M(H)$  at  $T = 5$  K.

cive field  $H_c$ , which will be used in the detailed analysis below.

To observe the onset of magnetic ordering in more detail, we studied the temperature dependence of EPR spectrum from 300 down to 77 K. A strong symmetric EPR signal with a line shape very close to Lorentzian is observed at room temperature. When the temperature is lowered, the linewidth decreases, passes through a minimum at  $T_{\min} \cong 220$  K, and increases on further cooling. Around 200 K ( $T_C$ ) the spectrum splits into two lines, indicating the appearance of spontaneous magnetization coexisting with a remainder of the paramagnetic phase [15]. It is noteworthy that it is near this temperature that both the resistance peak and sharp change in magnetization are observed (see Fig. 1). As the temperature is reduced further, the intensity of the resonance line corresponding to the paramagnetic phase decreases drastically, and this line almost completely disappears below  $\sim 170$  K.

In our opinion, both the sharp ferromagnetic transition and narrow hysteresis loop are evidence of rather good chemical and magnetic homogeneity of the sample. Both the value of  $M_s$  ( $\sim 85$  emu/g) and  $H_c$  ( $\leq 3$  mT) correlate well with other data reported in the literature [5,16,17]. Nevertheless, the Curie temperature  $T_C$  is much lower than that observed in stoichiometric  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  ( $T_C \cong 260\text{--}270$  K) [16–18]. To find out the reason for this discrepancy, we checked the chemical composition of the samples with  $x = 0$ ; 0.05; and 0.10,

using the x-ray fluorescence technique. The results of the analysis have shown that, across the series of samples, the atomic ratio between constituent metal atoms (La, Ca, Mn and Cu) keeps close to the nominal one (for each of the elements, deviation from the nominal value does not exceed 3%). Thus, the most likely reason for the lowered  $T_C$  in our case lies in a deviation of oxygen content from the stoichiometric value. Comparison of the data plotted in Fig. 1 with the results presented in Refs. 14, 17, 19, 20 shows that the parent sample is oxygen deficient, with  $\delta \sim 0.06$  (different methods give different values of  $\delta$  ranging from 0.04 to 0.08). Taking into account that all the samples of the  $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Cu}_x\text{O}_{3-\delta}$  family were synthesized under exactly the same conditions, we hold the opinion that  $\delta$  remains nearly constant as  $x$  varies from 0 to 0.15, although, at this stage, we are unable to determine its exact value.

The effect of oxygen nonstoichiometry on the electrical, magnetic, and resonance properties of perovskite manganite thin films was studied in detail by Rajeswari et al. [21]. It was found that a decrease in oxygen content strongly affected the sharpness of both the resistive and magnetic transitions and led to a significant growth in EPR linewidth. As one of the important results to be mentioned, the authors showed that the increase of  $\delta$  in epitaxial films of  $\text{Nd}_{0.67}\text{Ca}_{0.33}\text{MnO}_{3-\delta}$  could change the minimal peak-to-peak linewidth  $\Gamma_{\min}$  from about 20 to 100 mT. Turning to our EPR data,  $\Gamma_{\min}$  is equal to 34 mT for the parent ( $x = 0$ ) sample and is around 35 mT for LCMC with  $x = 0.05$ . These values are higher than those observed in high-quality epitaxial films of  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_{3-\delta}$  [21], but they are less than or comparable to  $\Gamma_{\min}$  in bulk polycrystalline samples synthesized by other researchers [4,22,23]. So, despite the considerable oxygen deficiency of our samples, this parameter is very close to the best values reported before, and it can serve as an additional conformation of the rather good quality of the materials synthesized in the present study.

