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The Effect on Highly Cr-Substituted Manganite $Nd_{0.6}Ca_{0.4}(Mn_{0.5}Cr_{0.5})O_3$

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Neutron powder-diffraction experiments on the highly Cr-substituted manganite, $Nd_{0.6}Ca_{0.4}(Mn_{0.5}Cr_{0.5})O_3$, at different temperatures and fields reveal that the structure retains the charge exchange-type of the parent compound, $Nd_{0.6}Ca_{0.4}MnO_3$. It is antiferromagnetic below 200 K and becomes a canted antiferromagnet below 50 K. The Mn and Cr form zig-zag ferromagnetic chains coupled antiferromagnetically in the *ac*-plane. These are stacked along the *b*-axis with opposite spins.

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1. Introduction

Doping of the Mn-sublattice by such magnetic cations as Cr, Ru, Co, in rich Mn^{4+} charge ordered (CO) and orbital ordered (OO) manganites with the charge exchange (CE) structure which are known to be antiferromagnets (AF) and insulators (I) induces a transition to ferromagnetic (FM) and metallic (M) states even in the absence of a magnetic field [1–8]. The appearance of ferromagnetism is attributed to phase separation [9]. For low doping of Cr, it has been observed that Cr forms FM clusters within the AF matrix which grow at the expense of the AF structure: as the doping of Cr is increased the FM clusters are spread into

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layers. The transition from an AF–I state to FM–M one is very interesting for their potential applications.

In the present paper, we present neutron powder neutron diffraction (NPD) experiments on the rich Cr doped manganite $Nd_{0.6}Ca_{0.4}(Mn_{0.5}Cr_{0.5})O_3$. The compound keeps the CE structure as the parent compound $Nd_{0.6}Ca_{0.4}MnO_3$ [10] but the CO–OO is destroyed. Mn and Cr form AF zig-zag chains on the basal plane and are coupled AF along the b axis of the orthorhombic *Pnma* structure.

2. Experimental

The sample was synthesized from simple oxides and carbonates at (1400–1500)°C in air using a conventional ceramic technology. X-ray diffraction at room temperature did not reveal extra lines, within the accuracy of the method, to indicate the presence of impurity phases.

NPD experiments were performed on the E6 diffractometer at BENSC in Hahn–Meitner Institute (Berlin), using a wavelength of 2.4422 Å from a pyrolytic graphite monochromator. The angular resolution was $10'$. The data were recorded over an angular range of 10–95° after no reflection was detected below 10° at any temperature in the range of 1.8–300 K within the instrumental resolution. At first, the 300 K pattern was recorded and after the sample was cooled down to 1.8 K. Between 1.8 and 300 K a number of patterns were recorded at 200, 100, 50 and 1.8 K. The obtained patterns were refined with the Rietveld method using the Fullprof program.

3. Results and discussion

3.1. Nuclear structure

NPD patterns at selected temperatures are shown in Fig. 1. The refinement of the room temperature NPD data confirmed the space group *Pnma* in agreement with the X-rays results. Neither additional reflections were observed nor any splitting in any of the reflection indicating CO–OO state at any temperature. Two very weak reflections appeared at the angles where the superstructure reflections 2,1.5,0 and 2,2.5,0 could appear if the sample adopted a CO–OO state. The intensity of these reflections was very weak and they did not change with temperature and they were almost diffused in the background. Thus, they were excluded from the refinement. It must be pointed out that the absence of any additional peaks cannot be taken as a proof for the absence of CO as the intensity of these peaks is often very low in neutron diffraction and need a high intensity powder diffractometer. In the refinement Mn and Cr share the same site $4a$ of the *Pnma* group. The lattice parameters that we obtained from the refinement at 200 K, above the transition temperature, are: $a = 5.4096(3)$, $b = 7.6144(2)$ and $c = 5.3870(3)$ and reliability factors $R_B = 1.33$, $R_f = 2.23$ and $\chi^2 = 5.6$. The relation of the lattice

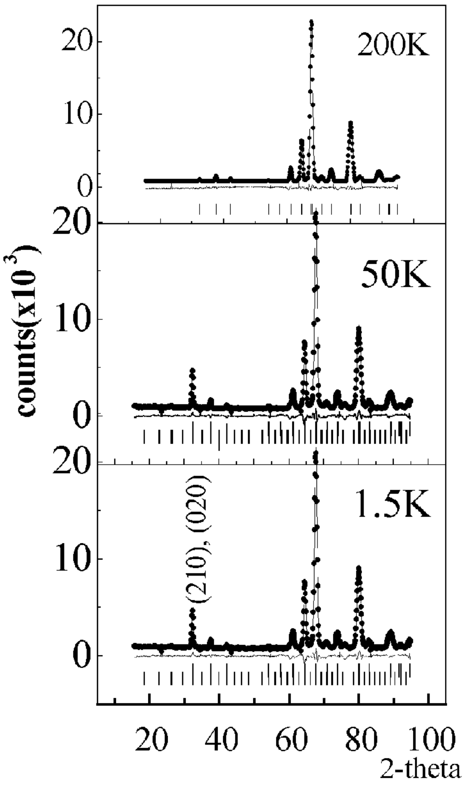

Fig. 1. Selected NPD patterns: points — the experimental data and line — the fitting: the vertical lines indicate the Bragg positions.

parameters is $c < b^{1/2} < a$ which indicates that the structure is of the O* type. This relation remains at all temperatures.

