ELSEVIER

Journal of Alloys and Compounds 262–263 (1997) 152–156

Journal of ALLOYS AND COMPOUNDS

Structural phase diagram of $La_{1-x}Sr_xMnO_3$ for low Sr doping

L. Pinsard[a,*], J. Rodríguez-Carvajal[b], A. Revcolevschi[a]

[a] Laboratoire de Chimie des Solides Bât. 414, URA 446 CNRS, Université Paris-Sud, 91405 Orsay Cedex, France
[b] Laboratoire Léon Brillouin (CEA-CNRS), CE de Saclay, 91191 Gif sur Yvette Cedex, France

Abstract

The Mn-based perovskite oxides are of strong current interest because they show a colossal negative magnetoresistance near the ferromagnetic ordering temperature. The samples become metallic below T_C for a content of approx. 30% Mn^{4+}. We present in this article a structural study of $La_{1-x}Sr_xMnO_3$ for compositions lying below the optimum magnetoresistance. At high temperature, the system is rhombohedral ($R\bar{3}c$). On cooling, two structural transitions to orthorhombic Pbnm phases (O and O′) take place successively. The transition from the O to the O′-phase is due to the setting up of co-operative Jahn–Teller distortions that become static in the O′-phase. The O′-phase is characterised by the presence of an anti-ferrodistorsive Mn^{3+} orbital ordering. This ordering is evidenced by a peculiar arrangement of distorted MnO_6 octahedra: the connection between octahedra in the basal plane (a, b) shows long Mn–O bonds adjacent to short Mn–O bonds. The peculiarity of samples around the composition $x=0.125$ is that they undergo another transition to an orthorhombic O″-phase at lower temperatures. This phase has the same average structural features as the O-phase but the Jahn–Teller distortion seems to be completely suppressed. © Elsevier Science S.A.

Keywords: Jahn–Teller effect; Structural transitions; Perovskite compounds

1. Introduction

The perovskite structure oxides containing Mn ions have recently been the object of a strong interest [1–4] due to the complicated interplay between electronic, magnetic and structural properties that gives rise to several interesting phenomena such as colossal magnetoresistance (CMR) and charge ordering (CO) effects. The parent compound, $LaMnO_3$, is an antiferromagnetic insulator in which an orbital ordering is established due to the co-operative Jahn–Teller (JT) effect. Doping this compound with Sr^{2+} allows hopping of the e_g electron, belonging to a Mn^{3+} ion, to neighbouring sites containing Mn^{4+} ions. This introduces a new exchange mechanism (double exchange) favouring the ferromagnetic interactions [5], due to a strong on-site Hund coupling, between neighbouring sites. Millis [6] has proposed that the influence of the JT effect, as a consequence of the presence of Mn^{3+} ions, plays an important role in the magnetic and transport properties in the lightly-doped manganese system. The degree of co-operative JT effect can be studied using diffraction techniques which allow the determination of the octahedral distortion. The diffraction results can be compared closely with the results obtained from macroscopic physical properties in order to gain insight into the involved physics.

Recently, x-T and x-P_{O_2} structural phase diagrams of $La_{1-x}Sr_xMnO_3$ have been studied by Kawano [7] and Mitchell [8], respectively. But apart from these recent articles providing a rough characterisation,

---

[*] Corresponding author. E-mail: pinsard@psisun.u-psud.fr

0925-8388/97/$17.00
PII S0925-8388(97)00371-X

there has been little work done on this system since Wollan and Koehler [9]. In the present article, we present new details of the phase diagram and preliminary results of a structural study performed on the solid solution $La_{1-x}Sr_xMnO_3$ $(0 \leq x \leq 0.20)$ using neutron powder diffraction. A more detailed and precise structural determination on single crystals is presently being undertaken.

2. Experimental

Powder samples were obtained by crushing crystalline ingots grown by the floating zone method. Such a procedure makes possible the preparation of materials of homogeneous composition. Transport and thermal properties are measured on the same ingots so that a clear correlation with the thermal behaviour of the structure can be established.

