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

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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 $(0q0)$ 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 $(0q0)$ 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 (“*o*-”) *RMnO*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 $\sim 1 \mu\text{C}/\text{cm}^2$ [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* = Ho, their order causes a dramatic increase in *P* [11].

In this study we are concerned with the case of *R* = Tm, situated in the center of the *E*-type phase [5]. Experimental work by Pomjakushin *et al.* [12] presented orthorhombic (*o*-)TmMnO₃ 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 $(0\frac{1}{2}0)$ reflection (in *Pbmn* 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 $T_N \approx 40$ K, and the multiferroic phase appears below $T_C \approx 32$ 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 Ba₃NbFe₃Si₂O₁₄ [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*-TmMnO₃. 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

o-TmMnO₃ films were grown on YAlO₃ [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 TmMnO₃ ceramic target with a fluence of 2.3–2.7 J cm⁻² at a repetition rate of 2 Hz in a N₂O 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 K α x-ray diffraction. Growth conditions are the same as for other *o*-RMnO₃ 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 RESOXS UHV diffraction end station [20] at the SIM beam line [21] of the Swiss Light Source (SLS). Photon energies used correspond to the Mn $L_{2,3}$ absorption edges ($2p \rightarrow 3d$, ~ 643 and ~ 652 eV) and to the Tm $M_{4,5}$ absorption edges ($3d \rightarrow 4f$, ~ 1505 and ~ 1460 eV). Linearly polarized incident light was used, with either π or σ polarization (electric field in the scattering plane or perpendicular to the scattering plane, respectively). Scattered intensities were collected using an IRD AXUV100 photodiode. Samples were mounted on the cold head of a Janis flow cryostat and cooled to temperatures as low as 9 K. Rotation of the sample around the momentum transfer vector $\mathbf{Q}$ (azimuthal rotation, see experimental geometry in Fig. 1) was conducted using a mechanical arm to a precision of $\pm 3^\circ$. For all results herein the azimuthal angle Ψ is defined as zero when the crystallographic $\hat{a}$ axis is in the scattering plane.

Nonresonant x-ray diffraction (XRD) was conducted using a 3 + 2 diffractometer at the Surface Diffraction end station of the Materials Science beam line of the SLS [22]. The photon energy was 8.45 keV, using linearly polarized light with the electric field in the synchrotron plane. Diffracted intensities were collected using a Pilatus 100K detector mounted on the detector arm. All diffracted intensities were corrected for the polarization factor and for variations in the scattering volume due to sample rotation. Samples were cooled to temperatures as low as ~ 16 K using a Janis flow cryostat.

III. RESULTS

A. Magnetic diffraction at the Mn $L_{2,3}$ edges

X-ray diffraction at the Mn $L_{2,3}$ absorption edges ($2p \rightarrow 3d$ transitions) is directly sensitive to the unpaired $3d$ electrons

¹Lattice parameters for the main *o*-TmMnO₃ film used, measured at 16.5 K : (a,b,c) = (5.226 Å, 5.789 Å, 7.387 Å). Error estimate for all lattice parameters: ± 0.001 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, $\vec{k}$ and $\vec{k}'$, respectively. θ is the Bragg angle and χ_0 is the angle between $\mathbf{Q}$ and the film surface normal $\hat{n}$. Ψ 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 $\Psi = 0$.

at the Mn³⁺ sites. This allows studying magnetic ordering solely of the Mn moments through magnetic reflections arising from their periodicity. Figure 2 presents the temperature dependence of the magnetic (0 q 0) reflection taken at 643 eV, with $q \approx 1/2$. The energy dependence of this reflection at 10 K is presented in the inset of Fig. 2, nicely showing the resonant enhancement of the diffraction signal. Temperature dependences of the integrated intensity and the magnitude of the ordering wave vector q are presented in Fig. 3. The reflection appears below $T_N \approx 40$ K, in agreement with

FIG. 2. (Color online) Temperature dependence of the (0 q 0) reflection taken at the Mn L_3 edge (643 eV) with incoming π -polarized light. Sample: 400-nm-thick [010]-oriented film. Inset: intensity of the (0 q 0) reflection as a function of incoming photon energy, measured with π - and with σ -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 σ light, as expected (see main text).