As can be seen from Fig. 1, the resistivity  $\rho$  of the  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{3-\delta}$  sample is several orders of magnitude greater than typical values reported for epitaxial films of the same composition [24]. This is not surprising for polycrystalline (ceramic) materials consisting of low-resistivity grains and high-resistivity intergrain regions. When high- and low-resistive regions are connected in series, the DC response is strongly dependent on the high-resistivity region. Thus in such materials the amount and quality (chemical composition, structural and mag-

netic disorder, etc.) of the intergrain regions greatly affects both the electrical resistance and magnetoresistance but scarcely influences most of other properties, since the relative volume of the intergrain region is negligibly small. To shed further light upon the origin of high-resistivity behavior of  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{3-\delta}$ , a part of the sample was subjected to different kinds of heat treatment. After it was annealed in air at  $800^\circ\text{C}$  for 1 h, its resistivity dropped by 3 orders. Further annealing at this temperature gave rise to a further decrease in  $\rho$  but neither the bulk magnetization nor the width of the insulator-to-metal transition was changed. This seems to indicate that this kind of heat treatment affects only the intergrain regions and that it apparently results in an improvement of their structure or/and a slight increase in oxygen content. However, these experiments have also led to a slight reduction in the low-temperature magnetoresistance, which is one of the crucial parameters for this class of materials. Therefore, in what follows we concentrate only on the properties of unannealed  $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Cu}_x\text{O}_{3-\delta}$  samples, keeping in mind that each one consists of perfectly crystallized grains divided by highly disordered or/and strongly oxygen deficient intergrain regions.

The structural parameters of the LCMC samples are listed in Table. The parent  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{3-\delta}$  compound belongs to  $O'$ -type orthorhombic structure [2] with lattice parameters  $a_0 = 5.4568 \text{ \AA}$ ,  $b_0 = 5.5017 \text{ \AA}$  and  $c_0 = 7.7126 \text{ \AA}$ , satisfying  $c_0/\sqrt{2} < a_0 < b_0$ . These data correlate well with the results of Ref. 5. The samples with  $0.05 \leq x \leq 0.15$  are rhombohedrally distorted with  $a \cong 2c_0$  and  $\alpha \cong 91.5^\circ$ . The fact that lattice constants are scarcely dependent on doping level seems to support the results of Ref. 9 showing that copper ions in manganites are in both  $2^+$  and  $3^+$  charge states. Unidentified phases with weak ( $< 5\%$ ) peaks at  $2\theta \cong 12.4^\circ$  and  $24.9^\circ$  were revealed in

Table

Room-temperature crystallographic parameters for rhombohedral samples of  $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Cu}_x\text{O}_{3-\delta}$

$x$	$a$ , $\text{\AA}$	$\alpha$ , deg
0.050	15.489	91.53
0.075	15.478	91.50
0.100	15.474	91.49
0.125	15.481	91.53
0.150	15.467	91.49

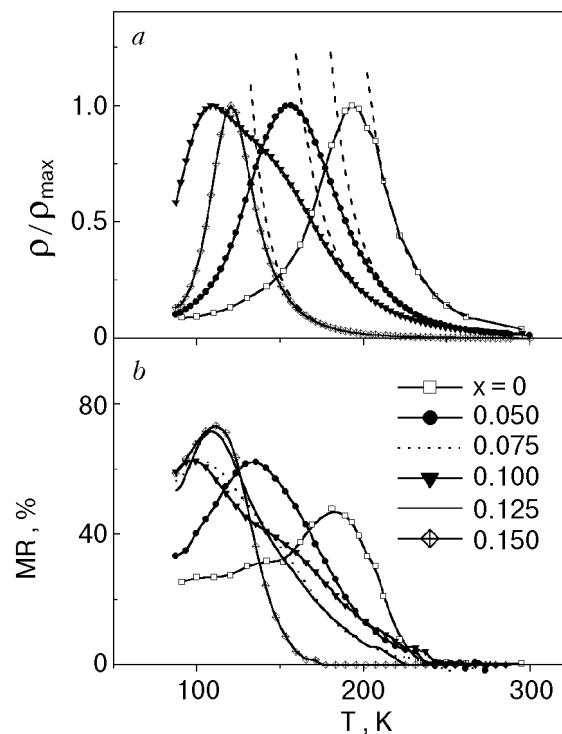


Fig. 2. Normalized resistance vs. temperature for polycrystalline  $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Cu}_x\text{O}_{3-\delta}$  samples. The dotted lines denote the resistance fitted according to the adiabatic small-polaron hopping model (a). Temperature dependence of the magnetoresistance in a field  $H = 1.5 \text{ T}$  (b).

