Unique coexistence of incommensurate and commensurate magnetic order in TbMnO₃ strained films

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Neutron diffraction studies on epitaxially strained orthorhombic (010) oriented TbMnO₃ thin films verify a theoretical prediction of an unusual magnetic phase with coexisting incommensurate and a commensurate order. Magnetic field dependent measurements of the (0 *q* 1) and (0 1 + *q* 1) Bragg reflections confirm that the magnetic intensity corresponding to an incommensurate *q* value has contributions from magnetic domains with both incommensurate and commensurate order. The ratio between the population of domains with commensurate and incommensurate order can be tuned by the magnetic field. In addition, the incommensurate order shows strong evidence of supporting the predicted *ab* cycloidal spin structure.

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I. INTRODUCTION

Magnetic phases in strongly correlated electron systems have generated a strong interest in the field of condensed matter physics. Orthorhombic TbMnO₃ represents a prototypical multiferroic where the magnetic ground state induces ferroelectric ordering [1]. It is a widely studied material having strong magnetoelectric coupling [2]. Magnetically, it transforms from a paramagnetic to an incommensurate (ICM) antiferromagnetic phase with a longitudinally modulated sinusoidal spin structure at $T_N \sim 41$ K [3]. The crystal symmetry remains unchanged and it stays paraelectric. On cooling below $T_C \sim 28$ K, the spin structure transforms to a *bc* cycloidal phase, which breaks the spatial inversion symmetry and induces a ferroelectric polarization (*P*) with $P||c$. The underlying mechanism depend purely upon the asymmetric Dzyaloshinskii-Moriya ($S \times S$)-type interaction between the Mn spins, which induces a displacement of the O²⁻ ion from the nonpolar equilibrium position in the Mn³⁺O²Mn³⁺ linear chain towards a polar orientation [4].

We have recently shown, that the multiferroic properties of coherently grown orthorhombic (o-) TbMnO₃ thin films can be drastically modified by epitaxial strain [5,6]. The effect of strain resembles the results of pressure-induced studies on bulk TbMnO₃ single crystals [7,8]. The multiferroic ground state is defined by a commensurate (CM) *E*-type antiferromagnetic order and a significantly enhanced ferroelectric polarization along the *a* axis as compared to $P||c$ in bulk. Microscopically, a symmetric exchange ($S \cdot S$)-type interaction seems to play a more dominant role for multiferroicity with $P||a$. Following theoretical studies, the large strain induced along the *b* axis favors an effective increase in the relative ratio between the exchange interactions $J_b/|J_{ab}|$, where J_b , J_{ab} are antiferromagnetic next-nearest-neighbor and ferromagnetic nearest neighbor exchange interaction coefficients, respectively. This enhancement is predicted to be responsible

for stabilizing the *E*-type ground state in RMnO₃ [5,6]. In addition and unlike in bulk, a unique high temperature ICM magnetic phase with ferroelectric order was observed below $T_N \sim 41$ K in the coherently grown thin films [9]. At present, a detailed understanding of this ferroelectric ICM phase is still lacking. A theoretical proposal by Mochizuki *et al.* predicted the coexistence of a metastable ICM spin state with CM *E*-type order. Their calculations demonstrate a strong dependence of the mixed magnetic state upon the size of J_b [4].

The existence of a mixed magnetic state was inferred from resonant soft x-ray diffraction experiments on YMnO₃ thin films [10]. From measurements of the (0, q_k , 0) magnetic reflection the ICM phase with $q_k < 0.5$ was identified. The *E*-type order, however, was only indirectly inferred from the effects of lattice distortions on the (0 1 0) reflection. Since the (0 1 0) reflection is forbidden for an orthorhombic symmetry, the existence of the (0 1 0) reflection in orthorhombic YMnO₃ was taken as evidence for the magnetic *E*-type order. A symmetry analysis for o-RMnO₃ confirmed that the existence of a forbidden nonmagnetic structural reflection implies purely a breaking of the rotational symmetry element along the *b* axis (2_b) [11]. This symmetry argument is supported by the simultaneous appearance of ferroelectric ordering and the (0 1 0) reflection. However, no direct evidence of a magnetic reflection at $q_k = 1/2$ was presented and the experimental verification of the proposed coexisting magnetic *E*-type order in RMnO₃ remained questionable. In this paper, we study the magnetic state of TbMnO₃ and provide direct evidence of the proposed coexistence state. Neutron diffraction is the ideal tool to test the unique mixed spin model. *Q*-dependent scans around the position of the magnetic reflection allow us to identify both the ICM and CM order. We further conduct magnetic field dependent measurements to confirm the magnetic character of the probed magnetic reflections.