Differential thermal analysis (DTA and DSC) experiments were carried out in a SETARAM TGDTA 92-16 device in a temperature range 150–1500 K, the experiments being performed under argon flow at a heating rate of 10°C min^{-1}. The temperatures defining the phase diagram have been obtained analysing the data of the DSC and DTA curves.

Several powder diffractometers of the Orphée Reactor at LLB were used in this study. The banana type diffractometer G4.1 ($\lambda = 2.43$ Å) and the high resolution powder diffractometers G4.2 ($\lambda = 2.59$ Å, or $\lambda = 1.99$ Å, $Q_{max} = 6.2$ $Å^{-1}$) and 3T2 ($\lambda = 1.22$ Å, $Q_{max} = 9.2$ $Å^{-1}$) were used for refining the crystal and magnetic structure as a function of temperature, using a standard Orange cryostat. The Rietveld method implemented in the program FULLPROF [10] has been used for crystal and magnetic structure refinements.

In this article we present the results obtained with the medium resolution diffractometer G4.1 because, even if the errors in position parameters are larger, with this equipment we obtain a good picture of the structural behaviour of the studied samples as a function of temperature.

3. Results and discussion

Recent studies [11,12] carried out on pure $LaMnO_3$ indicate that the compound undergoes two structural transitions at $T_{OO'}$ and T_{RO}, above room temperature. At room temperature, the orthorhombic *Pbnm* (O′) crystal structure shows the anti-ferrodistorsive orbital ordering due to the co-operative JT effect (Fig. 1). In this O′-phase, there is a large distortion of the MnO_6 octahedra. A transition from the O′-phase to the O-phase takes place at $T_{OO'}$. The O-phase is pseudo-cubic with $c/\sqrt{2} \approx b \approx a$ and the Mn–O bond lengths are almost equal, indicating that no orbital ordering occurs: the JT effect becomes dynamic. This transition does not change the average crystallographic symmetry; the space group remains *Pbnm*. At higher temperature, a transition to a rhombohedral phase ($R\bar{3}c$) occurs. Within the rhombohedral symmetry the JT distortion is not allowed, so the high temperature phase continues to display a dynamic JT effect. Through these transitions the average tilt angle of the MnO_6 octahedra evolves continuously towards a smaller value with increasing temperature [12].

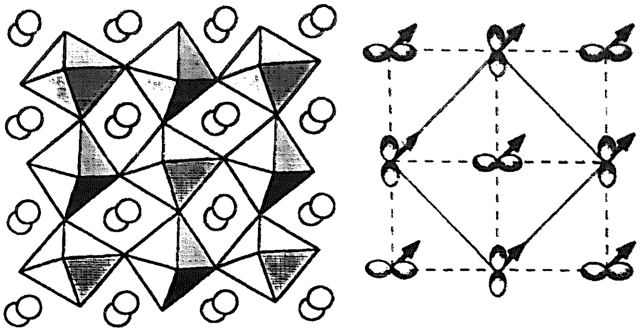

Fig. 1. Scheme of the crystal structure and the in-plane antiferrodistorsive orbital ordering observed in $LaMnO_3$.

These transitions continue to exist when pure $LaMnO_3$ is doped with divalent Sr^{2+} ions. We have studied the evolution of these structural transitions as a function of the Sr content that we assume to correspond to the amount of Mn^{4+} in the samples. This last assumption is consistent, within the experimental error, with the refinement of occupation factors. These have been fixed to the nominal values in the final refinements. The structural phase diagram of $La_{1-x}Sr_xMnO_3$ as a function of doping content x, is

