Transitions induced by a magnetic field in slightly doped TbMnO$_3$

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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 TbMn₁₋ₓAxO₃ (x≤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 Mn³⁺⁺Co³⁺→Mn⁴⁺⁺Co²⁺. The samples with 10% of non-magnetic doping, TbMn₀.₉Sc₀.₁O₃, TbMn₀.₉Al₀.₁O₃ and TbMn₀.₉Ga₀.₁O₃, 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 TbMn₀.₉Co₀.₁O₃. The application of an external magnetic field produces similar metamagnetic transitions in all TbMn₀.₉A₀.₁O₃ 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.

Highlights:
• We replace Mn by different cations in the multiferroic TbMnO₃.
• We monitor the effects of substitution in macroscopic properties.
• We determine the magnetic ground state of the doped compounds.
• We identify metamagnetic transitions in the Tb sublattice.
• We model the magnetic ordering at high magnetic fields.
1. Introduction.

TbMnO$_3$ 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 $\mathbf{k}_{\text{Mn}} = (0, q_{\text{Mn}} \sim 0.295, 0)$ 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 $\mathbf{k}_{\text{Tb}} = (0, q_{\text{Tb}} \sim 0.42, 0)$ [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$_x$O$_3$ series [10]. The couple Mn$^{4+}$-Co$^{2+}$ is more stable than the couple Mn$^{3+}$-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$_{0.1}$O$_3$ would be TbMn$_{0.8}^{3+}$Mn$_{0.1}^{4+}$Co$_{0.1}^{2+}$O$_3$ and the partial addition of Co may lead to competitive magnetic interactions such as the
ferromagnetic (FM) superexchange $\text{Mn}^{4+}$-$\text{O}$-$\text{Co}^{2+}$, the FM double exchange $\text{Mn}^{4+}$-$\text{O}$-$\text{Mn}^{3+}$ and the rest of antiferromagnetic (AFM) superexchange interactions: $\text{Co}^{2+}$-$\text{O}$-$\text{Co}^{2+}$, $\text{Mn}^{3+}$-$\text{O}$-$\text{Mn}^{3+}$ and $\text{Mn}^{4+}$-$\text{O}$-$\text{Mn}^{4+}$ [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 TbMnO$_3$ are well known [14]. These transitions were ascribed to the strong anisotropy of Tb$^{3+}$ ions whose spins behave as Ising-like ones confined into the $ab$-plane [15]. The replacement of Mn by other cations in TbMnO$_3$ strongly affects the magnetic coupling between both sublattices ($J_{\text{Mn-Tb}}$). In this way, we expect the presence of similar field induced magnetic transitions in doped TbMnO$_3$ 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$_x$O$_3$ ($x \leq 0.1$) 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 Tb$^{3+}$ 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 Tb$_4$O$_7$, MnCO$_3$ and the corresponding Ga$_2$O$_3$, Sc$_2$O$_3$ or Co$_3$O$_4$ were mixed and heated at 1000º C for 12 h in air. The resulting powders were
pressed into pellets and sintered at 1200º C for 24 h also in air. The last steps consisted on repressing and sintering the pellets at 1400º 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 Kα wavelength (λ=1.5418 Å). The patterns were collected in a range 18º ≤ 2θ ≤ 130º with a step Δθ = 0.03º. The x-ray powder diffraction patterns of all samples agree with a perovskite single phase adopting the expected orthorhombic structure with \textit{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\textsubscript{1-x}A\textsubscript{x}O\textsubscript{3} (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 1º ≤ 2θ ≤ 127º with Δθ =0.1º using a wavelength of 2.52 Å. A magnetic study was carried out for TbMn\textsubscript{0.9}Co\textsubscript{0.1}O\textsubscript{3} on this instrument with patterns collected at selected temperatures between 2 and 130 K, and at magnetic fields up to 30 KOe. Powder specimens of TbMn\textsubscript{0.9}Sc\textsubscript{0.1}O\textsubscript{3} and TbMn\textsubscript{0.9}Ga\textsubscript{0.1}O\textsubscript{3} were measured on the high intensity diffractometer D20 in an angular range 4º ≤ 2θ ≤ 130º with Δθ =0.1º 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 50 KOe. The refinement program used was \textit{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 -50 and 50 KOe.

