Interplay between magnetic order at Mn and Tm sites alongside the structural distortion in multiferroic films of o-TmMnO₃

Y. W. Windsor, M. Ramakrishnan, L. Rettig, A. Alberca, E. M. Bothschafter, and U. Staub
Swiss Light Source, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland

K. Shimamoto, Y. Hu, T. Lippert, and C. W. Schneider
General Energy Research Department, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland

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We employ resonant soft x-ray diffraction to individually study the magnetic ordering of the Mn and the Tm sublattices in single-crystalline films of orthorhombic (o-)TmMnO₃. The same magnetic ordering wave vector of \((0 q 0)\) with \(q \approx 0.46\) is found for both ionic species, suggesting that the familiar antiferromagnetic order of the Mn ions induces a magnetic order on the Tm unpaired \(4f\) electrons. Indeed, intensity variations of magnetic reflections with temperature corroborate this scenario. Calculated magnetic fields at the Tm sites are used as a model magnetic structure for the Tm, which correctly predicts intensity variations at the Tm resonance upon azimuthal rotation of the sample. The model allows ruling out a \(bc\)-cycloid modulation of the Mn ions as the cause for the incommensurate ordering, as found in TbMnO₃. The structural distortion, which occurs in the ferroelectric phase below \(T_C\), was followed through nonresonant diffraction of structural reflections forbidden by the high-temperature crystal symmetry. The \((0 q 0)\) magnetic reflection appears at the Mn resonance well above \(T_C\), indicating that this reflection is sensitive also to the intermediate sinusoidal magnetic phase. The model presented suggests that the Tm \(4f\) electrons are polarized well above the ferroelectric transition and are possibly not affected by the transition at \(T_C\). The successful description of the induced order observed at the Tm resonance is a promising example for future element-selective studies in which “spectator” ions may allow access to previously unobtainable information about other constituent ions.

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I. INTRODUCTION

Multiferroics are a class of materials in which two (or more) hysteretic spontaneous long-range orders occur simultaneously. Nowadays one usually refers to the combination of a magnetic order coexisting with a ferroelectric polarization \((P)\), although other cases are also discussed [1]. “Improper” (or “type-II”) multiferroics are a subfamily of this class. In these, one “ferroic” order drives the other, so very strong magnetoelectric coupling is inherent to these systems. Improper multiferroics have been investigated intensively since the discovery of multiferroicity in TbMnO₃ over a decade ago [2]. This is driven mainly by the prospect of controlling magnetism with electric fields (or vice versa), which would pave the way to highly efficient spintronic applications. To realize this, very strong magnetoelectric coupling, as observed in improper multiferroics, is required. Orthorhombic \(\text{(“o-“)}\) \(R\text{MnO}_3\) are a family of such materials \((R\) indicates a smaller rare-earth ion or \(Y\)), in which magnetic order lowers the crystal symmetry, resulting in ferroelectricity. Varying the \(R\) ion is known to change the Mn magnetic order of these systems, with the heaviest rare earths (and \(Y\)) producing the collinear \(E\)-type Mn order [3]. For these cases \(P\) can reach notably high values of \(\sim 1 \mu \text{C/cm}^2\) [4–6], which has sparked further theoretical interest into the mechanisms driving the multiferroic behavior [7–9]. To date, the mechanism stabilizing this phase is still under debate [10], although the experimental phase diagram [5] has been largely reproduced by Monte Carlo simulations [9]. Furthermore, the role of the \(R\) ions’ unpaired \(4f\) electrons remains unclear. These are expected to be purely paramagnetic down to very low temperatures, but at least in the case of \(R = \text{Ho}\), their order causes a dramatic increase in \(P\) [11].

In this study we are concerned with the case of \(R = \text{Tm}\), situated in the center of the \(E\)-type phase [5]. Experimental work by Pomjakushin et al. [12] presented orthorhombic \((o-)\text{TmMnO}_3\) as an example in which collinear antiferromagnetic order induces an exceptionally large electric polarization. Garganourakis et al. [13] measured the same polycrystalline sample and found the magnetic \((0 1/2 0)\) reflection (in \(Pbnm\) notation), showing that the Mn magnetic structure is in fact noncollinear, as predicted by Monte Carlo simulations [9]. Presently it is understood that a sinusoidal antiferromagnetic phase appears below \(T_N \approx 40\,\text{K}\), and the multiferroic phase appears below \(T_C \approx 32\,\text{K}\).