Since during cooling no additional lines or line splitting were detected in the specimen, the nuclear refinements at low temperatures were carried out in the *Pnma* space group, characteristic of the structure above the transition temperature. The lattice parameters variation with temperature is shown. Down to 130 K

TABLE I

Structural parameters (Å) as they were found from the data of neutron diffraction. Space group *Pnma*.

	200 K	100 K	50 K	1.8 K
a	5.4090(3)	5.4096(3)	5.4072(3)	5.4086(3)
b	7.6144(2)	7.6054(2)	7.6047(3)	7.6159(2)
c	5.3870(3)	5.4027(2)	7.6095(3)	5.3867(3)

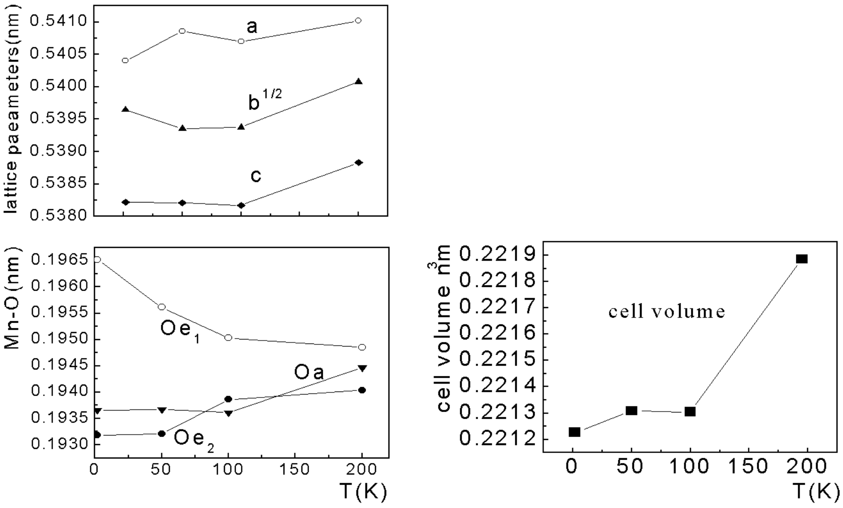

Fig. 2. The structural parameters vs. temperature. Oe and Oa are the equatorial and the apical bond lengths.

TABLE II

Selected atomic distances and angles at 200 and 1.8 K as they were found from the data of neutron diffraction. Space group *Pnma*. Oe, Oa basal and apical oxygens correspondingly.

	200 K	1.8 K
distances (Mn,Cr)–O (Å)		
(Mn,Cr)–Oe_1	1.9404(×2)	1.9345(×2)
(Mn,Cr)–Oe_2	1.9485(×2)	1.9423(×2)
(Mn,Cr)–Oa	1.9447(×2)	1.9345(×2)
angles O_1–Mn–O_2		
	88.56	91.73
angles (Mn,Cr)–O–Mn		
(Mn,Cr)–Oe–(Mn,Cr)	156.52(1.59)	159.02(1.59)
(Mn,Cr)–Oa–(Mn,Cr)	158.59(0.13)	156.50(0.13)
reliability factors		
R_B	1.93	4.46
R_p	5.63	12.0
R_{wp}	8.2	11.0
χ^2	4.89	6.2
R_{magn}		7.5

all parameters decrease monotonically. In the range of 50–130 K the a and b parameters remain unaltered while the a parameter increases slightly. Below 50 K the a parameter decreases while the b parameter increases. The absence of any sudden jump of the lattice parameters could be taken as an indication of the absence of CO state. The overall changes are 0.59, 0.10 and 0.08% for the lattice parameters a, c, and b, respectively. The structural parameters, the bond lengths of MnO_6 and the cell volume with respect to temperature are shown in Fig. 2, too, and Tables I, II. These octahedra blocks are randomly occupied by Mn^{3+}, Cr^{3+}, and Mn^{4+}. At 200 K the distortion is rather small. As the temperature decreases the apical bond length (Oa) and one of the equatorial lengths (Oe_2) decrease by 0.0051 and 0.0088 Å, respectively while the other equatorial one (Oe_1) increases by 0.167 Å. The net effect is a large breathing motion of the equatorial plane of the octahedron.