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 TbMnO$_3$ ($Pbnm$ space group). Figure 1 shows the pattern of a representative sample. The substitution of Mn by another cation leads to changes 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 $\Delta V = -8.3$ Å$^3$/x in this substitution range ($x \leq 0.1$). This is due to the great similarity between the ionic radii of Ga$^{3+}$ (0.62 Å) and Mn$^{3+}$ (0.645 Å). The greatest differences are obtained with the replacement of Mn$^{3+}$ by Sc$^{3+}$ (0.745 Å) and Al$^{3+}$ (0.535 Å) giving rise to the largest volume expansion ($\Delta V = +16.5$ Å$^3$/x) and volume shrinkage ($\Delta V = -22.5$ Å$^3$/x), respectively. In the case of Co substitution, we observe a volume contraction ($\Delta V = -18.9$ Å$^3$/x) similar to the Al substitution. This might be related with the addition of low spin (LS) Co$^{3+}$ with a similar size to Al$^{3+}$. However recent spectroscopic studies revealed that Co substitution is not isovalent, with an incomplete charge transfer from Mn$^{3+}$ to Co$^{3+}$ 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 Mn$^{4+}$.

This type of substitution, although very small, strongly affects the properties of TbMnO$_3$. Fig. 2 shows the heat capacity ($C_p$) measurements of these samples. The temperature dependence of $C_p/T$ of TbMnO$_3$ shows three anomalies as previously
reported [2]. On cooling, they correspond to the magnetic ordering of Mn\textsuperscript{3+} moments (\(T_{N1}=41.3\) K), the magnetic rearrangement of Mn\textsuperscript{3+} coupled to the ferroelectric transition (\(T_{N2}=T_{FE}=26.1\) K) and the magnetic ordering of Tb\textsuperscript{3+} moments (\(T_{N3}=6.5\) 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 \(T_{N1}^{Al}>T_{N1}^{Ga}>T_{N1}^{Sc}\). The small size of Al\textsuperscript{3+} seems to be less unfavorable to the ordering of Mn\textsuperscript{3+} moments than the small size mismatch of Ga\textsuperscript{3+} atoms. Sc\textsuperscript{3+}, 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 likely due to the mixed valence character of Mn and Co cations yielding competitive magnetic interactions which in addition to the induced structural disorder are very detrimental to the long range AFM ordering of Mn\textsuperscript{3+} moments.

The effect of these substitutions on the magnetic ordering of Tb\textsuperscript{3+} is more surprising. The intensity of the peak ascribed to this transition (and the concomitant entropy content) strongly decreases for any of these substitutions. The entropy content follows the sequence Al>Ga>Sc>Co. Again, there is a relationship to the dopant size and the isovalent replacement. For \(x=0.1\) samples, the peaks become more rounded and the shape resembles a Schottky anomaly (Figure 2b). This result reveals the strong correlation between the magnetic ordering of both sublattices. Any perturbation in the magnetic arrangement of the Mn-sublattice strongly influences the ordering of the Tb-sublattice.
Similar results are observed for the ferroelectric transition at $T_{N2}$. For $x=0.05$ samples, the temperature of the anomaly decreases, with $T_{N2}^{Al}> T_{N2}^{Ga}$, and no clear anomalies are noticeable for Sc- and Co-doped samples. For $x=0.1$, there is no peak specific for this transition in any of the samples. However, such peaks if present could be screened by the wide Schottky anomaly. In this way, anomalies in the dielectric constant have been reported for TbMn$_{0.9}$Ga$_{0.1}$O$_3$ and TbMn$_{0.9}$Al$_{0.1}$O$_3$. In the case of the Ga doped compound a ferroelectric state develops [6] below 15 K, while in the second sample a behavior typical of a relaxor has been found below 20 K [18]. These results agree with the importance of the non-linear magnetic structure of Mn-moments to develop ferroelectricity in Tb-based manganites [19]. In sample where this ordering is strongly weakened or vanished, there is not transition related to the ferroelectric transition in $C_p$ curves.