LCMC with  $x = 0.10$  and  $0.15$  but we believe that these phases have little effect on the transport and magnetoresistance properties of the samples.

Data on the normalized resistivity  $\rho/\rho_{\text{max}}$  as a function of temperature  $T$  are plotted in Fig. 2,a for LCMC samples with  $x = 0; 0.05; 0.10$ , and  $0.15$  (the data for  $x = 0.075$  and  $0.125$  are omitted for clarity). In all the samples  $\rho$  increases drastically with decreasing  $T$  to a maximum at  $T = T_p$ , after which a metallic behavior appears. The variation of  $T_p$  with  $x$  is nonmonotonous: its value first falls from  $193 \text{ K}$  ( $x = 0$ ) to  $108 \text{ K}$  ( $x = 0.10$ ) and then gradually grows, reaching  $120 \text{ K}$  at  $x = 0.15$ ;  $\rho_{\text{max}}$  decreases with increasing  $x$  from about  $6000$  ( $x = 0$ ) to  $1000$  ( $x = 0.15$ )  $\Omega\text{-cm}$ . Although at  $T < T_p$  the  $\rho(T)$  dependence is metallic ( $d\rho/dT > 0$ ) the resistivity at the lowest measured temperature ( $T = 77 \text{ K}$ ) is greater than  $\rho(300 \text{ K})$ . The lowest  $\rho(77 \text{ K})$ , which is  $\sim 150 \text{ \Omega-cm}$  for this series of samples, is much larger than  $\rho_{\text{Mott}} \approx 5\text{--}10 \text{ \Omega-cm}$  estimated from the Mott minimum metallic conductivity [25].

In the high-temperature region, the variation of the resistivity conforms well to the expression

$$\rho(T) = \rho_0 T \exp(E_a/kT) \quad (1)$$

predicted for small-polaron hopping conductivity [4,26]. The activation energy  $E_a$  is weakly dependent on  $x$  and is equal to 0.2 and 0.14 eV for the samples with extreme concentrations of Cu,  $x = 0$  and 0.15, respectively. When going from higher temperatures, the measured resistivity progressively deviates from that predicted by (1). The temperature at which difference between the experimental and fitted data exceeds 5% is denoted as  $T_a$ . It is the temperature, below which not only the electrical but also the magnetoresistive and magnetic properties deviate from those typical of an insulating paramagnet. For all the samples, the effect of magnetic field on the resistance becomes noticeable at  $T < T_a$  and reaches a maximum at  $T_{MR}$  slightly below  $T_p$  (Fig. 2, *b*). The peak values of the magnetoresistance  $MR_{\max}$  measured in a field of 1.5 T are about 48% and 73% for LCMC with  $x = 0$  and 0.15, respectively.

The field dependence of the magnetoresistance at  $T = 77$  K is presented in Fig. 3. For compositions with higher values of  $T_p$  ( $x \leq 0.05$ ) the  $MR(H)$  curves show a sharp drop at low fields ( $< 0.2$  T) followed by a more gradual change at  $H > 0.2$  T. In both the regions  $\rho$  changes almost linearly with  $H$ . It is now well established that the low-field  $MR$  component in manganites originates from a high degree of spin polarization of the conduction electrons, and it is ascribed to intergrain spin-polarized

tunneling [27] or spin-dependent scattering of polarized electrons at the grain boundaries [24].

The variation of  $MR$  with  $H$  is completely different in the samples with  $x > 0.05$ . All the curves are nonlinear in the whole field range examined and their hysteretic behavior is well pronounced, especially for the composition with  $x = 0.10$ . This effect may be a result of increased magnetic inhomogeneity caused by the introduction of Cu ions in the Mn sublattice, or it may indicate the appearance of other kinds of magnetic ordering [7,8]. To shed further light on the origin of the highly hysteretic behavior of  $MR(H)$ , we performed AC magnetic susceptibility measurements on LCMC with  $x = 0.10$ . The temperature dependence of both  $\chi$  and  $|d\chi/dT|$ , which are plotted in Fig. 4, seems to show that there is no other transition except for the paramagnetic-ferromagnetic one, but the transition region is extremely broadened.

