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Solid State Communications 137 (2006) 350–353

solid
state
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Chemical pressure effect on the magnetic order of the $La_{1.4}Sr_{1.6}Mn_2O_7$ bilayered manganite

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Received 5 October 2005; received in revised form 6 December 2005; accepted 12 December 2005 by S. Das Sarma

Abstract

In this paper we have studied, by means of high-resolution neutron powder diffraction, the structural and magnetic feature of pure $La_{1.4}Sr_{1.6}Mn_2O_7$ and Sr-doped (25%) $La_{1.4}Sr_{1.6}Mn_2O_7$.

Our data reveal the stabilization of the A-type AFM long-range order for the $La_{1.4}Sr_{1.6}Mn_2O_7$ bilayered manganites induced by the partial replacement of the Sr with the smaller Ca, keeping constant the hole doping. This can be in turn due to the change in the orbital character of the e_g electrons as a function of Ca-doping.

PACS: 75.47.Lx; 61.12.Ex; 71.70.Ej

Keywords: A. Manganites; A. Perovskites; C. Neutron diffraction

1. Introduction

In recent years there has been an increasing interest in studying the role of pressure, both external and internal (chemical), on the physical properties of different materials with the aim of shedding light on the basic properties of magnetic and other functional complex compounds. Significant efforts have been directed towards strongly correlated and layered materials such as manganites. Within this class most of the available theoretical and experimental work has, until now, been focused on the 3D perovskite structures, that is the $n=\infty$ end-member of the $A_{n+1}B_nO_{3n+1}$ Ruddlesden–Popper family, in which n 2D layers of BO_6 corner-sharing octahedra are joined along the stacking direction and separated by rock-salt AO layers.

The optimally-doped $n=2$ members of this family (La_{2-2x} $B_{1+2x}Mn_2O_7$ where B=Ca or Sr) behave analogously to the $n=\infty$ manganites in the sense that they undergo an insulating- to metallic-like state (I–M) transition coupled to a ferromagnetic transition at temperatures around 120–140 K; besides, they present a large magnetoresistance in this temperature range [1]. However, the change in dimensionality and resulting pronounced cation dependence of the electronic properties can produce physical properties which contrast strongly with the perovskite systems [2–6].

In this paper, we report about the effect induced by chemical pressure on the magnetic order within the $La_{1.4}Sr_{1.6}Mn_2O_7$ manganite. In particular, we prepared and studied, by means of neutron diffraction, the pure $La_{1.4}Sr_{1.6}Mn_2O_7$ sample and another sample in which about 25% of the Sr was replaced by the smaller Ca ($La_{1.4}Sr_{1.2}Ca_{0.4}Mn_2O_7$) while keeping the average Mn valence state constant.

2. Experimental

Samples have been prepared by solid state reaction starting from proper amounts of La_2O_3, Mn_2O_3, $CaCO_3$ and $SrCO_3$ (Aldrich >99.99%). Pellets were prepared from the thoroughly mixed powders and allowed to react first at 1273 K for 72 h and afterwards at 1573 K for 72 h. During the thermal treatments pellets were re-ground and re-pelletized at least three times. In order to control the Mn valence state

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0038-1098/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ssc.2005.12.022

the final thermal treatment was carried out in pure argon. Oxygen content was determined to be 7.00±0.02 through chemical analysis.

Neutron diffraction data were collected on the D1A instrument at the ILL Facility in Grenoble with a wavelength of 1.39 Å at room temperature and of 1.91 Å at 137, 94, 52 and 2 K.

Neutron data were refined by means of the Fullprofile software [7]. We stress that an impurity phase of perovskite structure has been detected and its amount estimated to be around 7%. The presence of this kind of spurious phase is very often encountered when working with double-layered manganites.

3. Results and discussion

Fig. 1(a) reports the neutron diffraction patterns for $La_{1.4}Sr_{1.6}Mn_2O_7$ collected at four different temperatures while Fig. 1(b) presents the same kind of measurements for the $La_{1.4}Sr_{1.2}Ca_{0.4}Mn_2O_7$ compound. Up to now we just measured the samples for a limited number of temperatures. However, even though the full development of the magnetic structure can not be followed through these *T* values, we remark that they cover the most significant *T*-range regarding the magnetic transitions which are placed at around 100 and 60 K for the pure and Ca-doped samples, respectively.

Fig. 1(a), which refers to $La_{1.4}Sr_{1.6}Mn_2O_7$, shows the intensity increase of some nuclear peaks (marked with an asterisk in the Figure) starting from 94 K due to evolution of the magnetic contribution to the intensity. These peaks can be indexed considering a magnetic cell where all the Mn spins are aligned in the same direction within the *a*–*b* planes of the single bilayer and all the successive bilayers are aligned in the same direction thus giving origin to a ferromagnetic (FM) long-range order.

