Oxidation states of copper ions and magnetic properties of $(La_{0.7}Sr_{0.3})(Mn_{1-x}Cu_x)O_{3\pm\delta}$ system

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Abstract.

The aim of the present work is to determine the actual oxidation state of copper ions and its correlation with magnetic properties of $(La_{0.7}Sr_{0.3})(Mn_{1-x}Cu_x)O_{3-\gamma}$ system ($0\leq x\leq 0.15$). It has been shown that solid solutions are formed in the whole investigated range of copper concentrations ($0\leq x\leq 0.15$), and their unit cell volume varied with x according to Vegard's law. There are two regions of concentrations with different character of the saturation magnetization dependence on x. At $x\leq 0.05$ the saturation magnetization changes slightly, whereas at $x>0.05$ it significantly decreases with x. These results can be explained in supposition of divalent copper ions in the $(La_{0.7}Sr_{0.3})(Mn_{1-x}Cu_x)O_{3-\gamma}$ system, which was verified and confirmed experimentally.

Key words: A. Powders-solid state reaction, B. X-ray methods, C. Magnetic properties, D. Perovskites, E. Functional applications

1 Introduction

The considerable interest in doped manganites with deformed perovskite-like structure, $La_{1-x}A_xMnO_3$ (A = rare-earth element), is due to a high sensitivity of their electrical properties to magnetic field (a colossal magnetoresistive effect), which makes this class of materials promising for use in magnetoelectronic devices [1]. However in most cases considerable changes in electrical resistance can be achieved only at strong fields or at low temperatures, which is dramatically restricting an area of practical application. It has been shown recently [2] that complex substitutions in $La_{1-x}A_xMnO_3$ cation sublattices can be efficient tools for an improvement of magnetoresistive properties.

A lot of attention has been paid to the investigation of lattice effects, which arise from the substitution of rare-earth elements of different sizes for lanthanum [3]. However, more substantial modifications of the interactions in the Mn^{3+}-O-Mn^{4+} chain should be expected for the case of the manganese sublattice doping. Substitutions of both magnetic (Co, Ni, Fe …) and nonmagnetic (Ge, Al, Cu …) elements for manganese were investigated in Refs [4-7]. It has been shown that magnetoresistance can be considerably enhanced, particularly by using a copper dope [7].

Rather contradictory data have been obtained during the last years about the influence of copper impurities on the magnetic properties of $La_{1-x}A_xMnO_3$ (A = Ca, Sr) [8-11] It seems the substitution of copper for manganese does not just weaken the double exchange, but also strongly changes the whole system of competing interactions in manganites.

It is difficult to analyze and predict properties of copper-doped manganites because there is still no agreement about one of the key parameters namely about the oxidation state of copper in these compounds. The data about the oxidation state of copper in such materials are inconsistent [8,10,12]. The incorporation of copper into the manganese sublattice results in rather complex processes and comprehensive investigation are needed to understand them.

The aim of the present work is to determine the oxidation state of copper ions in the $(La_{0.7}Sr_{0.3})(Mn_{1-x}Cu_x)O_{3\pm\delta}$ system based on the analysis of the interrelation between structural, magnetic, and resonance properties of the compounds.

