

Influence of oxygen content on the magnetic properties of B-site deficient lanthanum manganites

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ABSTRACT

The results of X-ray diffraction and magnetization measurements performed for $\text{LaMn}_{0.94}\text{O}_x$ ($2.91 \leq x \leq 3.00$) manganites have been presented. The solid solutions have been found to possess three different structural forms (orbitally ordered orthorhombic, orbitally disordered orthorhombic, and monoclinic ones), depending on the oxygen concentration. The transitions from an antiferromagnetic to an inhomogeneous ferromagnetic, and then to a spin-glass phase have been observed with increasing oxygen content. The experimental results have been discussed in the framework of the ionic distribution model adapted to the case of B-site deficient manganites.

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1. Introduction

Hole-doped lanthanum manganites with a perovskite-like structure are the model objects to study the interactions between magnetic, electronic and structural subsystems. Moreover, these materials are very promising from the viewpoint of their practical application in field of microelectronics and spintronics. Being initially recognized as compounds exhibiting colossal magnetoresistance effect [1,2], today they are also widely known as materials demonstrating a variety of magnetic and structural phase transitions, charge and orbital ordering, magnetic and structural phase separation, magnetic-field-induced insulator-to-metal transition, pressure-induced insulator-to-metal transition and many others intriguing physical phenomena.

The parent compound LaMnO_3 is an orbitally ordered A-type antiferromagnet ($T_N = 140 \text{ K}$) [3]. The antiferrodistortive ordering of the d_{z^2} orbitals is established below $T_{JT} = 750 \text{ K}$ [4] due to the cooperative Jahn–Teller effect breaking the degeneracy of the electronic configuration of the Mn^{3+} ions. Hole doping (i.e., the introduction

of Mn^{4+} ions), which is usually induced by a heterovalent substitution in the A sublattice of the ABO_3 perovskite or by oxidation of stoichiometric LaMnO_3 , leads to remarkable changes in the crystal structure, magnetic, and electrotransport properties of the compound. The crystal structure and magnetic state evolution of the $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ (A is alkali-earth metal) and $\text{LaMnO}_{3+\delta}$ solid solutions under hole doping have been well studied by now, and structural and magnetic phase diagrams of these systems have been already proposed [5,6]. Surprisingly, much less attention is paid to the so-called self-doped manganites (i.e. in which Mn^{4+} ions appear as a result of cation vacancies creation), though they show all the attractive properties which are peculiar to the low-doped manganites.

Recently, we performed a detailed study of the crystal and magnetic structure as well as elastic, magnetic, and electrotransport properties of $\text{La}_{0.88}\text{MnO}_x$ ($2.82 \leq x \leq 2.96$) solid solutions as a function of oxygen content [7]. Under oxygen doping, transition from an antiferromagnetic insulating to a ferromagnetic metallic state was observed. The transition was found to correlate with the change of the type of Jahn–Teller distortions from static to dynamic ones. It was shown that the dynamic orbital correlations favored ferromagnetic state, while A-type antiferromagnetic state was typical for the static Jahn–Teller distortions. The concentrational transition to ferromagnetic phase was shown to occur via the formation of inhomogeneous state with different types of orbital correlations and corresponding types of magnetic structures [7].

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Self-doping of LaMnO_3 by Mn^{4+} ions can be also realized through the creation of B-site vacancies. Only few articles have been devoted to structural and magnetic investigations of B-site deficient lanthanum manganites with varying oxygen stoichiometry [8] or Mn-vacancies concentration [9–11], the presented data being often contradictory (i.e., there is a large difference between the magnetic properties and magnetic phase transition temperatures for the compounds with the very similar chemical compositions). This is probably explained by the great sensitivity of properties of the materials to oxygen stoichiometry (i.e. to preparation conditions). To reveal the effect of oxygen content on the magnetic properties of Mn-deficient compounds we have performed synthesis and investigation of $\text{LaMn}_{0.94}\text{O}_x$ manganites (according to our investigation, this B-sublattice deficiency is the largest one allowing to obtain the single-phase perovskite structure using a solid-state reaction method; further increase of the B-site vacancies resulted in appearance of traces of La_2O_3 impurity phase) and compare the results with those obtained for La-deficient $\text{La}_{0.88}\text{MnO}_x$ system [7]. The difference in the magnetic properties of $\text{LaMn}_{0.94}\text{O}_x$ ($2.91 \leq x \leq 3.00$) and $\text{La}_{0.88}\text{MnO}_x$ ($2.82 \leq x \leq 2.96$) solid solutions is explained within the existing models of ionic distribution in cation-deficient manganites.