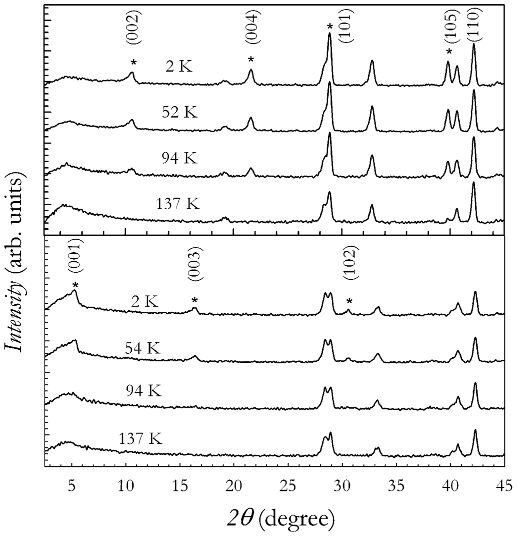

Fig. 1. Neutron patter for $La_{1.4}Sr_{1.6}Mn_2O_7$ (a) and $La_{1.4}Sr_{1.2}Ca_{0.4}Mn_2O_7$ (b) at four different temperatures. Asterisks mark the magnetic peaks whose index are reported in parentheses.

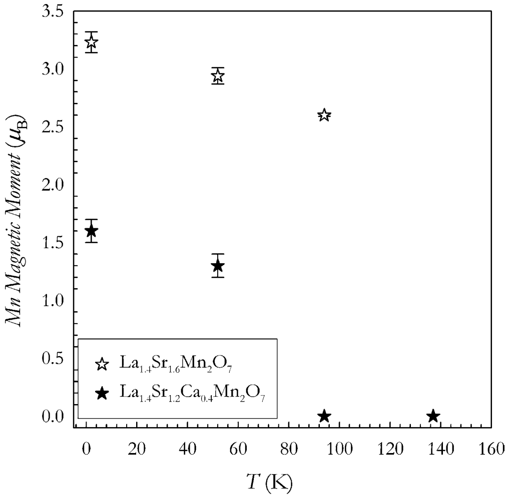

Fig. 2. Magnetic moment as derived from the Rietveld refinements of the magnetic structures for $La_{1.4}Sr_{1.6}Mn_2O_7$ (empty stars) and $La_{1.4}Sr_{1.2}Ca_{0.4}Mn_2O_7$ (full stars) as a function of temperature.

Fig. 1(b) shows that for the $La_{1.4}Sr_{1.2}Ca_{0.4}Mn_2O_7$ sample only the nuclear peaks are visible at 137 and 94 K while, starting from the 54 K pattern, the magnetic peaks become evident. These peaks can be indexed according to an antiferromagnetic (AFM) spin arrangement of the A-type where each layer of the bilayer is FM coupled but the order within the bilayer is AFM. No traces of FM long-range order is present besides the antiferromagnetism.

Fig. 2 shows the magnetic moment of the Mn ions for the two samples (in Bohr magnetons units) as calculated from the Rietveld refinements of the magnetic structure, as a function of temperature. For the $La_{1.4}Sr_{1.6}Mn_2O_7$ sample the value of the magnetic moment at 2 K is not far from the expected value of 3.70 μ_B, while for the $La_{1.4}Sr_{1.2}Ca_{0.4}Mn_2O_7$ sample it is lower, thus suggesting that some spin-canting may occur. In fact, a possible rotation along the *c*-axis of the AFM structure may not be ruled out even though it would be very small since no traces of long-range FM peaks in the $La_{1.4}Sr_{1.2}Ca_{0.4}Mn_2O_7$ pattern have been found. Also the possibility of a canting with respect to the parallel alignment of the spin in the two layers composing the bilayers would give origin to FM peaks. This relatively small moment might also originate from some spin disorder connected to the Ca-doping, which will lower the value of the net magnetic moment. However, the present data does not allow to get further insight into this topic that will be analysed by collecting more accurate data especially at low angles (<5°).

The striking feature of our finding is the marked difference in the magnetic behaviour between two samples presenting the same amount of hole doping. The presence of the same Mn valence state (∼3.30) was confirmed through extensive X-ray absorption spectroscopy (XAS) analysis at the Mn–K edge. Fig. 3 shows the edge region for the two samples presented in this paper, where the vertical line indicates the maximum position. It is clear that, within the experimental