TECHNICAL ARTICLE

Ferromagnetic ordering in $La_{0.7}Sr_{0.3}Mn^{3+}_{0.85}Nb^{5+}_{0.15}O_3$ manganite

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Structural measurements have been performed on the $La_{0.7}Sr_{0.3}Mn^{3+}_{0.85}Nb^{5+}_{0.15}O_3$ compound with oxidation state of manganese close to +3. The composition undergoes a structural transition from rhombohedral to orthorhombic symmetry below room temperature. The calculated structural parameters show that the orthorhombic phase is not long-range orbitally ordered and that the structural transition is associated with a steric effect. The compound is ferromagnetic with a Curie point of around 150 K and a magnetic moment of 3.1 μ_B/Mn. It is suggested that ferromagnetism is originated from superexchange interactions via oxygen. Covalence enhances the positive part of the superexchange interactions whereas structural disorder leads to suppression of ferromagnetism. © *2015 International Centre for Diffraction Data.* [doi:10.1017/S0885715615000032]

I. INTRODUCTION

$La_{1-x}A_xMnO_3$ (A = Ca, Sr, Ba) mixed valence manganites have been of interest for many years since they exhibit very intriguing magnetic and magnetotransport properties (Zener, 1951; Pirogov *et al.*, 1999; Dagotto *et al.*, 2001; Şen *et al.*, 2007). To explain the interplay between magnetic and transport properties Zener introduced a special form of exchange interactions through charge carriers (Mn^{4+}) – double exchange (Zener, 1951). However, it was found that the ferromagnetic state can be realized even in compounds containing only manganese of valence 3 (Bents, 1957; Goodenough, 1963; Troyanchuk *et al.*, 1997; Zhou *et al.*, 2001; Blasco *et al.*, 2002; Deisenhofer *et al.*, 2002; Troyanchuk *et al.*, 2002; Zhou *et al.*, 2008). For example the parent $LaMnO_3$ exhibits ferromagnetic interactions in the orbitally disordered phase (T > 750 K) with an approximate Curie point around 160 K (Zhou and Goodenough, 1999). Long-range ferromagnetism is observed in the $LaMn_{1-x}Ga_xO_3$ (0.2 < x < 0.6) and $LaMn_{1-x}Cr_xO_3$ (0.2 < x < 0.6) series containing only Mn^{3+}. Both these series show a gradual transition into an orbitally disordered state upon Ga^{3+}(x > 0.5) or Cr^{3+}(x > 0.35) substitution. The origin of the ferromagnetic state in single valent manganites is a matter of discussion. It has been suggested that ferromagnetism can occur in the d_z^2-orbitally ordered state by mixing of e_g-orbitals with different symmetry whereas orbital disorder leads to the frustration of magnetic interactions (Zhou *et al.*, 2008). However, it is an apparent contradiction to the fact that ferromagnetism is very strong in the orbitally disordered phases in $LaMn_{1-x}Ga_xO_3$ (x = 0.6) and $LaMn_{1-x}Cr_xO_3$ (0.35 < x < 0.6) (Blasco *et al.*, 2002; Deisenhofer *et al.*, 2002).

Optimally doped $La_{0.7}Sr_{0.3}(Mn^{3+}_{0.7}Mn^{4+}_{0.3})O_3$ has the highest critical temperature (T_C = 380 K) of the transition into the ferromagnetic state among mixed-valence manganites. The substitution of manganese ions with five-valence ions such as Nb^{5+} or Sb^{5+} leads to the reduction of the average manganese valence and hence, Mn^{3+}–O–Mn^{3+} superexchange interactions via oxygen should be dominant. In this work, we report the structure and properties of $La_{0.7}Sr_{0.3}Mn_{0.85}Nb_{0.15}O_3$ stoichiometric compound containing only Mn^{3+} species.