Resonant x-ray Bragg diffraction (RXD) is a powerful technique for studying periodic magnetic arrangements. Tuning the incoming photon energy to an absorption edge provides a resonant enhancement of otherwise weak magnetic Bragg reflections. The technique is element specific, as the signal from the resonant ion dominates others. As such, it allows studying the behavior of selected magnetic sublattices within complex materials, as recently shown for \(\text{Ba}_3\text{NbFe}_2\text{Si}_2\text{O}_{14}\) [14]. This technique is especially suitable for studying magnetism in thin films (as demonstrated on manganite and nickelate films [15–18]), as even small scattering volumes can be used due to the large resonant enhancement of magnetic scattering at the transition-metal \(L\) edges and rare-earth \(M\) edges.

Here we present diffraction experiments on single-crystalline epitaxial films of \(o\text{-TmMnO}_3\). By tuning the photon energy to the relevant absorption edges, we follow the magnetic order of the unpaired Mn \(3d\) and the Tm \(4f\) electrons separately. We show that these are linked to each other and can be described by a Mn-Tm induced order model.
We also utilize the high photon flux of a synchrotron light source to follow weak structural reflections directly sensitive to the ferroelectric distortion, which occurs as the multiferroic phase sets in.

II. EXPERIMENT

\(\alpha\)-TmMnO\(_3\) films were grown on Y\(\alpha\)IO\(_3\) [010] and [110] substrates (Crystec Co., Ltd.) by pulsed laser deposition. Pulsed beams from a KrF excimer laser (\(\lambda = 248\) nm, \(\tau = 25\) ns) were imaged onto a stoichiometric hexagonal TmMnO\(_3\) ceramic target with a fluence of \(2.3-2.7\) J cm\(^{-2}\) at a repetition rate of \(2\) Hz in a \(N_2\)O partial pressure of \(0.30\) mbar. The target-substrate distance was fixed at \(37\) mm and the substrate was heated to \(780\) °C during the film growth. The crystal structure and quality of the as-deposited films were investigated using Cu \(\alpha\) x-ray diffraction. Growth conditions are the same as for other \(\alpha\)-RMnO\(_3\) films, described in detail in Ref. [19]. Unless stated otherwise, all presented results are from a 400-nm-thick, [010]-oriented film.\(^1\)

Resonant soft x-ray diffraction experiments (RSXD) were conducted using the RESOX S UHV diffraction end station [20] at the SIM beam line [21] of the Swiss Light Source (SLS). Photon energies used correspond to the Mn values with respect to bulk values from Ref. [33]: 0.017\%, 0.335\%, all lattice parameters: at 16 K [010]-oriented film.1

Nonresonant x-ray diffraction (XRD) was conducted using a 400-nm-thick [010]-oriented film. Inset: a (\(=0\)) reflection taken at \(643\) eV, \(\sigma\)-polarized incoming light, at \(10\) K. The sample was oriented here with the \(c\) axis perpendicular to the scattering plane, suppressing the signal produced with incoming \(\sigma\) light, as expected (see main text).

\(^1\)Lattice parameters for the main \(\alpha\)-TmMnO\(_3\) film used, measured at 16.5 K: \((a,b,c) = (5.226\ \text{Å}, 5.789\ \text{Å}, 7.387\ \text{Å})\). Error estimate for all lattice parameters: \(\pm 0.001\ \text{Å}\). Corresponding compressive strain values with respect to bulk values from Ref. [33]: 0.017\%, 0.335\%, and −0.958\%.

FIG. 1. (Color online) Experimental geometry of the RSXD experiment on a film sample. The scattering plane contains the momentum transfer \(\mathbf{Q}\) and the directions of the incoming and outgoing beam, \(\mathbf{k}\) and \(\mathbf{k}'\), respectively. \(\theta\) is the Bragg angle and \(\chi_0\) is the angle between \(\mathbf{Q}\) and the film surface normal \(\hat{n}\). \(\Psi\) is an angle of sample rotation around the \(\mathbf{Q}\) direction. The bottom arrow (in green) indicates the \(a\)-axis direction within the film plane when \(\Psi = 0\).

