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

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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 $\text{R} = \text{Tb}$ 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 $\text{Tb}_{0.89}\text{Na}_{0.11}\text{MnO}_{2.90}$ 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.

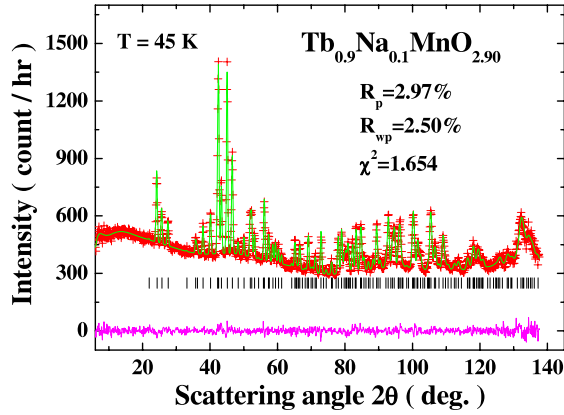


Figure 1. Observed (crosses) and fitted (solid lines) high-resolution neutron powder diffraction patterns of $\text{Tb}_{0.9}\text{Na}_{0.1}\text{MnO}_{2.9}$, collected at 45 K. The solid vertical lines shown below the pattern mark the calculated positions of Bragg reflections for the proposed structure,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

2. Crystalline structure

A 10% Na-doped polycrystalline sample of $(\text{Tb}/\text{Na})\text{MnO}_{3-\delta}$ was fabricated by employing the solid-state reaction technique. A stoichiometric mixture of high-purity powders of Tb_4O_7 , Na_2CO_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 Rietveld refinement method. All of the observed diffraction patterns could be described 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 $\text{Tb}_{0.9}\text{Na}_{0.1}\text{MnO}_{2.90}$. 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 $(\text{La}, \text{Na})\text{MnO}_{3-\delta}$ 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_2O_3 were found. We estimated any impurity phases in the sample to be less than 1%.

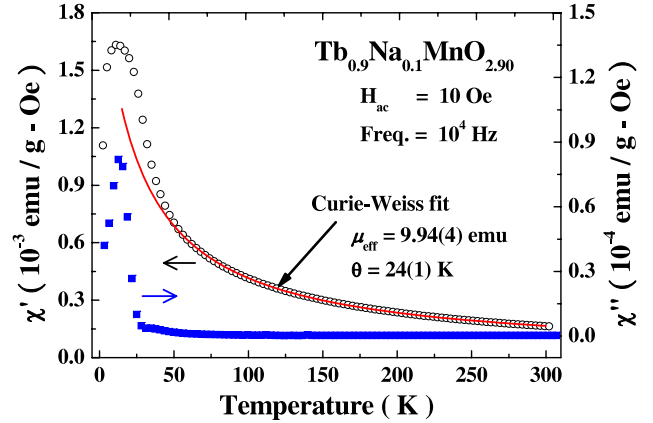


Figure 2. The in-phase (open circles) and out-of-phase (solid circles) components of the ac magnetic susceptibility χ' and χ'' , measured using a probing field with a root mean square (rms) strength of 10 Oe and a frequency of 10^4 Hz. The $\chi'(T)$ departs from the Curie–Weiss behavior (solid line) below 40 K, and reveals a peak at 9 K, at which a peak in χ'' is also evident.

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

$\text{Tb}_{0.9}\text{Na}_{0.1}\text{MnO}_{2.9}$						
$T = 45$ K, space group: $Pbnm$						
$a = 5.2965(6)$ Å, $b = 5.7717(6)$ Å, $c = 7.3804(8)$ Å						
Atom	x	y	z	Biso	Mult	Fraction
Tb	-0.0168(7)	0.0777(5)	1/4	0.69(7)	4	0.90(2)
Na	-0.0168(7)	0.0777(5)	1/4	0.69(7)	4	0.10(2)
Mn	1/2	0	0	0.23(11)	4	1
O(1)	0.1039(6)	0.04654(6)	1/4	0.08(8)	4	0.9659(9)
O(2)	-0.2956(5)	0.3251(5)	0.0520(4)	0.03(6)	8	0.9666(4)
$\chi^2 = 1.654$			$R_p = 2.97\%$		$R_{wp} = 2.50\%$	

