



Transitions induced by a magnetic field in slightly doped TbMnO₃



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ABSTRACT

We have investigated the magnetic properties of slightly doped multiferroic TbMnO₃ after application of a magnetic field. The study focused on compositions TbMn_{1-x}A_xO₃ ($x \leq 0.1$) with A = Ga, Sc, Co and Al. The replacement of Mn by Ga, Al or Sc proved to be isovalent while the addition of Co leads to a partial charge transfer as $\text{Mn}^{3+} + \text{Co}^{3+} \rightarrow \text{Mn}^{4+} + \text{Co}^{2+}$. The samples with 10% of non-magnetic doping, TbMn_{0.9}Sc_{0.1}O₃, TbMn_{0.9}Al_{0.1}O₃ and TbMn_{0.9}Ga_{0.1}O₃, preserve the long range antiferromagnetic ordering of the Mn sublattice with, however, reduced transition temperatures compared to TbMnO₃. New magnetic interactions in the Co-doped compound lead to the suppression of Mn ordering in TbMn_{0.9}Co_{0.1}O₃. The application of an external magnetic field produces similar metamagnetic transitions in all TbMn_{0.9}A_{0.1}O₃ compounds that are ascribed to the Tb-sublattice. Powder neutron diffraction was used to determine the changes in the magnetic structure with applied magnetic field revealing a strong increase of F- and C-type magnetic reflections in these compounds. These results are accounted for by the anisotropic response of the Tb sublattice to a magnetic field while the Mn sublattice remains unchanged.

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1. Introduction

TbMnO₃ belongs to the family of magnetoelectric multiferroics [1] and undergoes on cooling three consecutive transitions [2]. The Mn sublattice orders antiferromagnetically (A-type) at $T_{N1} \sim 41$ K. The order is incommensurate with a wave vector $\mathbf{k}_{\text{Mn}} = (0, q_{\text{Mn}}, 0) \sim (0, 0.295, 0)$ at T_{N1} [3]. The Mn moments are sinusoidally modulated and oriented along the *y*-direction [3,4]. On cooling, a spin rearrangement of the Mn moments yields an elliptical spiral in the *bc*-plane at $T_{N2} \sim 27$ K. This transition is coupled to a ferroelectric phase transition with spontaneous polarization parallel to the *c*-axis [2]. Finally, the Tb-sublattice develops an incommensurate magnetic ordering at $T_{N3} \sim 8$ K with a different propagation vector $\mathbf{k}_{\text{Tb}} = (0, q_{\text{Tb}}, 0) \sim (0, 0.42, 0)$ [5].

Replacing Mn by a non-magnetic ion weakens the magnetic ordering of the Mn-sublattice and is also detrimental to the ordering of the Tb moments and to the ferroelectric transition [6,7]. This fact reveals the great importance of the magnetic coupling between Mn and Tb moments, $J_{\text{Mn-Tb}}$, for the occurrence of ferroelectricity in this system. Moreover, small substitutions affect only slightly the magnetoelectric properties of the Mn sublattice but influence

strongly the magnetic ordering of the Tb moments suggesting that this ordering is determined by the competition between $J_{\text{Mn-Tb}}$ and the direct coupling between Tb moments, $J_{\text{Tb-Tb}}$ [6]. A different behavior is expected for the replacement of Mn by Co. This type of substitution is reported to be not isovalent in related systems [8,9] and more recently in the TbMn_{1-x}Co_xO₃ series [10]. The couple $\text{Mn}^{4+}\text{-Co}^{2+}$ is more stable than the couple $\text{Mn}^{3+}\text{-Co}^{3+}$ in the perovskite structure and hence, this dopant can be magnetic (Co^{3+} may adopt the non-magnetic low spin configuration in a perovskite lattice). To a first approximation, the ionic formula for the transition metals in TbMn_{0.9}Co_{0.1}O₃ would be TbMn_{0.8}³⁺Mn_{0.1}⁴⁺Co_{0.1}²⁺O₃ and the partial addition of Co may lead to competitive magnetic interactions such as the ferromagnetic (FM) superexchange $\text{Mn}^{4+}\text{-O-Co}^{2+}$, the FM double exchange $\text{Mn}^{4+}\text{-O-Mn}^{3+}$ and the rest of antiferromagnetic (AFM) superexchange interactions: $\text{Co}^{2+}\text{-O-Co}^{2+}$, $\text{Mn}^{3+}\text{-O-Mn}^{3+}$ and $\text{Mn}^{4+}\text{-O-Mn}^{4+}$ [10,11].