FIG. 2. (Color online) Temperature dependence of the \((0\ 0\ 0)\) reflection taken at the Mn \(L_1\) edge (643 eV) with incoming \(\pi\)-polarized light. Sample: 400-nm-thick [010]-oriented film. Inset: intensity of the \((0\ 0\ 0)\) reflection as a function of incoming photon energy, measured with \(\pi\)- and with \(\sigma\)-polarized incoming light, at 10 K. The sample was oriented here with the \(c\) axis perpendicular to the scattering plane, suppressing the signal produced with incoming \(\sigma\) light, as expected (see main text).
including \( \text{TbMnO}_3 \), which is known to possess a constant incommensurate value slightly below \( T_1 \approx 15 \text{ K} \), below which it converges to a \( \sigma \)-type phase \([9]\). Based on Monte Carlo simulations, they predicted an additional canting within the magnetic structure, not an \( E \)-type.

Figure 4 presents the variations in diffracted intensity as \( \Psi \) changes. The red triangles are the lines of expected intensity from Eqs. (1)a and (A1). We find an excellent agreement with the data and thus conclude that the model of a canted (noncollinear) \( E \)-type magnetic structure is in good agreement with the data available from the \( \text{Mn} \ L_3 \) edge.

A noncollinear model was also presented by Mochizuki \etal\ for the \( \text{Mn} \ E \)-type phase \([12,13]\). This is in contrast to results from bulk samples, in which a commensurate \( \sigma \) value is present down to \( T \approx 15 \text{ K} \), below which it converges to a \( \sigma \)-type phase \([9]\). Based on Monte Carlo simulations, they predicted an additional canting within the magnetic structure, not an \( E \)-type.

Following the formalism laid out by Hannon \etal\ and Hill and McMorrow \([25,26]\), the magnetic structure factor from resonant diffraction in the limit of a dipole transition is given by \([27]\)

\[
F(Q) = (e_i \times e') \cdot \sum_{i=1}^{N} m_i e^{2\pi i Q \cdot r_i},
\]

and the expected intensity follows \( I(Q) \propto F \cdot F^\ast \). Here \( Q \) represents the momentum transfer vector of the measured reflection, while \( e_i \) and \( e' \) represent the electric field axis of the incoming and outgoing light, respectively. The sum is over \( N \) resonant ions, with \( r_i \) and \( m_i \) the position in the unit cell and magnetic moment of the \( i \)-th resonant ion, respectively.

Calculating the magnetic structure factor for the \( (0 \ 0 \ 0) \) reflection with Eq. (1), one finds that the collinear \( E \)-type magnetic structure should produce no diffraction intensity, which is inconsistent with our observation. A nonzero structure factor can occur if a moment component exists along another axis. We therefore use a model with moments alternately canting along the \( c \) axis by an angle \( \pm \phi \), as depicted in Fig. 5. This model has been previously presented for \( \sigma \)-\( \text{RMnO}_3 \) systems \([13,15,16]\), and is an analogy to the behavior of mixed valence manganites, as shown by Jirak \etal\ \([28]\). This canting has been found to be directly connected to the ferroelectric distortion in \( \sigma \)-\( \text{LuMnO}_3 \), and is also strain dependent \([16]\). The diffraction intensities calculated from this model using Eq. (1) are plotted in Fig. 4 for \( \sigma \) and \( \pi \) linearly polarized incident light (see explicit expression in the Appendix). We find an excellent agreement with the data and thus conclude that the model of a canted (noncollinear) \( E \)-type magnetic structure is in good agreement with the data available from the \( \text{Mn} \ L_3 \) edge.

A noncollinear model was also presented by Mochizuki \etal\ for the \( E \)-type phase \([9]\). Based on Monte Carlo simulations, they predicted an additional canting within the \( ab \) plane of \( \pm 27.5^\circ \) away from the \( b \) axis, representing a noncollinear in-plane magnetic structure, and a canting in

Previous works \([5,12,13]\). The magnitude of \( q \) varies with temperature down to \( T \approx 15 \text{ K} \), below which it converges to a constant incommensurate value slightly below \( 1/2 \), as found for films of \( R = \text{Lu} \) and \( \text{Y} \) \([15,16,23]\). This is in contrast to results from bulk samples, in which a commensurate \( q = 1/2 \) value is reported in the antiferromagnetic \( E \)-type phase \([12,13]\).