II. SAMPLES AND CHARACTERIZATION

Pulsed laser deposition is used to grow epitaxial (0 1 0) oriented orthorhombic o-TbMnO₃ thin film with a thickness of 44 nm on (0 1 0) YAlO₃ substrates with structural properties similar as described in Ref. [5]. Crystallinity and the strain modified lattice parameters are estimated using reciprocal space mapping (not shown here) with lattice parameters $a = 5.182$ Å, $b = 5.936$ Å, $c = 7.371$ Å and the corresponding strain values ($\eta\%$) of $\eta_a = +2.1\%$, $\eta_b = -1.7\%$ and $\eta_c = +0.4\%$.

The magnetic order of the film is probed using neutron diffraction on the cold-neutron triple axis spectrometer RITA-II at the Swiss Spallation Neutron Source (SINQ) at the Paul Scherrer Institut (PSI) in Switzerland [12]. An incident wavelength of $\lambda_{\text{RITA-II}} = 4.21$ Å is selected by using the (002) reflection of a pyrolytic graphite (PG) monochromator and a 80' collimator is mounted after the monochromator. A PG filter between the monochromator and the sample and a cooled Be filter between the sample and the analyzer avoid higher order contaminations. The nine-blade analyzer in combination with an adjustable collimator before a position sensitive ³He detector uniquely provides an excellent signal-to-noise ratio and high q resolution. The sample was mounted in a He-flow cryostat with the (00 l) – (0 k 0) crystal axis in the horizontal scattering plane. This geometry gives access to the strongest magnetic peaks (0 q 1) and (0 1 + q 1) for the ICM and CM magnetic order as observed for similar films [9].

By utilizing vertical and horizontal cryomagnets, we were able to apply the external magnetic field along all three principle axes. The vertical magnet (maximum field 15 T) allows applying the external field along the crystallographic a axis, whereas the horizontal magnet (maximum field 6.9 T) was used to apply the external field along the b and c axis of the film. Due to geometrical constraints of the horizontal magnet [see Supplemental Material Fig. S1(a)] the strong magnetic (0 q 1) reflection was experimentally inaccessible and we therefore selected (0 1 + q 1) as the next strongest magnetic reflection, which is about 1.3 times weaker than (0 q 1).

III. RESULTS

A. Magnetic Properties

Recently, it was reported that o – RMnO₃ when grown as thin epitaxially strained films show unique changes in multi-ferroic properties [5,6,9]. At low temperatures the magnetic ground state is characterized by a CM E -type and a large ferroelectric polarization along the a -axis independent of the R -ion radii. To study the magnetic phase neutron scattering is used to measure the magnetic (0 q 1) reflections where q represented the magnetic modulation wave vector along the b axis in reciprocal space. The measured temperature dependence of q confirms that, below $T_N \sim 41$ K an ICM magnetic phase appears, which on cooling locks into an E type. In this article we use (0 1 0) TbMnO₃ films as described in Refs. [5,6] to study the ICM magnetic phase in more detail.

We measured the magnetic reflections (0 q 1) and (0 1 + q 1). The magnetic order of the Mn ion is found to give results similar as discussed in Ref. [5]. There is an ICM

phase with $q < 0.5$ at $T \sim 37.5$ K, which transformed into a CM E -type phase with $q = 0.5$ at $T \sim 31$ K. This CM order stays locked down to $T \sim 1.5$ K [Fig. 1(a)]. For a better understanding of the ICM phase, we conducted our measurements at $T \sim 37.5$ K. The peak shape of (0 q 1) reflection is found to be asymmetric with respect to the peak center implying a superposition of more than one peak. A careful analysis confirms, that a double-Gaussian function (Fig. 2) is necessary to reproduce the experimental peak shape and intensity which can be described by

$$I_{\text{cal}}(q) = I_0 + s \cdot q + \frac{A \cdot e^{-\frac{(q-q_A^c)^2}{w_A^2}}}{w_A \sqrt{\pi/2}} + \frac{B \cdot e^{-\frac{(q-q_B^c)^2}{w_B^2}}}{w_B \sqrt{\pi/2}} \quad (1)$$

with, I_{cal} the calculated intensity, I_0 is the offset representing the background intensity induced by incoherent scattering by the Al-made mechanical parts of the cryomagnet, s is the slope of the background, A, B = area under the curve corresponding to the integrated intensity of the incommensurate and commensurate contribution, respectively, q^c = peak center, and w = full width half maximum. We want to point out that the peak shape of the magnetic reflections is best described by two Gaussian peaks with the same q width [see for example Fig. 2(b)]. The width is given by the instrumental resolution, which implies a correlation length of several 100 Å for the corresponding magnetic domains. In our analysis we assume, that this long-range order is preserved at all temperatures and fields and therefore the width (w) in our global fit is fix. In magnetic reflections, the scattering intensity (I_{scatt}) is proportional to the ordered moment ($\langle m_i \rangle$) times the volume of magnetic domains V_m ; $I_{\text{scatt}} \propto (\langle m_i \rangle^2 V_m)$. In the calculated intensity function, the ratio between the areas $A : B$ represents the relative contribution of different magnetic domains and their corresponding magnetizations, and q^c is the magnetic order or periodicity of the magnetic unit cell.