2. Experimental

Polycrystalline samples of the $\text{LaMn}_{0.94}\text{O}_x$ manganites were prepared by a solid-state reaction method using high-purity La_2O_3 and Mn_2O_3 reagents. To remove absorbed water, a pre-firing of lanthanum oxide (1000°C , 1 h) was carried out. After that, the compacted mixture of reagents taken in necessary cation ratio was annealed at 950°C for 2 h, reground and pressed into pellets. The parent compound $\text{LaMn}_{0.94}\text{O}_{3.00}$ was obtained through a heat treatment performed at 1300°C for 6 h in air followed by a slow cooling at the rate of $30^\circ\text{C}\cdot\text{h}^{-1}$ down to room temperature. The oxygen content of the material was analyzed through the determination of oxidation equivalent of manganese by iodometric titration with an estimated error of ± 0.015 oxygen per formula. The reduction of the samples was carried out in evacuated quartz ampoules at $T = 1050^\circ\text{C}$ for 24 h using metallic tantalum. All the samples were quenched. The oxygen loss has been checked by the weighing of the samples before and after reduction. To verify the correctness of determination of the oxygen content in the reduced compounds iodometric titration was performed for selected samples. In all the cases, results showed a good agreement with expected values of the oxygen content. Single-phase compounds of $\text{LaMn}_{0.94}\text{O}_x$ manganites were obtained in the concentration range of oxygen $2.91 \leq x \leq 3.00$. This range corresponds to the average valence of manganese ions varying from 3 to ~ 3.19 . Reduction below the nominal value of the oxygen concentration $x = 2.91$ was found to lead to decomposition of the samples into La_2O_3 and MnO oxides. Structural characterization of the compounds has been performed with X-ray diffraction (XRD) experiments. XRD patterns were collected at room temperature using a DRON-3 diffractometer with $\text{Cr K}\alpha$ radiation. The refinement of the unit cell parameters has been carried out using the FullProf program. The measurements of temperature and field dependences of magnetization were performed with OI-3001 commercial vibrating sample magnetometer.

3. Results and discussion

As in the case of the La-deficient manganites $\text{La}_{0.88}\text{MnO}_x$ [7], the solid solutions $\text{LaMn}_{0.94}\text{O}_x$ ($2.91 \leq x \leq 3.00$) have been found to possess three different structural forms, depending on the oxygen content. According to X-ray diffraction data the $\text{LaMn}_{0.94}\text{O}_x$ ($2.91 \leq x \leq 2.95$) samples are characterized by O'-orthorhombic type of unit cell distortion ($b/\sqrt{2} < c < a$), space group $Pnma$ (Fig. 1). The unit cell parameters of the most reduced $\text{LaMn}_{0.94}\text{O}_{2.91}$ compound are very close to those characteristic of LaMnO_3 stoichiometric composition [4]. The unit cell volume decreases as the oxygen content increases, and the transition to the O-orthorhombic crystal structure ($b/\sqrt{2} \approx a < c$) occurs for $x = 2.97$ compound (Fig. 1). The O'-orthorhombic distortions in manganites are due to an antiferrodistortive ordering of the d_{z^2} orbitals of Mn^{3+} ions, while the O-orthorhombic structure corresponds to the orbitally disordered state [12]. Similarly to the most oxidized La-deficient compounds [7,13], the crystal structure of the $\text{LaMn}_{0.94}\text{O}_{3.00}$ parent