Figure 4 presents the variations in diffracted intensity as the sample is rotated about the momentum transfer vector \( Q = (0 \ 0 \ 0) \). The intensities are normalized to the intensity with unpolarized light \( (I_\sigma + I_\pi) \), which compensates for misalignment errors during sample rotation. We find that for \( \Psi = 90^\circ \) and \( 270^\circ \) the intensities for \( \pi \) and for \( \sigma \)-polarized incident light are equal, while for \( \Psi = 0^\circ \) and \( 180^\circ \) the intensity from \( \pi \) is maximal, and that from \( \sigma \) is absent. Similar results were reported for other \( \sigma \)-\( \text{RMnO}_3 \) systems \([15,16,24]\), including \( \text{TbMnO}_3 \), which is known to possess a \( bc \)-cycloid \( \text{Mn} \) magnetic structure, not an \( E \)-type.
FIG. 5. (Color online) Depiction of the commensurate canted $E$-type model, projected onto the $bc$ plane. E1 and E2 are the two equivalent $E$-type domains (labels as in Ref. [7]). Mn ions (large spheres) are shown with empty and filled (red) arrows, representing the collinear and $c$-axis canted Mn moments. The canting angle $\phi$ between them is indicated. The Tm ions (small spheres) are presented in bright (green) and dark (purple) shades indicating the local field magnitudes $m_1$ and $m_2$ at the Tm sites (see Table I). Dashed boxes indicate the chemical unit cell.

the $c$ direction which amounts to $\phi \approx \pm 9.7^\circ$. Calculating the magnetic structure factor for this model also agrees with our experimental observations. Unfortunately, we cannot distinguish between the models using our observations, as the $(0 q 0)$ reflection is insensitive to the canting in the $ab$ plane, and other magnetic reflections are not accessible at the Mn $L_{2,3}$ edges. As such, we do not consider this more complicated model in detail.

B. Magnetic diffraction at the Tm $M_5$ edge

The Tm $M_{4/5}$ absorption edges ($3d \rightarrow 4f$ transitions) occur at higher photon energies than the Mn $L$ edges, granting access to additional reflections. Resonant x-ray diffraction at these edges is a measure of the Tm magnetic moments. Figure 6 presents scans along the $(0 k 0)$ direction of reciprocal space at the Tm $M_5$ absorption edge, for $\sigma$- and $\pi$-polarized incident light. A commensurate $(0 1 0)$ reflection, which is forbidden in $Pbnm$ symmetry, is observed due to Templeton and Templeton scattering [29], along with a $(0 q 0)$ reflection that has the same incommensurate $q$ value as the magnetic reflection found at the Mn $L_3$ edge. We note the absence of a $(0 1-q 0)$ reflection, which was observed in TbMnO$_3$ above

the ordering temperature of the Tb moments [30,31]. The energy dependences of the scattering intensity at these $k$ values are presented in Fig. 7 for both incident linear polarizations. The intensity observed at the $M_5$ is much stronger than

FIG. 6. (Color online) Reciprocal space scan along the $(0 k 0)$ direction, taken at the Tm $M_5$ edge using incoming $\sigma$- and $\pi$-polarized light at 16 K.

FIG. 7. (Color online) Energy dependences of the $(0 q 0)$ and $(0 1 0)$ reflections measured at 10 K, using linearly polarized incoming light, of either $\pi$ (black symbols) or $\sigma$ (red symbols) polarizations.
at the $M_5$, as expected [32]. The intensity of $(0 q 0)$ from $\sigma$-polarized incident light is dominated by contributions from specular reflectivity and fluorescence at resonance, and is not of magnetic origin.

The temperature dependence of the $(0 q 0)$ reflection is presented in Fig. 8. A reciprocal space map around the $(0 0 1)$ position in the $k\perp$ plane is shown in the inset, which shows the absence of a $(0 1 q 1)$ reflection. Figure 9 presents azimuthal variations in intensity as the sample is rotated about the $Q = (0 0 0)$ and $Q = (0 1 q 1)$ momentum transfer vectors. The case of $(0 q 0)$ is qualitatively similar to that found at the Mn $L_3$ edge, albeit with a variation in curvature. For $(0 q 1)$ the dependence is no longer twofold symmetric. Instead, there are regions with $I_{\sigma} > I_{\pi}$ and others with $I_{\sigma} < I_{\pi}$.

The data for the $(0 q 1)$ reflection is taken from both [010]- and [110]-oriented samples. This is because they provide access to different angular regions in the azimuthal scan. These ranges are limited due to blocking of the incoming or outgoing beam upon azimuthal rotation (in both cases $x_0 \neq 0$). In general, due to such beam blocking, an azimuthal scan is limited to angular ranges of $\pm \sin^{-1}(-\tan \theta/\tan x_0)$ around the intersections between the surface plane and the plane spanned by $Q$ and the film normal $\theta$ is the Bragg angle, and $x_0$ is the angle between the film normal and $Q$, see Fig. 1). This limit is valid for $\theta - x_0$ combinations in which the beam can be blocked by the film upon azimuthal rotation (i.e., $|\tan \theta/\tan x_0| < 1$).