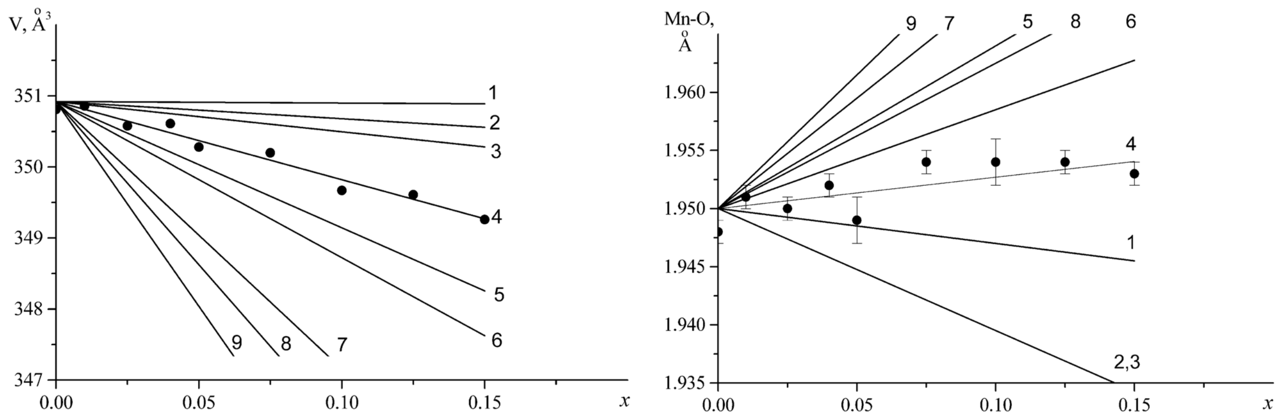
2 Experimental procedure

The polycrystalline $La_{0.7}Sr_{0.3}Mn_{1-x}Cu_xO_{3\pm\delta}$ (LSMC) samples with $x = 0 - 0.15$ were prepared using solid state sintering technique. High purity La_2O_3, Mn_2O_3 and chemical purity $SrCO_3$, CuO were used as the starting reagents. The produced blend was dried at 370–390 K, passed through a fosta nylon sieve (mesh 65), and calcined at $T_{calc} = 1270$ K (4 h). The synthesized powder was pressed into billets 12 mm in diameter and 3 mm in thickness, and then sintered at $T_{sint} = 1540 - 1600$ K (2 h).

The X-ray investigations were carried out on DRON 4-07 diffractometer (Co $K\alpha$ radiation; 40 kV, 20 мA). The structural parameters were refined by Rietveld full-profile. The manganese contents of the samples were determined using the titration of iodine with a sodium thiosulfate solution. The iodine was displaced from the potassium iodide solution by chlorine evolved from the dissolution of a weighed amount of manganite samples in hydrochloric acid. Shannon's system of ionic radii was used to analyze the crystal structure aspects of the substitution of copper for manganese [13]. The change of unit cell volume due to the lattice deformation associated with oxygen vacancy formation was considered to be equal to the volume of removed oxygen ions [14]. SQUID magnetometer (Quantum Design MPMS-5S) was used for the study of magnetic properties. Ferromagnetic resonance was measured using x-band (9.2 GHz) RADIOPAN spectrometer on the samples of parallelepiped shape (1x1x5 mm). The magnetic field was along the long axis.

3 Results and discussion

After sintering at 1300°C in air, ceramic $La_{0.7}Sr_{0.3}Mn_{1-x}Cu_xO_{3\pm\delta}$ samples had a perovskite structure with the space group R $\bar{3}$c. The crystal structure parameters of the ceramic samples were refined by Rietveld full-profile X-ray analysis. Figure 1a shows the experimental dependence (curve 4) of the unit cell volume of $La_{0.7}Sr_{0.3}Mn_{1-x}Cu_xO_{3\pm\delta}$ on copper content as well as theoretical curves calculated using the assumptions of different charge compensation mechanisms at substitution of copper for manganese. Based on the analysis of NMR spectra it has been shown [15] that manganese in manganites is in Mn^{3+} and Mn^{4+} states. Mn^{2+} can appear only when there is a considerable number of vacancies in the lanthanum sublattice. Vacancies in the oxygen sublattice do not lead to Mn^{2+} appearance [16]. So in the present work we assumed that manganese is in oxidation states 3+ and 4+ only, while copper can be in different states (1+, 2+, 3+). It was supposed in Ref [12] that the decrease in the unit cell volume is associated with the substitution of copper (3+) for manganese (3+). However it is clear from Fig. 1a (line 3), that the rate of this decrease is much lower than the experimentally observed one (Fig. 1a, curve 4). The calculations showed that a considerable decrease of the unit cell volume would be observed at the substitution of copper for manganese with the formation of oxygen vacancies (Fig. 1a, lines 5-9). The experimental dependence could be described in supposition of different charge compensation mechanisms taking place simultaneously. Some of them can lead to smaller (in comparison with experimental data) variation in unit cell volume (Fig. 1a, lines 1-3), while the other to larger variation (Fig. 1a, lines 5-9).



a

b

Fig. 1. Experimental plot of the unit cell volume (a) and the interatomic Mn–O distance (b) of $La_{0.7}Sr_{0.3}Mn_{1-x}Cu_xO_{3\pm\delta}$ samples as a function of copper content (4) and theoretical plots calculated based on the assumption of different charge compensation mechanisms at substitution of copper for manganese: $2Mn^{3+}\rightarrow Mn^{4+}+Cu^{2+}$ (1); $3Mn^{3+}\rightarrow 2Mn^{4+}+Cu^{1+}$ (2); $Mn^{3+}\rightarrow Cu^{3+}$ (3); $2Mn^{4+}\rightarrow 2Cu^{3+}+V_O^{\bullet\bullet}$ (5); $2Mn^{3+}\rightarrow 2Cu^{2+}+V_O^{\bullet\bullet}$ (6); $Mn^{3+}\rightarrow Cu^{2+}+V_O^{\bullet\bullet}$ (7); $Mn^{3+}\rightarrow Cu^{1+}+V_O^{\bullet\bullet}$ (8); $2Mn^{4+}\rightarrow 2Cu^{1+}+3\,V_O^{\bullet\bullet}$ (9).