The magnetic susceptibility of these samples has been already reported [10]. All compounds show a paramagnetic behavior at high temperature and the Curie-Weiss law is obeyed above 100 K with the expected contribution from the paramagnetic cations. At low temperature, the susceptibility curves show a peak at $\sim$5 K indicating the occurrence of magnetic ordering in the Tb sublattice. The only different behavior concerns TbMn$_{0.9}$Co$_{0.1}$O$_3$ where spin-glass-like properties are observed [10].

3.2. Magnetic phase at zero field.

The magnetic ground state was studied by powder neutron diffraction. Figure 3 shows the neutron patterns collected at 2 K for these samples. The compounds doped with non-magnetic cations exhibit similar patterns. Superstructure peaks arising from the antiferromagnetic ordering of the Mn moments are noticeable for TbMn$_{1-x}$A$_x$O$_3$ ($x=0.05$, 0.1; A=Al, Ga, Sc). The incommensurate propagation vector agrees with $k_{Mn}= (0, \sim \frac{1}{4},0)$ and the intensity of the magnetic peaks is weaker for the sample doped with
Sc$^{3+}$. Regarding the substitution with Co, the magnetic peaks are even weaker in TbMn$_{0.95}$Co$_{0.05}$O$_3$ and no sign of a magnetic ordering of the Mn sublattice is visible in TbMn$_{0.9}$Co$_{0.1}$O$_3$ in agreement with the previous results from the $C_p$ measurements.

As already deduced from the heat capacity data the ordering of the Tb$^{3+}$ moments is as well affected by the doping. In samples doped with non-magnetic cations the magnetic peaks ascribed to this ordering get more and more broadened in the sequence Al – Ga – Sc indicating an ordering getting more and more short ranged. At the same time the propagation vector of this magnetic order keeps the value of the modulation vector reported for TbMnO$_3$, $k_{\text{Tb}}=(0, ~0.42, 0)$. The increase in the doping ratio is very detrimental for the Tb-ordering and the associated peaks are strongly flattened for x=0.1 samples, especially for the Sc-based one. This effect is even more drastic in the Co-based samples where one cannot longer see broad peaks but only an anomalous background at low angles ascribed to diffuse scattering whose origin is not clear so far. These results confirm the intimate relationship between the magnetic orderings of both sublattices (Mn$^{3+}$ and Tb$^{3+}$) in TbMnO$_3$. Any inhomogeneity in the Mn-O-Mn-chains strongly affects the occurrence of long range AFM ordering in the Tb sublattice.

3.3. Metamagnetic transitions.

A common characteristic in the Tb-based perovskites, including TbMnO$_3$, is the existence of metamagnetic transitions [12,13], i.e. spin rearrangements induced by an external magnetic field [20]. We have recently characterized the nature of this type of transition in a single crystal of TbMn$_{0.9}$Al$_{0.1}$O$_3$ [18]. This section will be focused on the study of the metamagnetic transitions in TbMn$_{0.9}$A$_{0.1}$O$_3$ samples where A=Ga, Sc and Co. Figure 4 shows the magnetic hysteresis loops measured at 5 K for these samples. The isothermal magnetization shows an anomalous step at ~2 T for all samples revealing a field induced magnetic transition. The shape is the same for these
measurements independent of the existence (Sc- and Ga-doped samples) or non-existence (Co-based sample) of a magnetic ordering of the Mn-sublattice. This fact suggests that the Tb-sublattice plays an important role in determining the metamagnetic transitions. Finally, the magnetic moment at 5 T is similar for Ga- and Sc-based samples and slightly higher for the Co-doped sample. This effect may be ascribed to the additional paramagnetic contribution from Mn/Co-sublattice in the latter sample (lack of AFM order in the Mn-sublattice).