II. EXPERIMENTAL

Ceramic sample of $La_{0.7}Sr_{0.3}Mn_{0.85}Nb_{0.15}O_3$ series were prepared by a solid-state reaction technique using high purity oxides La_2O_3, Mn_2O_3, Nb_2O_5 and carbonate $SrCO_3$ taken in a stoichiometric ratio and thoroughly mixed in a planetary mill (Retsch, 300 rpm, 30 min). La_2O_3 was preliminary annealed at 1100 °C in air in order to remove moisture. The synthesis was performed at 1550 °C for 7 h in air, using a two-step procedure with an interim annealing at 1400 °C for 5 h followed by a thorough grinding. The sample was cooled from the synthesis temperature with a rate of 300 °C/h down to 300 °C. Neutron powder diffraction (NPD) measurements were performed on the high intensity D1B (λ = 2.520 Å) and high resolution D2B (λ = 1.594 Å) diffractometers (Institute Laue-Langevin, Grenoble).

III. RESULTS AND DISCUSSION

Neutron powder diffraction measurements show that the crystal structure at room temperature can be successfully described in the frame of the rhombohedral space group R-3c (Figure 1, Table I). However, the compound shows a structural transition with temperature decrease. This transition occurs above 180 K as evidenced by NPD data recorded at different temperatures. Rietveld refinement of the neutron diffraction

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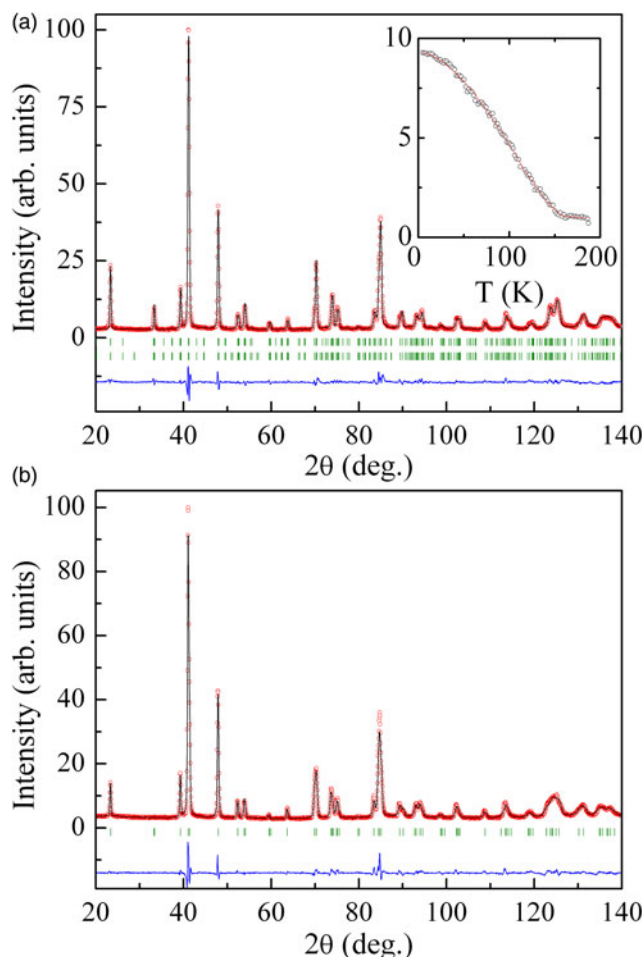
Figure 1. (Color online) NPD patterns were recorded at 300 and 2 K for $La_{0.7}Sr_{0.3}Mn_{0.85}Nb_{0.15}O_3$. The line and points refer to calculated and observed profiles and the bottom line represents their difference. The upper row of vertical ticks marks the Bragg reflections of the structural phase whereas the bottom row denotes ferromagnetic reflections. The inset of the top panel shows the temperature dependence of reflection (110).

patterns at low temperature has been performed using the *Pnma* space group resulting in a satisfied agreement between experimental data and calculated patterns (Figure 1). The connection between the lattice and orbital degrees of freedom, as investigated in several orthorhombic manganites (Deisenhofer *et al.*, 2002; Zhou and Goodenough, 2008) suggests that the development of orbital ordering results in a contraction of the *b* parameter, and if $b/\sqrt{2} < c \leq a$ the occurrence of orbital ordering can be conjectured. On the other hand, if $c > a \approx b/\sqrt{2}$, orbital disorder is expected. The observed relationship between the determined structural parameters ($c > a \approx b/\sqrt{2}$) is in agreement with the absence of orbital order in the orthorhombic phase of the sample. Rietveld refining of the neutron diffraction patterns using high-resolution data indicates that the refined oxygen contents correspond to a stoichiometric composition.