The temperature evolution of the $q$ parameter at the Mn $M_5$ is shown alongside that from the Mn $L_3$ edge in Fig. 3(b). The $q$ values from the Mn edge appear locked to those from Mn, strongly suggesting that the observed Mn magnetic order has the same origin as the one for Mn. The difference in $q$ is roughly constant, and likely due to slight differences in the index of refraction at different energies.

As the Tm$^{3+}$ ions are expected to order independently only below $\sim 4$ K [12,33], the observed order must be induced through the mean magnetic field from the Mn moments in their crystal environment. This would explain the agreement of modulation (described by $q$) for the Mn and Tm sublattices. Furthermore, the temperature dependences of intensity from the magnetic reflections at the Tm $M_5$ and the Mn $L_3$ do not scale with each other. At the Mn resonance, intensity follows a typical order parameter squared profile (for a second-order phase transition), whereas magnetic reflections at the Tm resonance follow a concave temperature dependence [see Fig. 3(a)].

The induced order on the Tm ions should follow a paramagnetic behavior in a temperature-dependent mean field, as found for the paramagnetic Nd$^{3+}$ ions in NdNiO$_3$ [17]. In this case, the moment on a magnetic sublattice can be described by

$$M_{Tm} \propto g \mu_B J \cdot B_f \left( g \mu_B J \frac{H}{k_B T} \right).$$

Here $B_f$ is the Brillouin function, $g$ is the Landé factor, $\mu_B$ is the Bohr magneton, $J$ is the total angular momentum on the Tm site, and $H$ is the magnitude of the local magnetic field. Since the dipole field is linear with the ordered Mn moment, the local field is described as $H \propto \sqrt{I_{Mn}}$, in which $I_{Mn}$ is the intensity of the magnetic $(0 q 0)$ reflection at the Mn $L_3$ edge.
This intensity is only sensitive to the c-axis canting of the Mn moment, but as its temperature dependence in Fig. 3(a) bears no signature of \( T_c \), one can assume it is proportional to the full Mn moment. Taking also \( M_{Tm} \propto \sqrt{T_m} \), we fit the magnetic intensity at the Tm \( M_5 \) to Eq. (2). The temperature dependence of \( I_m \), shown in Fig. 3(a), is used in the fitting to correctly account for the variation of \( H \) with temperature. The fit, shown as a solid line in Fig. 3(a), is in good agreement with the Tm RSXD data. This indicates that the observed magnetic order of the Tm moments is induced by the ordering of the Mn moments. As \( I_m \) is observed above \( T_c \) and appears to be insensitive to it, the model predicts that the induced Tm order is also insensitive to it. Indeed, magnetic intensity is observed at the Tm \( M_5 \) above \( T_c \), which is defined according to the appearance of the ferroelectric structural distortion (see next section).

The induced magnetic structure scales with the local magnetic fields experienced by the Tm ions. To model this, we shall calculate the motif of magnetic fields at the Tm sites within the magnetic unit cell. Such fields should vary within the crystal with the periodicity of the Mn magnetic structure, as is indeed found for \( q \) at the Tm edge in Fig. 3(b). The Tm ions sit at low-symmetry crystallographic orbits (Pbnm Wyckoff position 4c), which are defined by two structural parameters: \( x \) and \( y \) (values are taken from Ref. [33]). The fields experienced by these sites will depend on these parameters, as well as on the Mn canting angle \( \phi \). We assume a fully commensurate \( (q = 1/2) \) Mn magnetic structure (shown in Fig. 5), and sum up magnetic dipole field contributions at each Tm site from nearby Mn moments (up to a cutoff distance of 20 Å [34]). We find that the sums of all dipole fields at the Tm sites point only along the c axis. Furthermore, two distinct values for the field magnitude are found. We label these \( m_1 \) and \( m_2 \), and parametrize them as functions of \( \phi \) according to

\[
m_i = h_i \sin(\phi - \delta_i),
\]