It is evident that the unit cell volume depends on a number of factors (the oxidation states of manganese and copper, number of oxygen vacancies). Therefore, to determine the possible charge compensation mechanism, we additionally studied the variations of the interatomic Mn–O distance, saturation magnetization M_s and ferromagnetic resonance (FMR) spectra as a function of copper concentration.

Experimental data showed that the interatomic Mn–O distance increases with the copper concentration increase (Fig. 1b). The increase in the interatomic distance is possible only if there is a contribution from the charge compensation mechanisms involving oxygen vacancies formation. To describe the observed experimental dependences (Fig. 1) we assumed that there are only two charge compensation mechanisms. Based on this supposition we carried out the analysis of possible charge compensation mechanisms, which can provide a good agreement between the theory and experiment. It has been found that the experimental dependences observed in Fig. 1 can be explained by the simultaneous occurrence of the following substitution reactions:

$$2Mn^{3+} \rightarrow Mn^{4+} + Cu^{2+} \text{ and } 2Mn^{3+} \rightarrow 2Cu^{2+} + V_O^{\bullet\bullet} \qquad \text{(I)}$$

or

$$Mn^{3+} \rightarrow Cu^{3+} \text{ and } 2Mn^{4+} \rightarrow 2Cu^{3+} + V_O^{\bullet\bullet} \qquad \text{(II).}$$

It is clear from these reactions that the substitution for manganese can take place both with the participation of copper in 2+ oxidation state or 3+.

At that stage of investigations, it was difficult to make a choice between the mechanisms described by Eqs (I) or (II). The investigations of magnetic properties of $La_{0.7}Sr_{0.3}Mn_{1-x}Cu_xO_{3\pm\delta}$ materials were undertaken to clear up this question. All the samples, except one with $x = 0.15$, are saturated in magnetic fields of about 5 kOe at 10 K .

Figure 2 shows the concentration dependence of saturation magnetization M_s at 10 K. The character of M_s vs. x dependence is considerably changing near x=0.05: for low x (≤ 0.05), the saturation magnetization is practically constant, but at $x > 0.05$ M_s it significantly decreases with x increasing, the dependence being almost linear. The same figure shows calculated $M_s(x)$ plots for two charge compensation mechanisms described by reactions (I) and (II). For $x \leq 0.05$, the experimental data are fairly close to the calculated ones, though the accuracy of the experiment does not allow to give preference to some of the mechanisms. For x values exceeding 0.05 there is a large discrepancy between experimental and calculated curves.

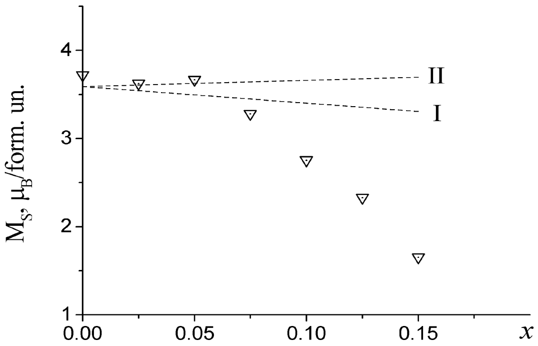


Fig. 2. Experimental plot of the saturation magnetization at 10 K vs. concentration (triangles) and theoretical dependences calculated for two charge compensation mechanisms (according to Eqs (I) and (II)).

To explain the observed experimental data (Fig. 2), we have analyzed the dependences of the Mn^{4+} fraction ($[Mn^{4+}]/[Mn_{total}]$) on copper concentration. At x=0, the Mn^{4+} fraction were determined from the results of a chemical analysis, and for x>0 they were calculated from Eqs (I) and (II) (Fig. 3). It is known [17] that a homogeneous ferromagnetic phase can exist in Sr-containing manganites if the Mn^{4+} content is in the 0.18-0.50 range (hatched area in Fig. 3). Out of this range, the tendency to antiferromagnetic ordering predominates, which gives rise to antiferromagnetism or more complex types of magnetic ordering [17].