The magnetic interactions of these materials can be influenced as well by a magnetic field. The existence of metamagnetic transitions in Tb-based perovskites [12,13] including TbMnO₃ are well known [14]. These transitions were ascribed to the strong anisotropy of Tb³⁺ ions whose spins behave as Ising-like ones confined into the *ab*-plane [15]. The replacement of Mn by other cations in TbMnO₃ strongly affects the magnetic coupling between both sublattices ($J_{\text{Mn-Tb}}$). In this way, we expect the presence of similar

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field induced magnetic transitions in doped TbMnO₃ but the influence of dopant is unknown. The aim of this work is thus the investigation of the magnetic field effects on the compounds TbMn_{1-x}A_xO₃ ($x \leq 0.1$) with non-magnetic (A = Al, Sc and Ga) and magnetic (A = Co) dopants. Magnetization measurements and powder neutron diffraction have been used for this purpose. We found that despite having different magnetic ground states at zero fields these samples present similar metamagnetic transitions which are caused by the magnetic transitions of the Tb-sublattice. The magnetism present in the Mn-sublattice remains unaltered by the external magnetic field up to 5 T. These results suggest that $J_{\text{Tb-Tb}}$ is much more sensitive to the strength of the magnetic field than $J_{\text{Mn-Mn}}$. Finally, we have determined the magnetic arrangement of Tb³⁺ moments from the symmetry analysis and the geometry of the diffraction measurement.

2. Experimental section

All the samples have been synthesized by solid state chemistry reaction. Stoichiometric amounts of Tb₄O₇, MnCO₃ and the corresponding Ga₂O₃, Sc₂O₃ or Co₃O₄ were mixed and heated at 1000 °C for 12 h in air. The resulting powders were pressed into pellets and sintered at 1200 °C for 24 h also in air. The last steps consisted on repressing and sintering the pellets at 1400 °C for 2 days in argon flow. The chemical composition of the samples was tested using a wavelength dispersive X-ray fluorescence spectrometer (Advant'XP+ from Thermo-ARL) and no significant differences were found between experimental and calculated compositions. X-ray diffraction patterns have been collected at room temperature using a Rigaku D/max-B diffractometer with a copper rotating anode and a graphite monochromator in order to select the Cu K_α wavelength ($\lambda = 1.5418 \text{ \AA}$). The patterns were collected in a range $18^\circ \leq 2\theta \leq 130^\circ$ with a step $\Delta\theta = 0.03^\circ$. The X-ray powder diffraction patterns of all samples agree with a perovskite single phase adopting the expected orthorhombic structure with *Pbnm* space group.

Neutron diffraction measurements were carried out at the Institut Laue-Langevin (ILL) in Grenoble (France) using two powder diffractometers. A preliminary study was performed on all TbMn_{1-x}A_xO₃ ($x = 0.05, 0.1$; A = Al, Co, Ga and Sc) compounds using the high flux powder diffractometer D1B between 80 and 2 K in an angular range $1^\circ \leq 2\theta \leq 127^\circ$ with $\Delta\theta = 0.1^\circ$ using a wavelength of 2.52 Å. A magnetic study was carried out for TbMn_{0.9}Co_{0.1}O₃ on this instrument with patterns collected at selected temperatures between 2 and 130 K, and at magnetic fields up to 3 T. Powder specimens of TbMn_{0.9}Sc_{0.1}O₃ and TbMn_{0.9}Ga_{0.1}O₃ were measured on the high intensity diffractometer D20 in an angular range $4^\circ \leq 2\theta \leq 130^\circ$ with $\Delta\theta = 0.1^\circ$ using a wavelength of 2.40 Å. The patterns were collected in a temperature range between 2 and 60 K, and in a magnetic field range between 0 and 5 T. The refinement program used was FULLPROF [16], both for X-ray and neutron diffraction measurements.

The temperature dependence of the dc magnetization and the ac magnetic susceptibility were measured on a commercial Quantum Design SQUID magnetometer from 2 K up to 295 K. Magnetic hysteresis loops were collected at selected temperatures between -5 and 5 T.