in which the constants \( h_i \) and \( \delta_i \) depend on \( x \) and \( y \). Values for \( h_i \) and \( \delta_i \) were calculated using structural data for \( o-TmMnO_3 \) from Ref. [33]. We find \( \delta_1 \) and \( \delta_2 \) at \(-94.2^\circ\) and \(-59.2^\circ\), respectively, and \( h_1 \) and \( h_2 \) are 0.155 and 0.113 T, respectively (fields are expressed in units of magnetic induction). For the latter values the Tesla units are normalized to the Mn moments in \( \mu_B \). Using 3.75\( \mu_B \) as the local Mn\(^{11}\) moment at low temperatures (reported for bulk \( o-TmMnO_3 \) [12]), we find the upper bounds for the local dipole fields: \( |m_1| \leq 0.581 \) T and \( |m_2| \leq 0.424 \) T. Adopting the 1.22\( \mu_B \) moment reported for the Tm\(^{21}\) ions at 2 K [12], we find that the interaction strength does not exceed 0.04 meV. This value is at least an order of magnitude lower than the expected Mn-Mn interaction strengths [9,10]. The Tm moments can thus be regarded purely as spectators, as their effect on the Mn order is negligible.

Table I summarizes the expressions for the magnetic field along the c axis at the Tm sites in the commensurate magnetic unit cell, following Eq. (3). Expressions are shown for fields induced by Mn domains E1 and E2, shown in Fig. 5.

<table>
<thead>
<tr>
<th>Position</th>
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<th>( 1/2 - x )</th>
<th>( x )</th>
<th>( x + 1/2 )</th>
<th>( -x )</th>
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<tr>
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<td>( 1/2 - y )</td>
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<td>1 + ( 1/2 - y )</td>
<td>1 - ( y )</td>
<td>1 + ( 1/2 + y )</td>
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<tr>
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<tr>
<td>Field (E2)</td>
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<td>( -m_2 )</td>
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C. Nonresonant x-ray diffraction

The appearance of the Mn E-type magnetic order is accompanied by a ferroelectric polarization \( P \). This is understood as a result of the magnetically induced lattice distortion, which lowers the crystal symmetry from \( Pbnm \) to \( P2_1nm \) [35]. The lattice distortion can be observed by following \( Pbnm \)-forbidden Bragg reflections, which are allowed by \( P2_1nm \). Their appearance is a clear indicator of the appearance of ferroelectricity, associated with the transition from the Mn sinusoidal magnetic order to the multiferroic phase.

Figure 10 presents the temperature dependence of the (0 3 3) reflection, which is one such reflection, measured at 8.45 keV (well below the Tm \( L_3 \) absorption edge). The signal appears clearly below \( T_c \approx 27 \) K, and intensifies as \( T \) is lowered. Weak intensity remains up to \( \sim 30 \) K. Integrated intensity of the (0 3 3) reflection is overplotted in Fig. 3(a), along
with the RSXD integrated intensities. Similar observations of \( Pbnm \)-forbidden reflections below \( T_C \) have been reported for \( o\)-YMnO\(_3\) and \( o\)-LuMnO\(_3\) films [15,16]. In the latter case, the distortion was estimated using the ratio of observed reflections. Such a ratio can be calculated if the actual crystal structure is known. The low-temperature symmetry of \( o\)-TmMnO\(_3\) has not been reported to date, but it has been reported for a single crystal of \( o\)-YMnO\(_3\), an isostructural material [36]. In that study (Ref. [35]), the largest displacement of Mn ions along the \( a \) axis was 0.0041 Å. Assuming that \( o\)-TmMnO\(_3\) distorts in the same way, we may interpolate between the \( Pbnm \) (50 K) and \( P2_1nm \) (21 K) structures reported in Ref. [35]. By doing so, we find that at the lowest measured temperature (16 K), the largest shift on Mn ions along the \( a \) axis is 0.0016 Å (±0.0001 Å).

IV. DISCUSSION

The structural distortion appears clearly only below \( T_C \approx 27 \) K, well below the appearance of \((0 \ 0 \ 0)\) intensity at the Mn edge at \( T_N \approx 40 \) K. \( T_C \) is slightly lower than bulk values (≈32 K), likely due to epitaxial strain. Nevertheless the temperature variation of the structural distortion below \( T_C \) follows a linear mean-field-like behavior. \( T_N \) is in excellent agreement with literature [5,33] but indicates that in the case of \( o\)-TmMnO\(_3\) the Mn \((0 \ 0 \ 0)\) is sensitive also to the sinusoidal magnetic order above the multiferroic phase. This differs from the case of \( o\)-LuMnO\(_3\) [16], where both orders occur nearly concomitantly, but agrees with the case of \( o\)-YMnO\(_3\) [15].