The additional intensity contribution to some structural peaks observed below 150 K for the $x = 0$ sample is associated with the ferromagnetic ordering [inset of Figure 1(a)]. The refined magnetic moment is 3.1 μ_B/Mn at 10 K.

The determined structural parameters prove that the orthorhombic distortion of the crystal lattice found at low temperatures is not caused by a long-range orbital ordering. Unit cell parameters correspond to the O-type orthorhombic phase. Apparently

the orthorhombic distortion is caused by steric effects similar to the case in optimally doped $La_{1-x}Ca_xMnO_3$ (Huang *et al.*, 1998).

Therefore, the ferromagnetism of the studied sample cannot be caused by orbital ordering or double exchange and is not associated with charge carriers. According to the Goodenough-Kanamori rules the sign of the 180°-superexchange interaction between $Mn(e_g)$–O–$Mn(e_g)$ cannot be determined for the Mn^{3+} ion if the orbital ordering is removed (Goodenough, 1963; Zhou and Goodenough, 1999). So, the antiferromagnetic and ferromagnetic components of the interactions can be equal. However, this statement is correct only in the case of a purely ionic bond (Troyanchuk, 2013a). However the chemical bond includes a covalent component and hybridization occurs between the e_g orbitals of manganese and the $2p$ orbitals of oxygen. This leads to a decrease of formal population of filled e_g orbitals of Mn as e_g electrons are partially located at the oxygen site and to an increase of the ferromagnetic component of the superexchange interactions. In the ionic model a similar effect results by partially replacing La^{3+} ions with two-valent alkaline earth ions, in this case Mn^{4+} ions appear. This substitution leads to the decrease of the antiferromagnetic contribution in the superexchange interactions as the e_g orbitals of Mn^{4+} are empty.

On the other hand structural disorder can decrease the covalence because of local variations of the bond angle Mn–O–Mn. This angle controls the hybridization of $2p$(O) and $3d$(Mn) orbitals (Goodenough, 1963). There is a critical value of the Mn–O–Mn angle associated with a change in sign of the superexchange interaction from positive to negative (Goodenough, 1963; Akahoshi *et al.*, 2003). The decrease of the Mn–O–Mn angle leads to gradual collapse of the long-range ferromagnetic order in both mixed and single valent manganites (Troyanchuk, 1998).

We will now try to discuss the interplay between magnetism and orbital ordering. The orbital order–disorder transition in the parent compounds $LnMnO_3$ (Ln-lanthanide) has a martensitic character (Kasper and Troyanchuk, 1996; Colin *et al.*, 2008). This means that there is a two phase regime under both doping and temperature variation. The orbitally ordered $LaMnO_3$ is A-type antiferromagnetic whereas the orbitally disordered $LaMnO_3$ has isotropic ferromagnetic interactions (Trokiner *et al.*, 2013). The experimental data for lightly doped $La_{1-x}A_xMnO_3$ ($A = Ca$, Sr; $x < 0.15$) provide no evidence for any homogeneous ferromagnetic state within a formally d_z^2-orbital ordered phase (Allodi *et al.*, 1997; Kumagai *et al.*, 1999; Korolyov *et al.*, 2000; Biotteau *et al.*, 2002; Choi *et al.*, 2010) Moreover, the ferromagnetic ordering in the lightly doped manganites leads to a magnetostructural first-order transition into a less distorted low temperature phase and concomitant localization of the charge carriers (Korolyov *et al.*, 2000; Biotteau *et al.*, 2002; Hennion and Moussa, 2005). The magnetostructural transition is accompanied by a significant increase of the spontaneous magnetic moment. However, the low temperature phase is not homogeneous. It contains inclusions of pure A-type antiferromagnetic phases as it was proved by NMR (Choi *et al.*, 2010) and NPD methods (Lia *et al.*, 2009; Troyanchuk, 2013b). Naturally one can suggest that these A-type antiferromagnetic inclusions arise from the local d_z^2 orbital ordering inherent to parent $LaMnO_3$. So the static d_z^2 orbital ordering seems to be incompatible with a pure ferromagnetic ordering in spite of mixing of d_z^2 and d_{x-y}^2 orbitals.