3. Magnetic structure

Figure 2 displays the temperature profiles of the in-phase component χ' (open circles) and the out-of-phase component χ'' (filled circles) of the ac magnetic susceptibility. We note that χ' measures the response of the system to the driving field, whereas χ'' signifies the dissipative loss of the driving field to the system. The $\chi'(T)$ departs from the Curie–Weiss behavior (solid curve) below 40 K, and reveals a peak at 9 K. Correspondingly, noticeable increases in χ'' with decreasing temperature are seen below 40 K, and a sharp peak develops at 9 K as well. The anomalies at 40 and 9 K are associated with the long-range Mn and quasi-long-range Tb spin orderings, respectively, as has been suggested for the parent compound [7, 11]. Interestingly, the anomaly in $\chi''(T)$ associated with the Tb ordering is significantly higher than that with the Mn ordering. Neutron magnetic diffraction is then used to determine the magnetic structure of the Mn spins. Figure 3 displays the magnetic diffraction pattern at 10 K, where the diffraction pattern taken at 45 K, serving as the non-magnetic background, has been subtracted. The negative counts appearing in figure 3 reflect that the background counts at 45 K are higher than those at 10 K, which may be expected since the magnetic signals normalize into magnetic peaks once the moments order. A series of

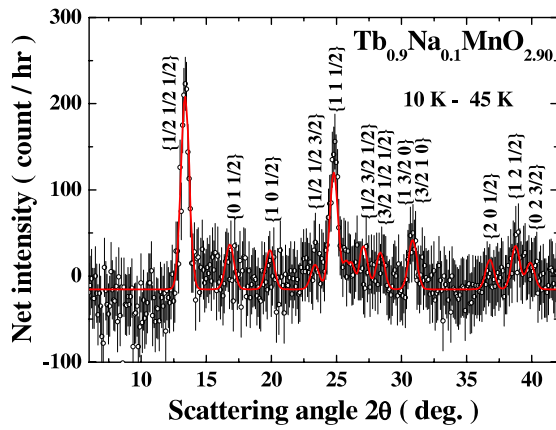


Figure 3. Observed (open circles) and calculated (solid curves) magnetic diffraction patterns associated with the Mn spin orderings developed from 45 to 10 K. It reveals a series of resolution-limited peaks that may be indexed using half-integers for all three Miller’s indices, when based on the nuclear unit cell. No modulation peaks are found.

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 $\text{Tb}_{0.9}\text{Na}_{0.1}\text{MnO}_{2.90}$. 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 $\{\frac{1}{2} \frac{1}{2} \frac{1}{2}\}$ 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 TbMnO_3 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

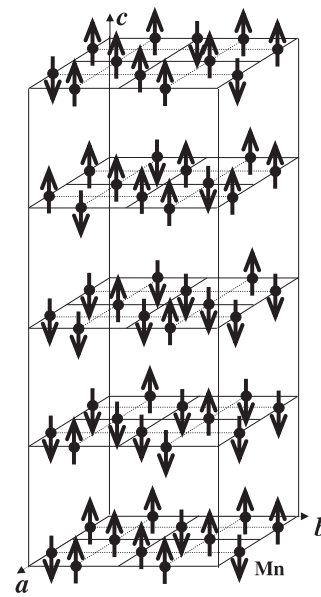


Figure 4. Proposed magnetic structure of the Mn ions in $\text{Tb}_{0.9}\text{Na}_{0.1}\text{MnO}_{2.9}$. This spin arrangement may be viewed as consisting of alternating ferromagnetic and antiferromagnetic chains along the [110] direction.

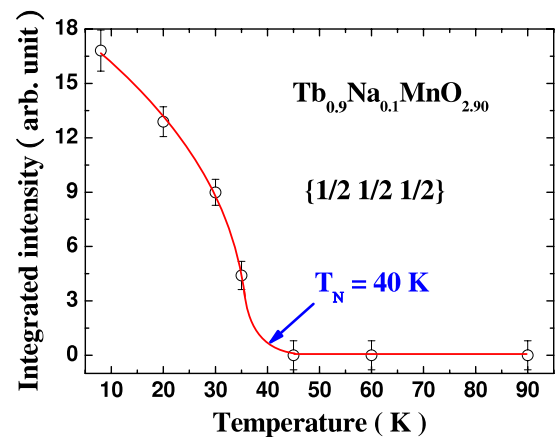


Figure 5. Plot of the thermal evolution of the $\{\frac{1}{2} \frac{1}{2} \frac{1}{2}\}$ integrated intensity, showing an ordering temperature, as determined to be at the inflection point, of $T_N \approx 40$ K for the Mn moments. The solid line is a guide to the eye only.

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 TbMnO_3 -related compounds.

Acknowledgments

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