Neutron patterns were collected at different magnetic fields to shed light on the changes induced by the field in the magnetic properties. Selected patterns are displayed in Fig. 5. Similar changes are observed for the three samples. Under the effect of the magnetic field the diffuse scattering associated to the short range magnetic ordering of Tb$^{3+}$ moments strongly decreases and for magnetic field values above ~1.5 T the growth of some existing and the appearance of new magnetic peaks is induced. These new or growing peaks can be indexed with a propagation vector $\mathbf{k}=(0,0,0)$ and the most significant increase corresponds to C- and F-type reflections as can be seen in Fig. 6 where the dependence on the magnetic field for some reflections is shown. It is well known that magnetic ordering of Mn-moments with $\mathbf{k}=(0,0,0)$ can be described, using symmetry analysis, by four modes denoted as A, C, F and G [21]. Similar modes can be used for the Tb-ordering but it is worth remembering that this atom is placed in different point symmetry and has different extinction conditions. For example, the C-type ordering of Tb-moments also shows magnetic contribution in the (0 1 1) reflection whereas a FM ordering also contributes to the (1 1 1) reflection. Such reflections only correspond to G- and A-type, respectively, in the ordering of Mn-sublattice.

The reflections ascribed to the Mn-ordering remain unchanged up to fields of 5 T in TbMn$_{0.9}$Ga$_{0.1}$O$_3$ and TbMn$_{0.9}$Sc$_{0.1}$O$_3$ samples (see Fig. 6a). The field dependence of
magnetic reflections ascribed to the Tb-order shows a similar trend for both types of doping (magnetic or not) as can be seen by comparing Fig. 6a and 6b. The temperature dependence of some magnetic peaks at 5 T is also shown in the Fig. 7. The magnetic Bragg peak reflecting the long range order of the Mn-sublattice appears in TbMn\(_{0.9}\)Sc\(_{0.1}\)O\(_3\) at \(\sim 35\) K in agreement with the anomaly observed in Fig. 2 under zero field conditions. This result reveals that magnetic fields up to 5 T do not affect significantly the magnetism of the Mn-sublattice. Regarding the magnetic reflections arising from the Tb-sublattice, there is an enhancement in their intensity below 40 K but C-type reflections start to be noticeable at \(\sim 60\) K. In the case of TbMn\(_{0.9}\)Co\(_{0.1}\)O\(_3\) less experimental points are available but the results are similar suggesting an onset for the C-type reflections between 70 and 50 K.

In order to ascertain the type of magnetic ordering induced by the magnetic field, we have refined the neutron patterns taking into account the previous results in related compounds [13]. Due to a strong Ising anisotropy, Tb\(^{3+}\) moments are usually ordered in non-collinear structures in the \(ab\)-plane and the interaction with an external magnetic field changes the magnetic alignment. Due to this anisotropy, the final configuration of each grain in a polycrystalline sample strongly depends on its geometric orientation with respect to the magnetic field. This makes a quantitative study on polycrystalline samples very difficult but important qualitative information can still be extracted. A study on a TbMn\(_{0.9}\)Al\(_{0.1}\)O\(_3\) single crystal [18] with \(\mathbf{H} || \mathbf{b}\) revealed a metamagnetic transition of the Tb\(^{3+}\) moments. At high fields, they adopt the C\(_x\)F\(_y\) structure following the Bertaut’s nomenclature [21]. This implies that moments are ferromagnetically aligned along the y-direction while a C-type AFM ordering is observed for the x-direction. This type of ordering also accounts for the occurrence of F- and C-type reflections in the neutron pattern at high fields for the present TbMn\(_{0.9}\)A\(_{0.1}\)O\(_3\) samples.
(A=Sc, Ga or Co). The ferromagnetic component along the field direction suggests that in the case of \( \mathbf{H} \parallel \mathbf{a} \), the most plausible magnetic structure would be \( \text{F}_x\text{C}_y \). Our attempts to refine the neutron patterns at high fields with a combination of both structures for Tb-moments (shown in figure 8) yielded satisfactory results with the only exception of the lack of intensity for (100) and (010) reflections. The absence of these reflections in the experimental pattern can be understood taking into account the geometry of our experimental setup outlined in figure 9. The magnetic field is vertical and perpendicular to the scattering vector. When the diffraction condition is fulfilled for the (1 0 0) reflection —or the (0 1 0) one— in a particular crystallite, its scattering vector is perpendicular (not parallel) to the magnetic field and therefore the FM ordering along the scattering direction in very disfavored so that this crystallite cannot adopt the \( \text{F}_x\text{C}_y \) magnetic structure —or the \( \text{C}_x\text{F}_y \) type magnetic structure for the (0 1 0) case— and there is no magnetic contribution to this reflection.