The ferromagnetic state in single-valent manganites likely arises from the removal of the static Jahn-Teller distortion. It

TABLE I. The results of crystal and magnetic structures refinement of $La_{0.7}Sr_{0.85}Nb_{0.15-x}Mg_xO_3$ samples

	x = 0		x = 0.08		x = 0.15	
T (K)	10	300	5	300	10	300
S.G.	Pnma	R-3c	Pnma	R-3c	R-3c	R-3c
a (Å)	5.521(1)	5.564(4)	5.495(7)	5.539(6)	5.493(5)	5.499(2)
b (Å)	7.810(2)	5.564(4)	7.774(2)	5.539(6)	5.493(5)	5.499(2)
c (Å)	5.557(7)	13.524(6)	5.541(1)	13.419(1)	13.297(1)	13.338(2)
V (Å³)	239.63(1)	362.66(1)	236.73(7)	356.62(1)	347.52(1)	349.31(6)
V_p (Å)	59.9	60.44	59.18	59.44	57.92	58.22
La/Sr						
X	0.509(1)	0	0.507(7)	0	0	0
Y	0.25	0	0.25	0	0	0
Z	0.00001	0.25	0.003(1)	0.25	0.25	0.25
Biso (Å²)	0.762(3)	1.066(3)	0.512(3)	0.624(4)	0.293(2)	0.458(2)
Mn/Mg/Nb						
X	0	0	0	0	0	0
Y	0	0	0	0	0	0
Z	0	0	0	0	0	0
Biso (Å²)	0.122(1)	0.141(7)	0.189(7)	0.257(2)	0.083	0.002
O1						
X	−0.008(2)	0.548(1)	−0.006(3)	0.548(1)	0.544(2)	0.542(3)
Y	0.25	0	0.25	0	0	0
Z	−0.059(7)	0.25	−0.058(9)	0.25	0.25	0.25
Biso (Å²)	0.838(6)	1.574(2)	0.627(4)	1.015(4)	0.673(2)	0.876(2)
O2						
X	0.258(1)	–	0.259(7)	–	–	–
Y	0.031(2)	–	0.030(4)	–	–	–
Z	0.238(6)	–	0.238(9)	–	–	–
Biso (Å²)	1.273(4)	–	0.967(1)	–	–	–
Mn–O1 (Å)	1.981(1)	1.980(4)	1.971(1)	1.969(4)	1.949(8)	1.951(8)
Mn–O2 (Å)	1.961(7)	–	1.960(8)	–	–	–
Mn–O2 (Å)	1.988(3)	–	1.973(2)	–	–	–
Mn–O1–Mn(deg.)	160.53(2)	164.48(2)	160.83(7)	164.46(1)	165.70(8)	166.31(1)
Mn–O2–Mn(deg.)	165.11(2)	–	165.40(3)	–	–	–
R-factors						
R_p/R_{wp} (%)	5.08/6.58	4.56/5.95	3.74/4.95	3.01/3.95	5.23/6.85	4.96/6.26
R_{Bragg} (%)	6.07	3.54	4.44	3.03	4.45	3.88
Magnetic moment at Mn ion						
μ_x (μ_B)	–	–	–	–	1.2(6)	–
μ_z (μ_B)	3.1(1)	–	2.7(7)	–	–	–
R_m	11.5	–	9.89	–	9.21	–

was suggested that the formally Jahn-Teller distorted $LaMn_{0.5}Ga_{0.5}O_3$ ($b/\sqrt{2} < c < a$) is a homogeneous ferromagnet. According to magnetic study, this compound is magnetically inhomogeneous. In comparison to $LaMn_{0.5}Ga_{0.5}O_3$ the completely orbitally disordered $LaMn_{0.4}Ga_{0.6}O_3$ is characterized by a larger Weiss constant thus indicating an enhancement of the ferromagnetic correlations (Blasco et al., 2002). One can suggest that Ga^{3+} doping leads to nanoscale structural separation into nanodomains with fast and slow orbital dynamic. The fast orbital dynamic corresponds to ferromagnetic ordering whereas the slow orbital dynamic favors antiferromanetism.

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