FIG. 3. (Color online) (a) Temperature dependence of integrated intensities. Blue and black circles represent the $(0q0)$ reflection measured with RSXD at the Mn L_3 and Tm M_5 edges, respectively. These reflections were measured in the same experiment. The solid line is a fit of the Tm RSXD dataset to an induced order moment [Eq. (2), see main text] using the Mn RSXD dataset to account for the temperature variation in the magnetic field. The red triangles are the (033) reflection measured with XRD. (b) Temperature dependence of the modulation parameter q , from the Mn L_3 and Tm M_5 edges (measured in the same experiment).

previous works [5,12,13]. The magnitude of q varies with temperature down to $T \approx 15$ K, below which it converges to a constant incommensurate value slightly below $1/2$, as found for films of $R = \text{Lu}$ and 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 $\mathbf{Q} = (0q0)$. The intensities are normalized to the intensity with unpolarized light ($I_\pi + I_\sigma$), which compensates for misalignment errors during sample rotation. We find that for $\Psi = 90^\circ$ and 270° the intensities for σ - and for π -polarized incident light are equal, while for $\Psi = 0^\circ$ and 180° the intensity from π is maximal, and that from σ is absent. Similar results were reported for other o -RMnO₃ systems [15,16,24], including TbMnO₃, which is known to possess a bc -cycloid Mn magnetic structure, not an E -type.

FIG. 4. (Color online) Variation of integrated intensity of the $(0q0)$ reflection upon azimuthal rotation, measured at the Mn L_3 edge at 16 K, using σ and π linearly polarized light. Solid lines are calculations of expected intensity from Eqs. (1) and (A1).

Following the formalism laid out by Hannon *et al.* and Hill and McMorro [25,26], the magnetic structure factor from resonant diffraction in the limit of a dipole transition is given by [27]

$$F(\mathbf{Q}) = (\mathbf{e}' \times \mathbf{e}) \cdot \sum_{i=1}^N \mathbf{m}_i e^{2\pi i \mathbf{Q} \cdot \mathbf{r}_i}, \quad (1)$$

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

Calculating the magnetic structure factor for the $(0\frac{1}{2}0)$ 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 canted along the c axis by an angle $\pm\phi$, as depicted in Fig. 5. This model has been previously presented for o -RMnO₃ systems [13,15,16], and is an analogy to the behavior of mixed valance manganites, as shown by Jirak *et al.* [28]. This canting has been found to be directly connected to the ferroelectric distortion in o -LuMnO₃, and is also strain dependent [16]. The diffraction intensities calculated from this model using Eq. (1) are plotted in Fig. 4 for π and σ 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 Mn L_3 edge.

A noncollinear model was also presented by Mochizuki *et al.* 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

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 ϕ 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 σ - and π -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 TbMnO₃ above

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

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. 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 π (black symbols) or σ (red symbols) polarizations.

FIG. 8. (Color online) Temperature dependence of the $(0q0)$ reflection measured at the Tm M_5 absorption edge. Inset: a reciprocal space map of the $(0q1)$ reflection at 10 K, measured on a $[110]$ -oriented film using π -polarized light.

at the M_4 , as expected [32]. The intensity of $(0q0)$ from σ -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 $(0q0)$ reflection is presented in Fig. 8. A reciprocal space map around the $(0q1)$ position in the k - l plane is shown in the inset, which shows the absence of a $(01-q1)$ reflection. Figure 9 presents azimuthal variations in intensity as the sample is rotated about the $\mathbf{Q} = (0q0)$ and $\mathbf{Q} = (0q1)$ momentum transfer vectors. The case of $(0q0)$ is qualitatively similar to that found at the Mn L_3 edge, albeit with a variation in curvature. For $(0q1)$ 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 $(0q1)$ reflection is taken from both $[010]$ - and $[110]$ -oriented films. This is because they provide access to different angular ranges in the azimuthal scan. These ranges are limited due to blocking of the incoming or outgoing beam upon azimuthal rotation (in both cases $\chi_0 \neq 0$). In general, due to such beam blocking, an azimuthal scan is limited to angular ranges of $\pm \sin^{-1}(-\tan \theta / \tan \chi_0)$ around the intersections between the surface plane and the plane spanned by $\mathbf{Q}$ and the film normal (θ is the Bragg angle, and χ_0 is the angle between the film normal and $\mathbf{Q}$, see Fig. 1). This limit is valid for θ - χ_0 combinations in which the beam can be blocked by the film upon azimuthal rotation (i.e., $|\tan \theta / \tan \chi_0| \leq 1$).