Therefore, we have modeled the powder neutron patterns excluding the 20 range of (010) and (100) reflections and including the magnetic contributions of the AFM ordering of the \( \text{Mn}^{3+} \) moments and of the two magnetic structures of the \( \text{Tb}^{3+} \) moments (Fig. 8a and 8b). For the Co-doped compound, only the magnetic contribution from the Tb-sublattice was considered (Fig. 8c). The refined magnetic moment for Mn atoms is 2.89(6) and 3.92(6) for \( \text{TbMn}_{0.9}\text{Sc}_{0.1}\text{O}_3 \) and \( \text{TbMn}_{0.9}\text{Ga}_{0.1}\text{O}_3 \) samples, respectively. These results suggest a more complete Mn-ordering in the Ga-based sample in agreement with its larger \( \lambda \)-anomaly in the Cp-measurements (see Fig. 2).

Regarding the ordering of Tb moments, only qualitative information can be extracted. Our refinement suggests a higher contribution from the \( \text{F}_x\text{C}_y \) phase with respect to the \( \text{C}_x\text{F}_y \) one. This may indicate that the Ising direction is closer to the \( \mathbf{a} \)-axis. Previous studies in related systems [12,13] found the Ising direction at 34-40º from the
a-axis in agreement with our hypothesis. Nevertheless, further studies on single crystals with different geometries are desirable to determine the Tb-ordering with accuracy.


The substitution of Mn in TbMnO$_3$ by small amounts of different cations leads in the case of non-magnetic atoms (Al, Ga, Sc) to a weakening of the Mn-O-Mn interaction with a gradual decrease of $T_{N1}$. The weakening increases with increasing the cationic size of the non-magnetic dopant, but long range AFM ordering is preserved in the Mn-sublattice. In the Co-based sample, the non-isovalent substitution produces competitive magnetic interactions preventing the Mn ordering. All of these substitutions are very detrimental to the magnetic ordering of Tb moments observed in the parent TbMnO$_3$ compound. Upon 10% of doping diffuse scattering is present in the neutron patterns indicating short range magnetic ordering of the Tb-moments. This indicates that a perfectly ordered magnetic Mn-sublattice is required to develop the incommensurate AFM ordering of Tb$^{3+}$ observed in TbMnO$_3$ [5]. This agrees with previous suggestions that this ordering arises from the interplay between $J_{\text{Mn-Tb}}$ and $J_{\text{Tb-Tb}}$ interactions [22].

The application of external magnetic fields favors the $J_{\text{Tb-Tb}}$ interaction and disturbs the coupling between Mn and Tb sublattices. While the Tb-sublattice gets realigned in the $ab$-plane the Mn-sublattice remains unchanged, i.e. with an AFM order in Ga- and Sc-based samples or disordered in the Co-doped sample ($J_{\text{Mn-Mn}}$ is practically insensitive to the magnetic field). The Tb$^{3+}$ moments are ordered in a $F_{i}C_{j}$ mode ($i\neq j=x,y$) depending on the magnetic field orientation as the crystal field anisotropy fixes the direction of the moments [12,13].