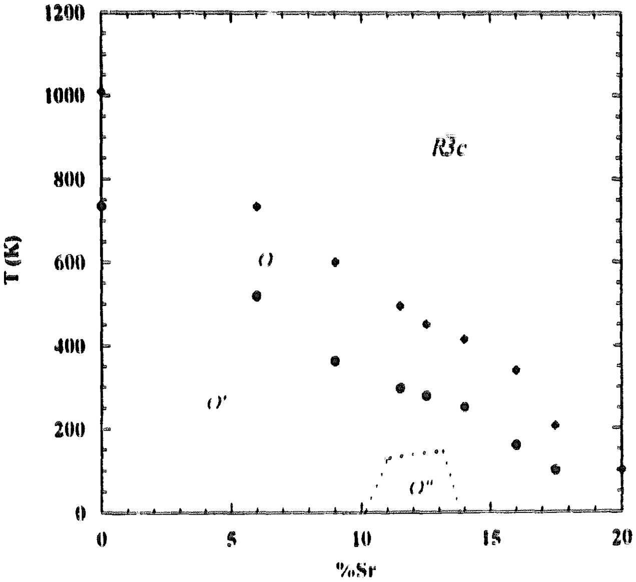

Fig. 2. Structural phase diagram of $La_{1-x}Sr_xMnO_3$ as a function of Sr content.

shown in Fig. 2 (we have labelled all samples by their nominal Sr concentrations). For Sr concentrations within the $0 \leq x \leq 0.20$ range, the three phases $R\bar{3}c$, O and O′ observed in LaMnO$_3$, are unambiguously observed. When the concentration of Sr^{2+} increases, we note a nearly linear decrease of the transition temperatures. This behaviour can be explained qualitatively: in all cases we observed that at $T_{OO'}$, upon heating, the distortion of the octahedra when going from the O′-phase to the O-phase diminishes drastically, indicating the disappearance of the co-operative orbital ordering due to the JT effect associated with the Mn^{3+} ions. The introduction, through the doping with Sr^{2+}, of Mn^{4+} ions which have empty e_g orbitals on the octahedral sites, reduces the number of ions participating in the distortion of the octahedra. At the same time, the effective tolerance ratio increases towards unity. Consequently, temperatures of the structural transitions, $R\bar{3}c \rightarrow$ O, driven mainly by steric effects and O → O′, driven by the JT electron-phonon coupling, decrease upon increasing the concentration of Mn^{4+}.

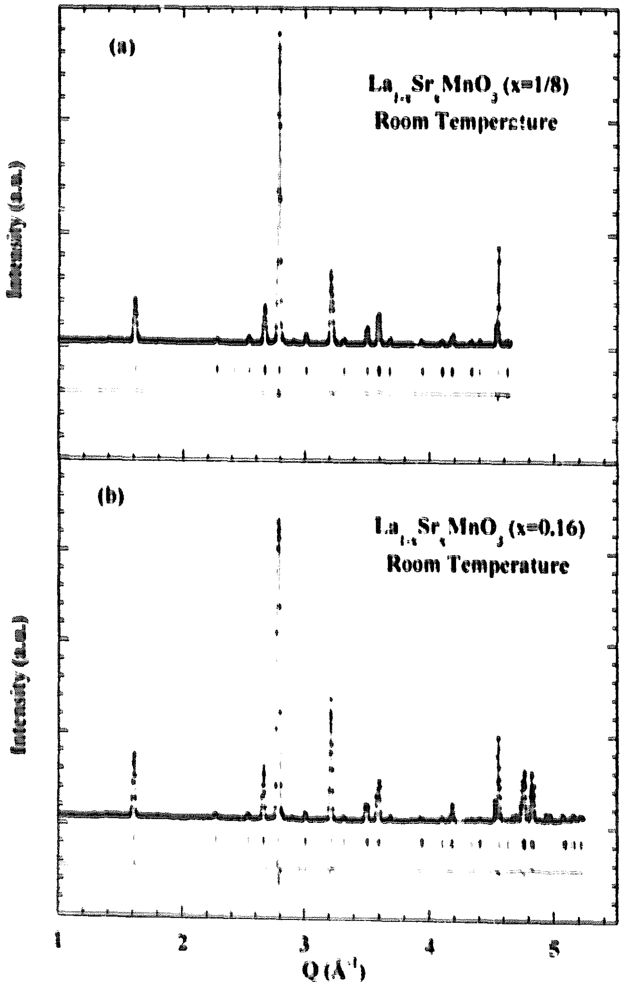

Fig. 3. Observed and calculated neutron powder diffraction patterns of the compound La$_{7/8}$Sr$_{1/8}$MnO$_3$ (a) and La$_{0.84}$Sr$_{0.16}$MnO$_3$ (b) (Phase O) at room temperature.