The concentration dependence of the characteristic temperatures  $T_a$ ,  $T_p$ , and  $T_{MR}$  is displayed in Fig. 5, *a*. It is seen, that apart from  $T_a$ , which tends to decrease gradually with increasing  $x$ , the rest of the quantities do not change monotonically as function of  $x$ . Such unusual behavior seems to be closely connected with the considerable broadening of both the resistive and magnetic transitions observed near  $x = 0.10$ . To give a clear visual demonstration of this relationship, we used the difference between  $T_a$  and  $T_p$  for a quantitative characterization of the width of the resistive transition and plotted it as a function of copper content in

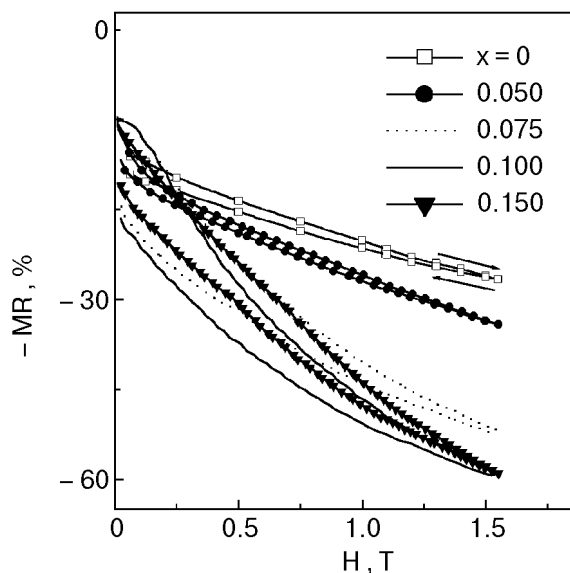


Fig. 3. Magnetoresistance vs. field for  $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Cu}_x\text{O}_{3-\delta}$  measured at  $T = 77$  K (the data for  $x = 0.125$  are omitted).

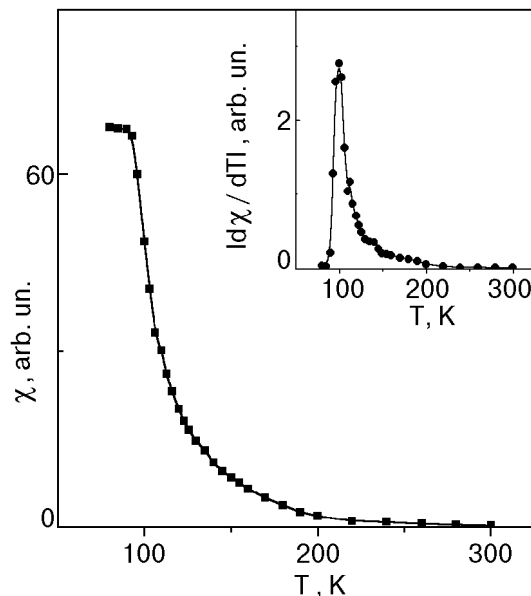


Fig. 4. AC magnetic susceptibility  $\chi$  of  $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.90}\text{Cu}_{0.10}\text{O}_{3-\delta}$  and the absolute value of its derivative  $|d\chi/dT|$  as functions of temperature.