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References.


FIGURE CAPTIONS

Figure 1. X-ray powder diffraction pattern for TbMn$_{0.9}$Al$_{0.1}$O$_3$ 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$_x$O$_3$ ($x\leq0.1$) samples. The type of dopant (A) is given for each curve.

Figure 2. Temperature dependence of the specific heat divided by temperature for (a) TbMn$_{0.95}$A$_{0.05}$O$_3$ and (b) TbMn$_{0.9}$A$_{0.1}$O$_3$ samples (A=Al, Ga, Sc and Co).

Figure 3. Neutron powder diffraction at 2 K and zero magnetic field for (a) TbMn$_{0.95}$A$_{0.05}$O$_3$ and (b) and TbMn$_{0.9}$A$_{0.1}$O$_3$ samples (A=Al, Ga, Sc and Co). The patterns have been shifted vertically for the sake of comparison.

Figure 4. Magnetic hysteresis loops at 5 k for TbMn$_{0.9}$Sc$_{0.1}$O$_3$, TbMn$_{0.9}$Ga$_{0.1}$O$_3$ and TbMn$_{0.9}$Co$_{0.1}$O$_3$.

Figure 5. Neutron powder diffraction at 2 K and at different magnetic fields for (a) TbMn$_{0.9}$Sc$_{0.1}$O$_3$, (b) TbMn$_{0.9}$Ga$_{0.1}$O$_3$ and (c) TbMn$_{0.9}$Co$_{0.1}$O$_3$.

Figure 6. Peak intensity of selected Bragg reflections vs. magnetic field intensity for (a) TbMn$_{0.9}$Sc$_{0.1}$O$_3$ and (b) TbMn$_{0.9}$Co$_{0.1}$O$_3$.

Figure 7. Peak intensity of Bragg reflections vs. temperature for (a) TbMn$_{0.9}$Sc$_{0.1}$O$_3$ and (b) TbMn$_{0.9}$Co$_{0.1}$O$_3$.

Figure 8. Rietveld refinements of the neutron powder diffraction at 2 K and $\mu_0H=3$ T for (a) TbMn$_{0.9}$Sc$_{0.1}$O$_3$, (b) TbMn$_{0.9}$Ga$_{0.1}$O$_3$ and (c) TbMn$_{0.9}$Co$_{0.1}$O$_3$.

Figure 9. Geometry in the diffraction measurement at D1B/D20. Magnetic field is located vertically, ie perpendicular to the plane composed by scattering vector $\mathbf{Q}$ and both the incoming and outgoing neutron beam (indicated by the vectors $\mathbf{k}$). Left and right pictures show the arrangement for (0 1 0) and (1 0 0) planes, respectively.
Figure 1.
Figure 2.

(a) $C_p/T$ (J/mol K\(^2\))

(b) $C_p/T$ (J/mol K\(^2\))

- $\text{TbMnO}_3$
- $\text{TbMn}_{0.95}\text{Al}_{0.05}\text{O}_3$
- $\text{TbMn}_{0.95}\text{Ga}_{0.05}\text{O}_3$
- $\text{TbMn}_{0.95}\text{Sc}_{0.05}\text{O}_3$
- $\text{TbMn}_{0.95}\text{Co}_{0.05}\text{O}_3$
Figure 3.

(a) and (b) show the X-ray diffraction patterns for different elements: Mn, Tb, Al, Ga, Sc, Co. The intensity (counts) is plotted against 2θ (°) for each element.
Figure 4.

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\begin{align*}
\text{TbMn}_{0.9}\text{A}_{0.1}\text{O}_3
\end{align*}
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Figure 5.
Figure 6.
Figure 7.
Figure 8.
Figure 9.