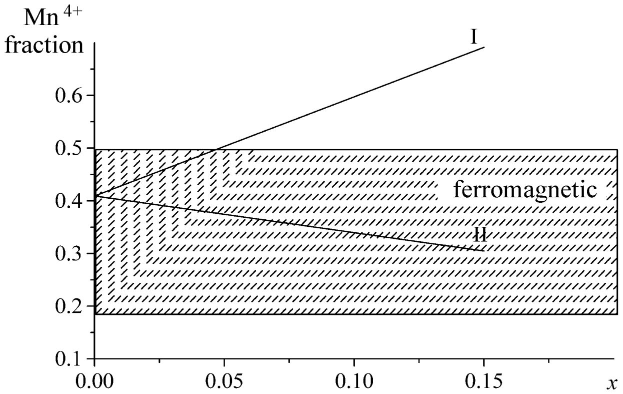


Fig. 3. Mn^{4+} fraction for $La_{0.7}Sr_{0.3}Mn_{1-x}Cu_xO_{3\pm\delta}$ samples calculated in assumption of different charge compensation mechanisms: Eqs I (line I) and II (line II). Hatched area shows the region of existence of a homogeneous ferromagnetic phase.

According to Fig. 3 in the case of the second mechanism (Eqs II) a stable ferromagnetic phase should be observed in the all investigated copper concentration range. Meanwhile in the case of the first mechanism (Eqs. I), the ferromagnetic phase should be stable only up to x~0.05. At higher concentrations of copper it is reasonable to assume a decomposition of the compound into two magnetic phases: ferromagnetic and weak- or non-magnetic, which cannot be saturated even at 50 kOe. To verify this assumption, we run ferromagnetic resonance experiments on $La_{0.7}Sr_{0.3}Mn_{1-x}Cu_xO_{3\pm\delta}$ samples.

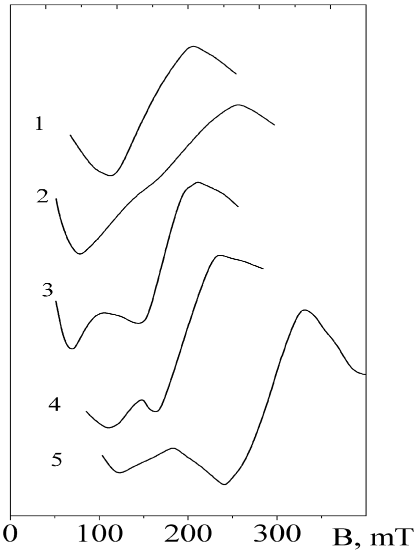


Fig. 4. Ferromagnetic resonance spectra of $La_{0.7}Sr_{0.3}Mn_{1-x}Cu_xO_{3\pm\delta}$ samples with different copper content: $x = 0.025$ (1); 0.050 (2); 0.075 (3); 0.100 (4); 0.150 (5). T=77 K.

Figure 4 shows the evolution of FMR spectra with the variation of copper content. For samples with $x = 0$ and 0.025, the resonance spectrum is a single line with parameters that correspond to the ferromagnetic state of manganites and similar to obtained in other works for $La_{0.7}Sr_{0.3}MnO_3$ samples [18]. For the sample with $x = 0.050$, the line is substantially broadened, indicating an increase in magnetic inhomogeneity. The characteristic feature of the magnetic resonance spectra recorded on the samples with $x > 0.050$ is the presence of two well-defined absorption lines, which correspond to two different magnetic phases. These data are in good agreement with the assumption that the first charge compensation mechanism (Eqs I) takes place. In this case, a homogeneous ferromagnetic phase must be observed up to $x \sim 0.05$, while at $x > 0.05$ a decomposition into two magnetic phases will lead to appearance of the second peak. Thus the substitution of copper ions for manganese in the $La_{0.7}Sr_{0.3}Mn_{1-x}Cu_xO_{3\pm\delta}$ is described by Eqs (I) and copper oxidation state is 2+.

4 Conclusions

Based on the investigations of dependences of the unit cell volume, interatomic Mn–O distances, saturation magnetization, and FMR spectra on copper content, it has been shown that the substitution of copper for manganese in $La_{0.7}Sr_{0.3}Mn_{1-x}Cu_xO_{3\pm\delta}$ compounds can be described by the simultaneous reactions $2Mn^{3+} \rightarrow Mn^{4+} + Cu^{2+}$ and $2Mn^{3+} \rightarrow 2Cu^{2+} + V_O^{\bullet\bullet}$.

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