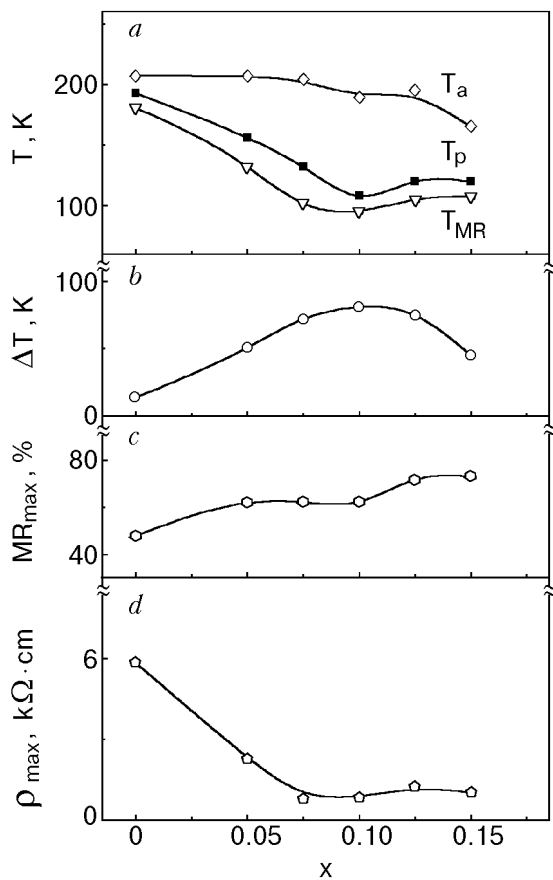


Fig. 5. Concentration dependence of the characteristic temperatures  $T_a$ ,  $T_p$ , and  $T_{MR}$  (a); the temperature width of the resistive transition (b); the maximum value of the magnetoresistance in a field  $H = 1.5$  T (c); the maximum value of the resistivity  $\rho_{\max}$  (d).

Fig. 5, b. A very narrow transition region ( $\Delta T = 14$  K) is observed at  $x = 0$ . As  $x$  grows,  $\Delta T$  first increases, exhibits a maximum near  $x = 0.10$  ( $\Delta T_{\max} = 81$  K), and then gradually decreases and reaches 45 K at  $x = 0.15$ . Such a strong broadening of the resistive transition near  $x = 0.10$  suggests the presence of structural or magnetic inhomogeneities and it can be a reason for reduced sensitivity of the electronic transport to magnetic field. As can be seen from Fig. 5, c,  $MR_{\max}(x)$  exhibits a local minimum in the vicinity of  $x = 0.10$ , although it grows continuously at  $x \leq 0.075$  and  $x > 0.10$ .

An unusual effect of Cu doping on electronic transport properties was observed earlier in the  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{1-x}\text{Cu}_x\text{O}_{3-\delta}$  system [7,8]. The authors carried out a careful examination of compounds with  $x = 0, 0.1, 0.2 \dots$ . It was found that substitution of 10% Cu lowers the Curie temperature from 320 to 280 K, and 20% Cu is enough to completely destroy the ferromagnetic state. At low tempera-

tures, the samples with  $x = 0$  and 0.1 were found to be metallic ferromagnets, while in those with  $x \geq 0.2$  a semiconducting spin glass state was revealed. Contrary to  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$ , in which a sharp change near the Curie temperature was observed on the magnetization vs. temperature curve, in  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.9}\text{Cu}_{0.1}\text{O}_{3-\delta}$  the magnetic transition was quite broadened, and the  $\rho$  vs.  $T$  dependence exhibited two peaks. For the latter sample, the authors attributed the low-temperature resistance peak to enhanced scattering of spin polarons on «frozen-in» magnetic disorder, which might exist below  $T_C$ .

An issue of crucial importance for the analysis of Cu-doped manganites, although it has remained unclear hitherto, is the valence state of Cu ions. It is known that copper in perovskite compounds may appear in  $2^+$  and  $3^+$  states [7–9, 11]. The authors of Refs. 7–9 analyzed their experimental results at the assumption that the Cu ions are divalent. Nevertheless, Tikhonov et al. carried out careful analysis of the structural properties of  $\text{La}_{1-z}\text{Sr}_z\text{Mn}_{1-x}\text{Cu}_x\text{O}_3$  ( $z = 0, 0.1, 0.3$ ;  $x = 0-0.5$ ) system and concluded that copper is trivalent in these compounds, but in the low-doping region ( $0 < x \leq 0.1$ ) a fraction of the Cu ions may also be found in the  $2^+$  state. It seems that these results show the way to understand the quite complex behavior of Cu-doped manganites.