We have investigated by neutron powder diffraction two selected compositions $x = 1/8$ and $x = 0.16$. We have refined the average crystal and magnetic structures of both compounds in the whole investigated temperature range with the space group Pbnm that perfectly fits the observed powder diffraction patterns (see Fig. 3). The same main feature for the O-phase and the O′-phase, previously described for LaMnO$_3$, is observed, namely a clear reduction upon heating of the JT distortion through the transition O′ → O at $T_{OO'}$. This transition is accompanied by an inversion of the lattice parameters: a, b for La$_{7/8}$Sr$_{1/8}$MnO$_3$ and b, $c/\sqrt{2}$ for La$_{0.84}$Sr$_{0.16}$MnO$_3$ (see Fig. 4). The evolution of the Mn–O bond lengths as a function of temperature is shown in Fig. 5. It is clear that for $x = 0.16$ only the transition O′ → O occurs at low temperature. The compound remains within the O′ phase at low temperature.

For doping near $x = 1/8$ [13], the system undergoes another transition to an orthorhombic O″-phase at lower temperature $T_{O'O''}$. This phase has the same average structural features as the O-phase: the JT distortion seems to be suppressed (see Fig. 5). In Table 1, we have summarized the structural parame-

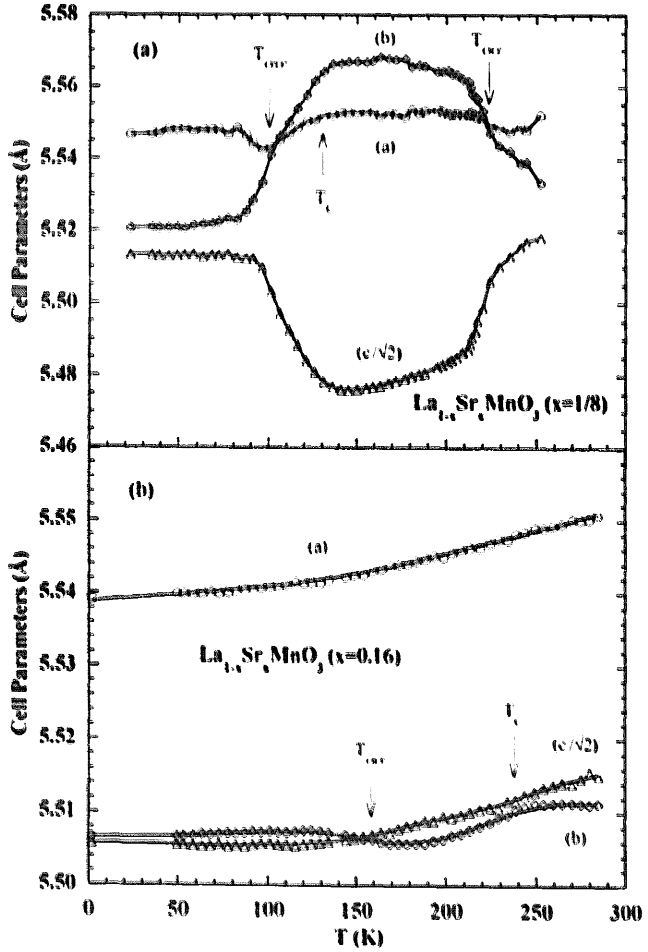

Fig. 4. Lattice parameters a, b and $c/\sqrt{2}$ as a function of temperature for (a) La$_{7/8}$Sr$_{1/8}$MnO$_3$ and (b) La$_{0.84}$Sr$_{0.16}$MnO$_3$.