3. Results

3.1. Macroscopic properties

All samples are isostructural as can be deduced from the X-ray patterns. They adopt the orthorhombic structure typical of TbMnO₃ (*Pbnm* space group). Fig. 1 shows the pattern of a representative sample. The substitution of Mn by another cation leads to changes

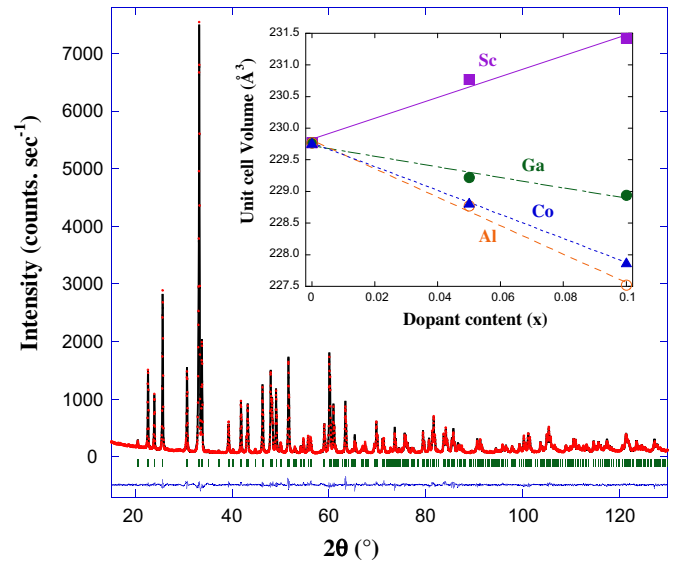


Fig. 1. X-ray powder diffraction pattern for TbMn_{0.9}Al_{0.1}O₃ at room temperature (points). The solid curve is the best fit from the Rietveld refinement while the bottom curve shows the difference between calculated and observed intensities and the vertical bars indicate the allowed Bragg reflections. Inset: unit cell volume vs. dopant concentration for TbMn_{1-x}A_xO₃ ($x \leq 0.1$) samples. The type of dopant (A) is given for each curve.

in the unit cell size in accordance with the tabulated size of the inserted cation [17]. The inset of Fig. 1 shows the effect of these substitutions on the cell volume. Ga substitution produces the smallest change with a volume decrease of $\Delta V = -8.3 \text{ \AA}^3/x$ in this substitution range ($x \leq 0.1$). This is due to the great similarity between the ionic radii of Ga³⁺ (0.62 Å) and Mn³⁺ (0.645 Å). The greatest differences are obtained with the replacement of Mn³⁺ by Sc³⁺ (0.745 Å) and Al³⁺ (0.535 Å) giving rise to the largest volume expansion ($\Delta V = +16.5 \text{ \AA}^3/x$) and volume shrinkage ($\Delta V = -22.5 \text{ \AA}^3/x$), respectively. In the case of Co substitution, we observe a volume contraction ($\Delta V = -18.9 \text{ \AA}^3/x$) similar to the Al substitution. This might be related with the addition of low spin (LS) Co³⁺ with a similar size to Al³⁺. However recent spectroscopic studies revealed that Co substitution is not isovalent, with an incomplete charge transfer from Mn³⁺ to Co³⁺ yielding a mixed valence character to both cations and the formal equilibrium $\text{Mn}^{3+} + \text{Co}^{3+} \rightleftharpoons \text{Mn}^{4+} + \text{Co}^{2+}$ shifted to the right [10]. Therefore the contraction observed on Co substitution may also be ascribed to the formation of small Mn⁴⁺.

This type of substitution, although very small, strongly affects the properties of TbMnO₃. Fig. 2 shows the heat capacity (C_p) measurements of these samples. The temperature dependence of C_p/T of TbMnO₃ shows three anomalies as previously reported [2]. On cooling, they correspond to the magnetic ordering of Mn³⁺ moments ($T_{N1} = 41.3 \text{ K}$), the magnetic rearrangement of Mn³⁺ coupled to the ferroelectric transition ($T_{N2} = T_{FE} = 26.1 \text{ K}$) and the magnetic ordering of Tb³⁺ moments ($T_{N3} = 6.5 \text{ K}$). All substitutions are detrimental to the three transitions but the exact change depends on the nature of the dopant cation. T_{N1} decreases with increasing the concentration of non-magnetic cations. This is an expected result but, for a given concentration, the T_{N1} diminution depends on the dopant size in the way $T_{N1}^{\text{Al}} > T_{N1}^{\text{Ga}} > T_{N1}^{\text{Sc}}$. The small size of Al³⁺ seems to be less unfavorable to the ordering of Mn³⁺ moments than the small size mismatch of Ga³⁺ atoms. Sc³⁺, with the largest ionic radius and a large size mismatch, is the most detrimental to the Mn order among non-magnetic dopants. In the case of Co substitution, the antiferromagnetic ordering of Mn is strongly weakened for $x = 0.05$ and it vanishes for $x = 0.1$. This is

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