Manganese ions play a key role in the determination of both the electrical and magnetic properties of the materials under consideration. The electrical conductivity and ferromagnetism are described in terms of the transfer of electrons between  $\text{Mn}^{3+}(t_{2g}^3 e_g^1)$  to  $\text{Mn}^{4+}(t_{2g}^3 e_g^0)$  ions; the magnetic interaction is double exchange that is sensitive to the Mn–O–Mn overlap. The conductivity depends on the electron spin alignment of the hopping electron and is enhanced by application of a magnetic field that reduces spin disorder. The double exchange, which favors itinerant electron behavior, is opposed by strong electron–phonon coupling due in part to a Jahn–Teller splitting of the Mn  $e_g$  states, by antiferromagnetic superexchange, and by charge and orbital ordering, all of them favoring insulating behavior. Thus the introduction of copper ions in the Mn sublattice is expected to drastically affect all these competing interactions, and this may cause profound changes in the magnetic and electrical properties. First, Cu substitution for Mn is expected to suppress ferromagnetism because of the absence of the double-exchange interaction between neighboring Mn and Cu ions [7, 11–13]. In our case, the general reduction of  $T_a$  with growing Cu content seems to support this idea. Nevertheless, the

introduction of Cu ions in the Mn sublattice also gives rise to local structure, spin, and charge distortions, especially when the copper is in the  $2^+$  state. If Cu is divalent, two different effects might occur as the amount of copper increases. First, there is a local change in the lattice constant caused by the incorporation of the significantly bigger ion, that might lead to enhancement of structural and magnetic inhomogeneity and, as a result, to temperature broadening of the magnetic transition. At the same time, this effect might also be accompanied by a drop in electrical resistivity due to relieving of the local strain in the rest of the sample [11–13]. Second, according to the charge neutrality condition, insertion of divalent Cu ions in the system converts part of the  $\text{Mn}^{3+}$  into  $\text{Mn}^{4+}$  which might lead to the appearance of regions with improved conductivity due to the rise in the  $\text{Mn}^{4+}/\text{Mn}^{3+}$  ratio [7,11].

The effect in which the resistivity decreases upon Cu doping was observed in Refs. 7, 11–12 as well as in this study. Figure 5,*b* shows  $\rho_{\text{max}}$  for the samples under investigation as a function of copper concentration. It is seen that  $\rho_{\text{max}}$  drastically drops with  $x$  for  $x < 0.10$ , while it remains almost constant at  $0.10 \leq x \leq 0.15$ . It is difficult to explain this character of  $\rho_{\text{max}}(x)$  by any kind of Cu segregation, but by assuming a mixed valence of Cu ions in the region  $0 \leq x \leq 0.10$ , this curve well supplements those presented in Fig. 5,*a-c*.

### Conclusions

Based on the present investigations, we draw the following conclusions.

(i) Substitution of Cu for Mn tends to suppress ferromagnetism in the compound  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{3-\delta}$  due to the absence of the double-exchange interaction between neighboring Mn and Cu ions.

(ii) Significant temperature broadening of both ferromagnetic and resistive transitions near  $x = 0.10$  leads to anomalous behavior of  $T_p$ ,  $T_{MR}$  and  $MR_{\text{max}}$  as a function of copper concentration.

(iii) The concentration dependence of  $\rho_{\text{max}}$ , which mainly reflects the properties of intergrain area for each sample with a fixed value of  $x$ , substantially changes its character in just the same range of  $x$  where anomalies of the other electrical and magnetic parameters are observed (i.e., near  $x = 0.10$ ).

(iv) All of the above peculiarities are well explained, by assuming that copper is trivalent in the  $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Cu}_x\text{O}_{3-\delta}$  system while in the low-doping region ( $0 < x \leq 0.1$ ) a fraction of the Cu ions is also in the  $2^+$  state.

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