This shows that for TmMnO\(_3\) there is already a \( c \)-axis spin canting in the sinusoidal phase. Our data put into question the idea of coexisting Mn magnetic phases, proposed in Ref. [15]. A coexisting phase of commensurate \( E \) type without spin canting cannot be observed at the Mn \( L_3 \) edges, as its structure factor is zero. However, such a phase would induce magnetic commensurate order on the Tm moments. This would produce reflections with \( q = 1/2 \) at the Tm edge, even in the absence of Mn spin canting \((\phi = 0)\). As these are clearly absent, this excludes the coexistence of a commensurate Mn magnetic phase. Furthermore, from Eq. (3) we find that small variations in canting angle (e.g., due to strain) are only expected to cause small differences in the induced fields.

Kenzelmann et al. [37] explored the sinusoidal ("HTI") and multiferroic ("LTI") phases of TbMnO\(_3\), a scenario similar to the present one. They showed that the multiferroic behavior is well described by a trilinear coupling term in the Landau free energy \( V = \sum_{\nu \gamma} a_{\nu \gamma} \sigma_{\nu} \sigma_{\gamma} (-k) P_{\nu \gamma} \), in which \( \sigma_{\nu} \) are the magnetic order parameters associated with different irreducible representations (IRREP), and \( a_{\nu \gamma} \) is a strength parameter. In this picture, the sinusoidal (HTI) phase was described by one IRREP, while the multiferroic phase (LTI) was described by an additional one, which appears at lower \( T \)'s, and thus allows for a nonzero \( P \). In analogy, for the present case of \( o\)-TmMnO\(_3\), one could argue that the observed \( Pbnm \)-forbidden reflections are only sensitive to the low-temperature IRREP, corresponding to the collinear \( E \)-type phase \((\phi = 0)\). The \((0 \ q \ 0)\) at the Mn edge is clearly sensitive to the high-temperature IRREP, as it is sensitive also to the sinusoidal phase. Therefore we note that the induced order fit in Fig. 3(b) uses only this IRREP as the \( T \) dependence of the magnetic field. Also, unlike the case of TbMnO\(_3\), here we do not observe the \((0\ 1- q \ 0)\) or \((0 \ 1- q \ 1)\) reflections within the multiferroic phase.

As the \( E \)-type Mn order has been reported for polycrystalline \( o\)-TmMnO\(_3\), it is safe to assume this order (with a slight sinusoidal modulation) in the multiferroic phase for the present case as well. Nevertheless, the azimuthal angle dependences in Figs. 4 and 9 can also agree with the canted \( ab \)-cycloid described in Ref. [15]. A \( bc \) cycloid, however, would produce an azimuthal dependence which does not agree with the data in Fig. 9, and is therefore ruled out. The model presented by Mochizuki et al. also agrees with the observations but cannot be distinguished from the model presented herein. The in-plane \((a-b)\) angle in their model has a profound impact on the field magnitudes experienced by the Tm sites, as well as on the ratio between fields experienced at different sites.

The ordering wave vector found at 10 K is \((0 \sim 0.46 \ 0)\) and varies with temperature. This is in contrast to the fixed \((0 \ 1/2 \ 0)\) vector found for bulk [12,13]. The departure from \(1/2\) and the variation of \( q \) with temperature have been recently reported for a number of other \( o\)-R MnO\(_3\) systems with small \( R \) ions, when studied as epitaxial films [15,16,23]. A strain effect is therefore a likely cause, but a sufficient explanation of this is still absent. However, comparison of the values in the footnote of page 2 with Ref. [16] indicates that the \( b \)-axis strain is quite low (0.33%), while the \( a \)- and \( c \)-axis values are similar to those reported for \( o\)-LuMnO\(_3\) films. A metastable state with \( q = 0.458 \) was predicted for \( o\)-R MnO\(_3\) by Monte Carlo simulations [9]. Appropriate variation of epitaxial strain may be responsible for tipping the balance in favor of this phase over the commensurate phase.