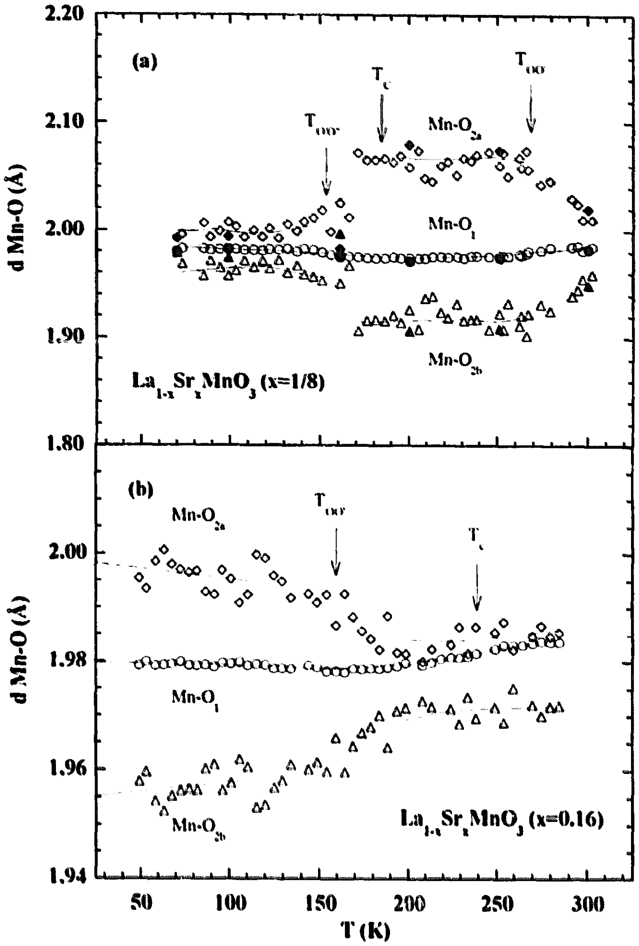

Fig. 5. Mn–O distances as a function of temperature for (a) $La_{7/8}Sr_{1/8}MnO_3$ and (b) $La_{0.84}Sr_{0.16}MnO_3$: $Mn–O_1$ apical distance; $Mn–O_2$ equatorial distance. The full symbols in (a) correspond to the results obtained from data collected on the G4.2 diffractometer; they are more precise than the other.

ters obtained by the Rietveld method. The O″-phase has been called a re-entrant phase [7,13] because it bears a strong similarity with the O-phase. Kawano et al. consider that the system exhibits a re-entrant structural transition of the type O → O′ → O (actually, these authors called O* the O-phase). However, recent investigations carried out with single crystals [14] allow us to disregard this denomination for the O″-phase. Yamada et al. [14] have found a set of superstructure reflections for samples $x = 0.10$ and $x = 0.15$ that occur in the low temperature phase of these compounds. These authors mention a 'polaron-ordered phase' that orders with a propagation vector $\mathbf{q} = (0, 0, 1/2)$ with respect to the *Pbnm* setting. They have proposed a scheme of the Mn^{3+}–Mn^{4+} ordering based on the observed superstructure peaks, but no quantitative analysis of the diffracted intensities were performed, so they do not give any indication of the octahedral distortions accompanying the two Mn species. It is clear to us that a charge localisation occurs in the O″-phase. The transport properties of the compound clearly indicate a metal-to-insulator transition on cooling at $T_{O'O''}$. The transition temperature coincides with the appearance of a very small canting of the ferromagnetic order ($T_{CA} \approx 150$ K). We have detected the canting by monitoring, as a function of temperature, the intensity of the reflection (003) using a single crystal. This reflection is forbidden for the crystal structure and for pure ferromagnetism. The appearance of a net intensity below $T_{O'O''}$ indicates the presence of a canting. This study shows the existence of a strong coupling between JT distortion, ferromagnetic ordering and transport properties in this compound. The disappearance or the reduction of the static JT effect upon the setting up of ferromagnetic ordering is a common characteristic of all Mn-perovskites showing CMR (namely for $x \approx 0.3$) and can be qualitatively understood. When the ferromagnetic ordering sets up, it favours the charge mobility, due to the double exchange mechanism; so that the co-operative static JT effect which is caused by the presence of a high concentration of Mn^{3+} ions disappears (or is strongly reduced) in the solid when charge carriers, that should be some kind of JT-polarons, become mobile. The puzzling question raised by this study is the origin of the charge localisation observed below $T_{O'O''}$. This charge localisation seems to be not accompanied by a restoration of the JT effect, so a new type of electronic ordering should take place. On the other hand, it is quite surprising that a small canting of the ferromagnetic structure could be at the origin of this localisation.