The temperature evolution of the q parameter at the Tm M_5 is shown alongside that from the Mn L_3 edge in Fig. 3(b). The q values from the Tm edge appear locked to those from Mn, strongly suggesting that the observed Tm 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 Tm³⁺ ions are expected to order independently only below ~ 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

FIG. 9. (Color online) Variation in RSXD intensity from the $(0q0)$ and $(0q1)$ reflections upon azimuthal rotation, measured at 10 K at the Tm M_5 edge (~ 1460 eV) with incoming σ - or π -polarized linear light. Data are normalized by the sum of intensities from σ and π light (see figure legend). Triangles and circles correspond to data from $[110]$ -oriented or $[010]$ -oriented samples, respectively. Solid lines are calculations based on Eqs. (1), (A2), and (A3). Dashed lines are the equivalent calculation of an induced Tm order from a Mn bc cycloid.

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 Nd³⁺ ions in NdNiO₃ [17]. In this case, the moment on a magnetic sublattice can be described by

$$M_{\text{Tm}} \propto g\mu_B J \cdot B_J \left(g\mu_B J \frac{H}{k_B T} \right). \quad (2)$$

Here B_J is the Brillouin function, g is the Landé factor, μ_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 $H \propto \sqrt{I_{\text{Mn}}}$, in which I_{Mn} is the intensity of the magnetic $(0q0)$ reflection at the Mn L_3 edge.

TABLE I. Expressions for the magnetic field along the c axis at all 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.

Position	x	$x + 1/2$	$-x$	$1/2 - x$	x	$x + 1/2$	$-x$	$1/2 - x$
	y	$1/2 - y$	$-y$	$y + 1/2$	$1 + y$	$1 + 1/2 - y$	$1 - y$	$1 + y + 1/2$
	$1/4$	$3/4$	$3/4$	$1/4$	$1/4$	$3/4$	$3/4$	$1/4$
Field (E1)	$-m_2$	$-m_2$	$-m_1$	$-m_1$	m_2	m_2	m_1	m_1
Field (E2)	m_1	$-m_1$	$-m_2$	m_2	$-m_1$	m_1	m_2	$-m_2$

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 $M_{\text{Tm}} \propto \sqrt{I_{\text{Tm}}}$, we fit the magnetic intensity at the Tm M_5 to Eq. (2). The temperature dependence of I_{Mn} , 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_{Mn} 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 ϕ . 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 ϕ according to

$$m_i = h_i \sin(\phi - \delta_i), \quad (3)$$

in which the constants h_i and δ_i depend on x and y . Values for h_i and δ_i were calculated using structural data for o -TmMnO₃ from Ref. [33]. We find δ_1 and δ_2 at -94.2° and -59.2° , 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 μ_B . Using $3.75\mu_B$ as the local Mn³⁺ moment at low temperatures (reported for bulk o -TmMnO₃ [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 Tm³⁺ 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 doubled unit cell, induced by Mn domains E1 and E2. The allocation of m_1 and m_2 labeling to the Tm sites is also shown in Fig. 5. As the moments at the Tm sites scale with the local magnetic fields, we adopt this structure to calculate the expected intensities at the Tm edge using Eq. (1). The calculated azimuthal angle dependence of intensity from the (0 q 0) and (0 q 1) reflections is presented as solid lines in Fig. 9. Explicit expressions are given in the appendix. For (0 q 1) the experimental Bragg angle $\theta = 42^\circ$ is used in the calculation, as the curves' shape depends on it. Excellent agreement is found for (0 q 0), and qualitatively good agreement is found for (0 q 1). The deviations are most likely due to variations in Bragg angle between the two samples and due to the $q = 1/2$ approximation used. This agreement shows that the dipolar field induced order model adequately describes the behavior of the RSXD data at the Tm M_5 edge. The dashed lines in the same figure indicate the calculated azimuthal dependence of these reflections, if the Tm order would be induced by a Mn bc cycloid. As the data clearly do not agree with the model, a Mn bc -cycloid scenario can be ruled out as the cause for the incommensurability.

