Ferromagnetic ordering in La$_{0.7}$Sr$_{0.3}$Mn$_{3+0.85}$Nb$_{0.15}$O$_3$ manganite

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(Received 29 September 2014; accepted 30 December 2014)

Structural measurements have been performed on the La$_{0.7}$Sr$_{0.3}$Mn$_{3+0.85}$Nb$_{0.15}$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 $\mu_B$/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]

Key words: neutron diffraction, Rietveld analyses, manganites, superexchange

I. INTRODUCTION

La$_{1-x}$A$_x$MnO$_3$ (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$_x$O$_3$ (0.2 < x < 0.6) and LaMn$_{1-x}$Cr$_x$O$_3$ (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 $d^5$-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$_x$O$_3$ (x = 0.6) and LaMn$_{1-x}$Cr$_x$O$_3$ (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$^{5+}$ 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$_2$O$_3$, Mn$_2$O$_3$, Nb$_2$O$_5$ and carbonate SrCO$_3$ taken in a stoichiometric ratio and thoroughly mixed in a planetary mill (Retsch, 300 rpm, 30 min). La$_2$O$_3$ 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 ($\lambda$ = 2.520 Å) and high resolution D2B (\(\lambda = 1.594 \text{ Å}\)) 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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patterns at low temperature has been performed using the Pnma space group resulting in a satisfactory 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√2 < c ≤ a the occurrence of orbital ordering can be conjectured. On the other hand, if c > a = b√2, orbital disorder is expected. The observed relationship between the determined structural parameters (c > a ≈ b√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 μB/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_{x}MnO_{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 eg orbitals of manganese and the 2p orbitals of oxygen. This leads to a decrease of formal population of filled eg orbitals of Mn as eg 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 eg 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_{x}MnO_{3} (A = Ca, Sr; x < 0.15) provide no evidence for any homogeneous ferromagnetic state within a formally d_{x^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_{x^2} orbital ordering inherent to parent LaMnO_{3}. So the static d_{x^2} orbital ordering seems to be incompatible with a pure ferromagnetic ordering in spite of mixing of d_{x^2} and d_{x^2−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$_{0.3}$Nb$_{0.15}$MgO$_3$ samples

<table>
<thead>
<tr>
<th>$x$ (La/Sr)</th>
<th>0</th>
<th>0.08</th>
<th>0.15</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T$ (K)</td>
<td>10</td>
<td>300</td>
<td>5</td>
</tr>
<tr>
<td>S.G.</td>
<td>Pnma</td>
<td>R-3c</td>
<td>Pnma</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>5.521(1)</td>
<td>5.564(4)</td>
<td>5.495(7)</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>7.810(2)</td>
<td>5.564(4)</td>
<td>7.774(2)</td>
</tr>
<tr>
<td>$d$ (Å)</td>
<td>13.524(6)</td>
<td>13.419(1)</td>
<td>13.297(1)</td>
</tr>
<tr>
<td>$V$ (Å$^3$)</td>
<td>362.66(1)</td>
<td>356.62(1)</td>
<td>347.52(1)</td>
</tr>
<tr>
<td>$V_p$ (Å$^3$)</td>
<td>59.9</td>
<td>59.18</td>
<td>59.18</td>
</tr>
</tbody>
</table>

| $X$         | 0.509(1) | 0.507(7) | 0.503(1) | 0.505(7) | 0.503(1) | 0.505(7) |
| $Y$         | 0.25    | 0.25    | 0.25    | 0.25    | 0.25    | 0.25    |
| $Z$         | 0.00001 | 0.003(1) | 0.005(7) | 0.003(1) | 0.005(7) | 0.003(1) |
| Biso (Å$^2$) | 0.762(3) | 0.51(2) | 0.624(4) | 0.51(2) | 0.624(4) | 0.51(2) |

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$_{0.5}$Ga$_{0.5}$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.

ACKNOWLEDGEMENT

This work was supported by Russian Foundation for Basic Research (grant 12-02-01252).


