Effects of oxygen deficiency on the magnetic ordering of Mn in Tb$_{0.9}$Na$_{0.1}$MnO$_{2.9}$

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Abstract

Monovalent Na$^+$ ions have been incorporated into a multiferroic TbMnO$_3$ compound. Structural studies, using high-resolution neutron diffraction patterns, show that monovalent Na$^+$-doping results in a noticeable oxygen deficiency in the compound. The alternations in crystalline and magnetic structures due to oxygen deficiency are investigated by neutron diffraction and magnetic susceptibility measurements. Na-doping turns the modulated incommensurate Mn spin structure, observed for the parent compound, into a simple commensurate one. The observed magnetic diffraction patterns agree very well with that calculated assuming a D-type arrangement for the Mn spins, with the moments pointing along the $c$-axis direction. No significant alternation in the ordering temperature of the Mn moments is found.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The interplay between the occurrence of spontaneous ferroelectric order and the formation of modulated magnetic structure of the Mn moments in multiferroic RMnO$_3$, where R = Tb or Ho, is currently under intensive investigation [1–6]. It is known that incorporation of small ions onto the rare-earth sites of perovskite-type manganese oxides causes a significant GdFeO$_3$-type distortion along with a staggered $(d_{3x^2−r^2}/d_{3y^2−r^2})$-type orbital ordering. A noticeable difference in the next-nearest-neighbor (NNN) Mn–Mn superexchange (SE) interaction, via the (Mn–O)–(O–Mn) path, along the two in-plane crystallographic directions may then result, which in turn gives rise to a modulated magnetic structure for the Mn spins [7]. A sinusoidal antiferromagnetic order of the Mn spins has been found [3] to develop below 41 K in TbMnO$_3$, with a modulation vector that propagates along the second longest ($b$-axis) crystallographic direction. The magnitude of the modulation vector gradually decreases with decreasing temperature, and stabilizes at a transition $T_{ME}$ (~30 K) where a new magnetic order parameter develops simultaneously with ferroelectric order [6]. The ferroelectric polarization has been found [8] to develop with the polarization vector pointing along the longest crystallographic direction ($c$-axis) below $T_{ME}$. In this article, we report on the results of studies made on the crystalline and magnetic structures of an oxygen-deficient Tb$_{0.89}$Na$_{0.11}$MnO$_{2.90}$ compound. The oxygen vacancies interrupt the (Mn–O)–(O–Mn) superexchange (SE) paths, which reduces the significance of the next-nearest-neighbor interactions of the Mn ions. A simple commensurate magnetic structure for the Mn moments was found.
2. Crystalline structure

A 10% Na-doped polycrystalline sample of (Tb/Na)MnO$_3$ was fabricated by employing the solid-state reaction technique. A stoichiometric mixture of high-purity powders of Tb$_2$O$_3$, Na$_2$CO$_3$ and MnCO$_3$ was sintered in air at 1450°C for 24 h. The sample was characterized by the neutron powder diffraction technique. High-resolution neutron powder diffraction (HRPD) patterns, taken at selective temperatures, were collected on the HRPD powder diffractometer at the Australia Nuclear and Standard Technology Organization (ANSTO), employing the standard setup. The diffraction patterns were analyzed using the GSAS program, which follows the Riveted refinement method. All of the observed diffraction patterns could be very well by the orthorhombic symmetry, with the space group Pbnm, as reported previously [2]. Figure 1 displays the observed (crosses) and the calculated (solid lines) diffraction patterns, taken at 45 K, which is above the Mn magnetic ordering temperature (see below). Refinements that allowed Na to enter the Mn sites gave an unacceptable occupancy factor for Na. A poorer fit resulted when it was assumed that the O sites were fully occupied. Analysis of the occupancy factors shows that the Na content agree well with the stoichiometric content, while both the in-plane and axial O are noticeably deficient. The refined structural parameters are listed in table 1, and the chemical formula that we obtained from the fit is Tb$_{0.9}$Na$_{0.1}$MnO$_{2.9}$. This refined stoichiometric composition indicates that the Mn ions are trivalent, which agrees with what is obtained from the XANES Mn K-edge and Mn L-edge studies using synchrotron x-ray sources. Similar results have also been found for the (La, Na) MnO$_3$ system [9, 10]. Na-doping results in decreases in the two basal plane lattice parameters together with an increase in the axial one, so that the MnO$_6$ octahedra are more distorted than that of the parent compound. No traces of impurity phases such as MnO, MnO$_2$, and Mn$_2$O$_3$ were found. We estimated any impurity phases in the sample to be less than 1%.

Figure 1. Observed (crosses) and fitted (solid lines) high-resolution neutron powder diffraction patterns of Tb$_{0.9}$Na$_{0.1}$MnO$_{2.9}$, collected at 45 K. The solid vertical lines shown below the pattern mark the calculated positions of Bragg reflections for the proposed structure, while the differences between the observed and the fitted patterns are shown at the bottom.