It is obvious that the $x = 1/8$ concentration plays a

Table 1
Refined parameters of the *Pbnm* phase for $La_{7/8}Sr_{1/8}MnO_3$ for three selected temperatures

T (K) phase		100 K O″	200 K O′	300 K O
a (Å)		5.5351(4)	5.5489(4)	5.5448(2)
b (Å)		5.5187(3)	5.5598(4)	5.5258(2)
c (Å)		7.7903(4)	7.7375(4)	7.7927(3)
La (4c)	x	0.0005(9)	−0.0023(7)	−0.0031(6)
	y	0.0217(6)	0.0249(6)	0.0191(5)
O1 (4c)	x	0.0659(10)	0.0678(8)	0.0664(7)
	y	0.4900(8)	0.4910(9)	0.4923(8)
O2 (8d)	x	0.7251(9)	0.7358(15)	0.7308(9)
	y	0.2779(8)	0.2865(7)	0.2785(7)
	z	0.0360(4)	0.0358(4)	0.0353(3)
Mn μ_B		3.36(3)	—	—
R_{nucl}		4.14	5.68	3.08
R_{mag}		1.84	—	—
χ^2		1.98	2.60	1.07

Data collection has been performed on the diffractometer G4.2, using a wavelength of 2.59 Å.

crucial role in the present system. The commensurability of the hole concentration may be determinant for the existence of the low temperature phase transitions. Nevertheless, a deeper investigation using single crystal neutron diffraction, of the structural and magnetic features of the samples around $x = 1/8$ is needed to properly understand the fascinating behaviour of these manganites.

References

[1] R. von Helmont, J. Wecker, B. Holzapfel, L. Schultz, K. Samwer, Phys. Rev. Lett. 71 (1993) 2331.
[2] S. Jin, T.H. Tiefel, M. McCormack, R.A. Fastnacht, R. Ramesh, L.H. Chen, Science 264 (1994) 413.
[3] Y. Tokura, A. Urushibara, Y. Moritomo, et al., J. Phys. Soc. Jpn 63 (1994) 3931.
[4] A. Urushibara, Y. Moritomo, T. Arima, A. Asamitsu, G. Kido, Y. Tokura, Phys. Rev. B 51 (1995) 14103.
[5] P.G. de Gennes, Phys. Rev. 118 (1960) 141.
[6] A.J. Millis, P.B. Littlewood, B.I. Shraiman, Phys. Rev. Lett. 74 (1995) 5144.
[7] H. Kawano, R. Kajimoto, M. Kubota, H. Yoshizawa, Phys. Rev. B 53 (1996) R14709.
[8] J.F. Mitchell, D.N. Argyriou, C.D. Potter, D.G. Hinks, J.D. Jorgensen, S.D. Bader, Phys. Rev. B 54 (1996) 6172.
[9] E.O. Wollan, W.C. Koehler, Phys. Rev. 100 (1960) 141.
[10] J. Rodríguez-Carvajal, Physica B 192 (1993) 55.
[11] P. Norby, I.G. Krogh Andersen, E. Krogh Andersen, N.H. Andersen, J. Solid State Chem. 119 (1995) 191.
[12] J. Rodríguez-Carvajal, M. Hennion, F. Moussa, L. Pinsard, A. Revcolevschi, Physica B 234-236 (1997) 848-850.
[13] L. Pinsard, J. Rodríguez-Carvajal, A.H. Moudden, A. Anane, A. Revcolevschi, C. Dupas, Physica B 234-236 (1997) 856-858.
[14] Y. Yamada, O. Hino, S. Nohdo, R. Kanao, T. Inami, S. Katano, Phys. Rev. Lett. 77 (1996) 904.