For completeness, we also tested the noncollinear model for Mn order from Ref. [9]. The order induced in this case also agrees with the observed azimuthal dependence, and the local fields at the Tm sites are also purely along the c direction. Using the same magnetic moments reported for the Mn and Tm, we find that the ions experience fields m_1 and m_2 of 1.0 and 0.5 T. Dipolar interactions then reach over 0.07 meV, which are still small compared to expected Mn-Mn interactions.

C. Nonresonant x-ray diffraction

The appearance of the Mn E -type magnetic order is accompanied by a ferroelectric polarization $\mathbf{P}$. 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 ~ 30 K. Integrated intensity of the (0 3 3) reflection is overplotted in Fig. 3(a), along

FIG. 10. (Color online) Temperature dependence of the structural (0 3 3) reflection, forbidden by the high-temperature space group.

with the RSXD integrated intensities. Similar observations of $Pbnm$ -forbidden reflections below T_C have been reported for o -Y MnO_3 and o -Lu MnO_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 -Tm MnO_3 has not been reported to date, but it has been reported for a single crystal of o -Y MnO_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 -Tm MnO_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 q 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 -Tm MnO_3 the Mn (0 q 0) is sensitive also to the sinusoidal magnetic order above the multiferroic phase. This differs from the case of o -Lu MnO_3 [16], where both orders occur nearly concomitantly, but agrees with the case of o -Y MnO_3 [15]. This shows that for Tm MnO_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 Tb MnO_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 $V = \sum_{uv\gamma} a_{uv\gamma} \sigma_u(k) \sigma_v(-k) P_\gamma$, in which σ_i are the magnetic order parameters associated with different irreducible representations (IRREP), and $a_{uv\gamma}$ 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 -Tm MnO_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 Tb MnO_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 -Tm MnO_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 ~ 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 -RMnO $_3$ 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 -Lu MnO_3 films. A metastable state with $q = 0.458$ was predicted for o -RMnO $_3$ 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 -Tm MnO_3 single-crystalline films. Both are found to have the same magnetic ordering parameter ≈ 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 *Pbnm*-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 4*f* 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 TbMnO₃.

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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 1/2 0) reflection at the Mn absorption edge. Intensities for π and σ linearly polarized incident light are

$$\begin{aligned} I_\pi &\propto \sin^2\phi \cdot (\cos^2\theta\cos^2\Psi + \sin^22\theta\sin^2\Psi) \\ I_\sigma &\propto \sin^2\phi \cdot \cos^2\theta\cos^2\Psi, \end{aligned} \quad (A1)$$

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 π and σ linearly polarized incident light. For the (0 1/2 0) reflection, we find

$$\begin{aligned} M^{(0\ 1/2\ 0)} &= 4\cos^2\theta[1 + \sin(2\pi y)][h_1 \sin(\gamma_1 - \phi) - h_2 \sin(\gamma_2 - \phi)]^2 \\ I_\pi^{(0\ 1/2\ 0)} &\propto M^{(0\ 1/2\ 0)}[3 - \cos(2\Psi) - 4\cos(2\theta)\sin^2\Psi] \\ I_\sigma^{(0\ 1/2\ 0)} &\propto 2M^{(0\ 1/2\ 0)}\cos^2\Psi \end{aligned} \quad (A2)$$

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

$$\begin{aligned} M^{(0\ 1/2\ 1)} &= \left(\frac{1}{5}\right)(h_1^2[1 - \cos 2(\gamma_1 - \phi)] + h_2^2[1 - \cos 2(\gamma_2 - \phi)])[1 + \sin(2\pi y)] \\ I_\pi^{(0\ 1/2\ 1)} &\propto M^{(0\ 1/2\ 1)}\left(\frac{1}{4}\right)[49 - 36\cos 2\theta - 5\cos 4\theta - 4\cos^2\theta(5\cos 2\theta - 3)\cos 2\Psi - 16\sqrt{5}\sin 2\theta\sin \Psi] \\ I_\sigma^{(0\ 1/2\ 1)} &\propto M^{(0\ 1/2\ 1)}(11 - 9\cos 2\theta - 2\cos^2\theta\cos 2\Psi + 4\sqrt{5}\sin 2\theta\sin \Psi) \end{aligned} \quad (A3)$$

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

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