3.2. Magnetic structure

The NPD patterns below 160 K show an additional intensity in some of the diffraction peaks, Fig. 1. Although nuclear scattering is allowed at this position, the refinement in the *Pnma* structure is very poor. Finally, the best refinement was obtained quadrupling the volume of the original orthorhombic unit cell, $2a \times b \times 2c$, known as the CE structure. The Cr and Mn ions are distributed in the sixteen sites developed by the b-site of the *Pnma* space group. Their moments are opposite directed forming zig-zag AF chains in the basal plane, $z = 0$. These chains are alternatively AF coupled with the chains in the plane $z = 1/2$. The magnetic moments are directed along the a-axis and their values are given in Table III. At 100 K a compensation point is obtained. Below 50 K a better fitting was obtained with a small FM moment along the c-axis. With the present data it was not possible to decide whether the FM moment was originated from canting or phase separation.

TABLE III

The components of the magnetic moments at different sites.

	100 K	50 K	1.8 K		100 K	50 K	1.8 K
1/4,0,0		−2.10	−2.2	0,0,1/4	1.84	2.07	2.37
3/4,0,0	−1.83	−2.10	−2.0	0,0,3/4	1.84	2.07	2.37
1/4,0,1/2	−1.83	−2.10	−2.2	1/2,0,1/2	1.84	2.07	2.37
3/4,0,1/2	−1.83	−2.10	−2.2	1/2,0,3/4	1.84	2.07	2.37
1/4,1/2,0	1.84	2.21	2.34	0,1/2,1/4	−1.84	−2.22	−2.25
3/4,1/2,0	1.84	2.21	2.34	0,1/2,3/4	−1.84	−2.22	−2.25
1/2,1/2,0	1.84	2.21	2.34	1/2,1/2,1/2	−1.84	−2.22	−2.25
3/4,1/2,1/2	1.84	2.21	2.34	1/2,1/2,3/4	−1.84	−2.22	−2.25

The Nd sublattice did not indicate any ordering down to the lowest temperature which is an indication of no correlation between Mn and Nd.

4. Summary

In the highly doped manganite with Cr^{3+} $Nd_{0.62}Ca_{0.38}Mn_{0.5}Cr_{0.5}O_3$ the magnetic unit cell doubles the nuclear along the a and c axis and keeps the CE structure of the parent compound $Nd_{0.6}Ca_{0.4}MnO_3$ and melts the CO–OO. The collapse of the CO–OO state by Cr doping has been also observed in light doping by Cr [11]. The structure consists of Cr and Mn forming AF chains lying on the ac plane and at low temperatures there is an indication of a slight canted AF structure.

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References

[1] R. Gundakaram, A. Arulraj, P.V. Vanitha, C.N.R. Rao, N. Gayathri, A.K. Raychaudhuri, A.K. Cheetham, *J. Solid State Chem.* **127,** 354 (1996).

[2] B. Raveau, A. Maignan, C. Martin, *J. Solid State Chem.* **130,** 162 (1997).

[3] C. Martin, A. Maignan, F. Damay, M. Hervieu, B. Raveau, Z. Jirak, G. André, F. Bourée, *J. Magn. Magn. Mater.* **202,** 11 (1999).

[4] G.H. Rao, J.R. Sun, A. Kattwinkel, L. Haupt, K. Bärner, E. Schmitt, E. Gmelin, *Physica B* **269,** 379 (1999).

[5] O. Toulemonde, F. Studer, A. Barnabé, B. Raveau, J.B. Goedkoop, *J. Appl. Phys.* **86,** 2616 (1999).

[6] B. Raveau, A. Maignan, C. Martin, R. Mahendiran, M. Hervieu, *J. Solid State Chem.* **151,** 330 (2000).

[7] B. Raveau, C. Martin, A. Maignan, M. Hervieu, R. Mahendiran, *Physica C* **341,** 711 (2000).

[8] I.O. Troyanchuk, M.V. Bushynski, N.V. Pushkarev, H. Szymczak, K. Bärner, *J. Magn. Magn. Mater.* **225,** 331 (2001).

[9] R. Mahendiran, B. Raveau, M. Hervieu, C. Michel, A. Maignan, *Phys. Rev. B* **64,** 064424 (2001).

[10] J. López, P.N. Lisboa-Filho, W.A.C. Passos, W.A. Ortiz, F.M. Araujo-Moreira, O.F. de Lima, D. Schaniel, K. Ghosh, *Phys. Rev. B* **63,** 224422 (2001).

[11] T. Kimura, Y. Tomioka, R. Kumai, Y. Okimoto, Y. Tokura, *Phys. Rev. Let.* **83,** 3940 (1999).