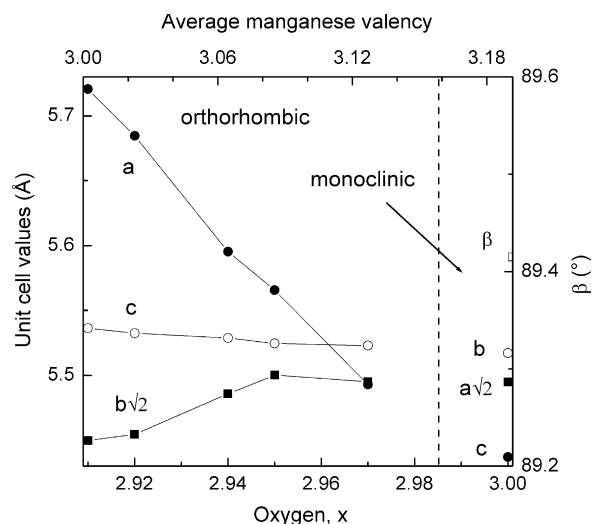


Fig. 1. Room-temperature unit cell parameters of $\text{LaMn}_{0.94}\text{O}_x$ ($2.91 \leq x \leq 3.00$) compounds.

compound can be described within the monoclinic space group $I2/a$ (Fig. 1). It is interesting to note that unit cell parameters of the Mn-deficient compounds are close to those obtained for the La-deficient manganites with corresponding $\text{Mn}^{4+}/\text{Mn}^{3+}$ ratio [7].

The magnetic properties of the most reduced $\text{LaMn}_{0.94}\text{O}_{2.91}$ sample have been found to be similar to those for LaMnO_3 one. The transition to paramagnetic state is observed at $T_N = 140\text{ K}$ (Fig. 2(a)). The compound is characterized by very small spontaneous magnetic moment (about $0.09\mu_B$ per manganese ion) and large coercive field (about 13 kOe), as shown in Fig. 3. Under oxygen doping, the Neel temperature decreases from 140 K for $x = 2.91$ –110 K for $x = 2.94$ (Fig. 2(a–c)). At the same time, increase of the net magnetization and decrease of the coercive field take place (Fig. 3). No change of magnetic ordering temperature is observed for $x = 2.95$ compound in comparison with $x = 2.94$ sample, but significant increase of spontaneous magnetic moment from 1 to $1.7\mu_B/\text{Mn}$ occurs (Figs. 2(d) and 3). For O-orthorhombic $\text{LaMn}_{0.94}\text{O}_{2.97}$ compound, the temperature of the transition to paramagnetic state increases to 128 K. At the same time, slight decrease of spontaneous magnetization value occurs (Fig. 3). Low-temperature behavior of FC and ZFC magnetizations indicates the appearance of a spin-glass component (Fig. 2(e)). In contrast to La-deficient series [7], in which an enhancement of the net magnetization is observed with increasing oxygen content, considerable decrease of spontaneous magnetic moment takes place for monoclinic $x = 3.00$ sample (Fig. 3). The temperature dependence of magnetization of this compound is typical for spin-glasses [14,15]. Super-paramagnetic behavior is developed below 136 K. The temperature of magnetic moments freezing is about 36 K (Fig. 2(f)).

The properties of the most strongly reduced $\text{La}^{3+}\text{Mn}_{0.94}^{3+}\text{O}_{2.91}^{2-}$ samples are similar to the properties of the stoichiometric $\text{La}^{3+}\text{Mn}^{3+}\text{O}_3^{2-}$. Both the compounds have the same $T_N = 140\text{ K}$ (Fig. 2(a)), are weak ferromagnets (Fig. 3), and exhibit the features of the cooperative orbital ordering (Fig. 1 and [8]). On the other hand, the reduced $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{2.85}$ manganite, which also does not contain Mn^{4+} ions, is a spin-glass with the low temperature of the freezing of magnetic moments. No features of the cooperative orbital ordering are observed for the compound [16]. This results from an appearance of oxygen vacancy changing the character of exchange interactions between manganese ions and removing the orbital ordering [16]. Really, d_{z^2} orbitals of Mn^{3+} ions in pentahedron coordination are directed as a rule to oxygen

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