V. SUMMARY

We have used resonant soft x-ray diffraction to study the magnetic order of the Mn and the Tm sublattices in \( o\)-TmMnO\(_3\) single-crystalline films. Both are found to have the same magnetic ordering parameter \( \approx 0.46 \), instead of \( q = 1/2 \) as expected from bulk. The intensity variations with temperature
from both resonances fit nicely to a model in which the ordered Mn ions project a magnetic field on the paramagnetic Tm ions. The mean dipole fields from the Mn are calculated at the Tm sites and are used as a model for the Tm order. Calculations from this model fit well with measured azimuthal dependences of magnetic reflections at the Tm resonance. A c-axis canted incommensurate E-type magnetic structure for the Mn moments agrees well with all data; however, an ab-cycloid cannot be ruled out either. A bc cycloid can be ruled out for the Mn, as the structure it would induce on the Tm ions would not yield the same azimuthal dependence of magnetic reflections at the Tm resonance. We have also used nonresonant hard x-ray diffraction to record the intensity variation of Phmm-forbidden reflections with temperature. These appear below $T_C$ and serve as an indicator for the onset of the multiferroic phase. We find that the Mn (0 q 0) magnetic reflection appears well above $T_C$, indicating that this reflection is sensitive also to the sinusoidal magnetic phase. The models presented indicate that the Tm 4f electrons are magnetically polarized well above the ferroelectric transition and do not appear to be affected by the transition at $T_C$.

Lastly, the successful description of the induced order observed at the Tm resonance provides a promising route for future element-selective studies. Such “spectator” ions may allow access to previously unobtainable information about other constituent ions (in this case Mn), or the magnitude of interatomic electronic interaction terms. In the present case the model allowed ruling out a possible Mn bc cycloid, as found in TbMnO$_3$.

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APPENDIX

This Appendix presents explicit calculations for the expected diffraction intensities from the model presented in Fig. 5. The canted Mn magnetic structure may be used with Eq. (1) to estimate the diffraction intensity from the (0 1/0) reflection at the Mn absorption edge. Intensities for $\pi$ and $\sigma$ linearly polarized incident light are

$$I_\pi \propto \sin^2 \phi \cdot (\cos^2 \theta \cos^2 \Psi + \sin^2 2\theta \sin^2 \Psi)$$

$$I_\sigma \propto \sin^2 \phi \cdot \cos^2 \theta \cos^2 \Psi,$$

which vanish for $\phi = 0$, as expected from the collinear E-type structure. The proportionality parameter for both expressions is the same.

By plugging the assumed Tm order from Eq. (3) and Table I into Eq. (1), explicit expressions are deduced for scattered intensity from magnetic reflections when using $\pi$ and $\sigma$ linearly polarized incident light. For the (0 1/0) reflection, we find

$$M^{(0,1/0)} = 4 \cos^2 \theta [1 + \sin(2\pi y)][h_1 \sin(\gamma_1 - \phi) - h_2 \sin(\gamma_2 - \phi)]^2$$

$$I_\pi^{(0,1/0)} \propto M^{(0,1/0)} [3 - \cos(2\Psi) - 4 \cos(2\theta) \sin^2 \Psi]$$

$$I_\sigma^{(0,1/0)} \propto 2 M^{(0,1/0)} \cos^2 \Psi$$

in which the term $M^{(0,1/0)}$ is merely defined for clarity. Doing the same for (0 1/2 1), we reach

$$M^{(0,1/2)} = \left( \frac{1}{2} \right) (h_1^2 [1 - \cos 2(\gamma_1 - \phi)] + h_2^2 [1 - \cos 2(\gamma_2 - \phi)]) [1 + \sin(2\pi y)]$$

$$I_\pi^{(0,1/2)} \propto M^{(0,1/2)} \left( \frac{1}{4} \right) [49 - 36 \cos 2\theta - 5 \cos 4\theta - 4 \cos^2 \theta (5 \cos 2\theta - 3) \cos 2\Psi - 16\sqrt{5} \sin 2\theta \sin \Psi]$$

$$I_\sigma^{(0,1/2)} \propto M^{(0,1/2)} \left( \frac{1}{4} \right) [11 - 9 \cos 2\theta - 2 \cos^2 \theta \cos 2\Psi + 4 \sqrt{5} \sin 2\theta \sin \Psi]$$

in which the term $M^{(0,1/2)}$ is also just for clarity. For each reflection the proportionality parameter is the same in the $I_\pi$ and $I_\sigma$ expressions.

INTERPLAY BETWEEN MAGNETIC ORDER AT Mn AND Tm . . . PHYSICAL REVIEW B 91, 235144 (2015)

[26] This formalism adequately describes intensities from magnetic moments along single crystallographic axes only, which is the present case.
[33] This procedure is not generally valid, because the dipole sum does not generally converge as the cutoff distance is increased (for example, in the case of a ferromagnet). However, in the present case of an antiferromagnet, the procedure is a valid assumption. This is because most contributions cancel each other out, so the dipole field at the Tm sites varies indefinitely by ±2% around a constant value as the cutoff distance is increased.