Table 1. Refined structural parameters of Tb$_{0.9}$Na$_{0.1}$MnO$_{2.9}$ at 45 K.

<table>
<thead>
<tr>
<th>Atom</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>Biso</th>
<th>Multi Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tb</td>
<td>$-0.0168(7)$</td>
<td>$0.0777(5)$</td>
<td>$1/4$</td>
<td>$0.69(7)$</td>
<td>$4$</td>
</tr>
<tr>
<td>Na</td>
<td>$-0.0168(7)$</td>
<td>$0.0777(5)$</td>
<td>$1/4$</td>
<td>$0.69(7)$</td>
<td>$4$</td>
</tr>
<tr>
<td>Mn</td>
<td>$1/2$</td>
<td>$0$</td>
<td>$0$</td>
<td>$0.23(11)$</td>
<td>$4$</td>
</tr>
<tr>
<td>O(1)</td>
<td>$0.1039(6)$</td>
<td>$0.0465(6)$</td>
<td>$1/4$</td>
<td>$0.08(8)$</td>
<td>$4$</td>
</tr>
<tr>
<td>O(2)</td>
<td>$-0.2956(5)$</td>
<td>$0.3251(5)$</td>
<td>$0.0520(4)$</td>
<td>$0.03(6)$</td>
<td>$8$</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>$1.654$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_p$</td>
<td>$2.97%$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_{wp}$</td>
<td>$2.50%$</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

3. Magnetic structure

Figure 2 displays the temperature profiles of the in-phase component $\chi'$ (open circles) and the out-of-phase component $\chi''$ (filled circles) of the ac magnetic susceptibility $\chi'$. $\chi'$, measured using a probing field with a root mean square (rms) strength of 10 Oe and a frequency of $10^3$ Hz. The $\chi''(T)$ departs from the Curie–Weiss behavior (solid line) below 40 K, and reveals a peak at 9 K, at which a peak in $\chi''$ is also evident.

Figure 2. The in-phase (open circles) and out-of-phase (solid circles) components of the ac magnetic susceptibility $\chi'$ and $\chi''$, measured using a probing field with a root mean square (rms) strength of 10 Oe and a frequency of $10^3$ Hz. The $\chi''(T)$ departs from the Curie–Weiss behavior (solid line) below 40 K, and reveals a peak at 9 K, at which a peak in $\chi''$ is also evident.
resolution-limited peaks are seen. All of these magnetic peaks may be indexed using half-integer Miller’s indices, when based on the nuclear unit cell. No modulation peaks are found. This magnetic diffraction pattern observed at 10 K represents a relatively simple magnetic structure for the Mn moments in the 10% Na-doped oxygen-deficient TbnNa0.1MnO2.90. The observed magnetic diffraction pattern agrees very well with the pattern (solid curve shown in figure 3) calculated assuming a D-type arrangement [11] for the Mn spins, with the moments pointing along the c-axis direction. The simple commensurate Mn spin structure observed for the 10% Na-doped compound is completely different from the incommensurate one observed for the parent compound. Structural analysis shows that no Na atoms may enter the Mn sites. It is then mainly the oxygen deficiency that turns the incommensurate Mn magnetic structure into a commensurate one. Figure 4 displays the proposed magnetic structure, where the in-plane Mn ions may be viewed as consisting of alternating ferromagnetic and antiferromagnetic chains along the [110] direction. Note that this proposed magnetic structure was obtained on a powder sample and using data of large statistical fluctuations, and it should be considered as a tentative one. Studies using a single crystal sample are needed to uncover the details of the magnetic structure. The low-temperature moment that we obtained for the Mn spins at 10 K is $\langle \mu_z \rangle = 3.9(2) \mu_B$. The ordering temperature for the Mn moments may be determined from the order parameter measurement shown in figure 5, where it displays the temperature dependence of the $\{1/2 1/2 1/2\}$ integrated intensity and reveals an ordering temperature of $T_N \approx 40$ K for the Mn moments.

4. Conclusion

The modulated magnetic structure for the Mn moments in TbMnO3 is currently understood [7] to be due to the differences in the NNN SE interactions between the Mn ions along the two in-plane crystallographic directions. These NNN SE interactions are known to be mediated through the nearby oxygen ions. Na-doping creates oxygen vacancies, which in turn alters the in-plane (Mn–O)–(O–Mn) SE paths. The suppression of magnetic modulation of the Mn spins may then be understood as the differences in the NNN SE interactions along the two in-plane crystallographic directions being reduced by Na-doping. Our observation shows directly that oxygen ions also play a decisive role in affecting the magnetic structure in TbMnO3-related compounds.

Acknowledgments

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References