The magnetic intensity of (0 q 1) shows a best convergence with the calculated intensity profile using Eq. (1). Two distributions centered at $q_{\text{IC}} \sim 0.485$ and $q_{\text{CM}} \sim 0.5$ representing an ICM and CM order, respectively, are needed to reproduce the measured intensity profile and asymmetry of the line shape. The ratio A / B is 3 : 1, implying that domains with ICM order have a dominant contribution [blue shade in Fig. 2(a)] to the overall magnetic intensity as compared to domains with CM order (black shade) in the absence of an external magnetic field. Here the coexisting mixed phase is present but the peak feature is subtle. Therefore, an external perturbation is necessary to verify the contributions with ICM and CM order and reveal unambiguously the magnetically mixed state in coherently strained TbMnO₃ thin films.

B. $H \parallel a$

To resolve and demonstrate the feature representing the coexistence of ICM and CM order a vertical magnetic field is applied along the a axis and (0 q 1) measured at $T \sim 37.5$ K as shown in Figs. 2(a)–2(d). The most prominent effect in the field dependent q scans is observed at $\mu_0 H = 2$ T [Fig. 2(b)]. A clear redistribution of the relative contribution from ICM and CM domains is observed. The intensity contribution from

FIG. 1. (a) Phase diagram showing temperature dependence of magnetic wave vector (q_k). Cartoon of E -type order and q_k values for $T = 5, 15, 25, 31$, and 38 K are taken from Refs. [5,7], (b) Magnetic intensity profile of $(0\ q\ 1)$ at different temperatures $T = 10, 31, 37.5$, and 60 K.

the CM order becomes more dominant with a ratio A/B of approximately 1:1.5. This reversal of domain population most clearly highlights the existence of the mixed magnetic state. In particular on ramping up the field from $\mu_0 H = 1-10$ T, the increase of the CM peak (black shade) and concurrent decrease in the ICM peak (blue shade) is observed for all fields. This effect is also accompanied by a decrease in the ICM modulation vector $q_{IC} \sim 0.48$ with increasing field, whereas the CM order stays pinned to $q_{CM} \sim 0.50$. On further ramping up the field the contribution of CM order gets more

pronounced with the relative ratio $A:B$ rising up to 1: 2.3 at $\mu_0 H = 13$ T (not shown).

C. $H||b$ and $H||c$

We measured the $(0\ 1 + q\ 1)$ reflection following the constraint of the experimental geometry using a horizontal magnetic field in the bc plane. To compensate for the reduction in the magnetic intensity of $(0\ 1 + q\ 1)$ compared to $(0\ q\ 1)$, the measurement was performed at the lower temperature

FIG. 2. Plots showing $(0\ q\ 1)$ reflections at $T = 37.5$ K with a set of different magnetic fields applied along the a axis (a) $\mu_0 H = 0$ T, (b) $\mu_0 H = 2$ T, (c) $\mu_0 H = 10$ T, and (d) $\mu_0 H = 13$ T. The solid line shows the best fit with the experimental data. Black and blue lines represent peaks corresponding to the CM and ICM phase, respectively.

FIG. 3. Plot showing the magnetic field dependence of the commensurate magnetic volume fraction for $H||a$ and $H||b$.

$T \sim 33$ K, but still within the ICM phase (as shown in Ref. [13]). Fitting the data with Eq. (1), it is found that contributions from both kinds of domains are necessary to reproduce the measured magnetic intensity as measured for $H||a$. Similar to $H||b$, the dominant contribution to the intensity also switches from ICM to CM domains with applied field [13]. At the highest field measured, $\mu_0 H = 6.5$ T, the ratio $A/B = 1 : 2.7$. The slight increase in the overall intensity of $(0\ 1 + q\ 1)$ is caused by an increase in the magnetization component normal to the scattering vector q . This increase in the magnetization component is due to a flipping of spins away from the field axis $\parallel b$.

For $H||c$, the peak shape does not change with field and no redistribution of the magnetic intensity between the CM and ICM domains occurs [13]. This implies that the magnetization components along the c axis are small and spins flipping away from the field axis $\parallel c$ fail to induce any effect to the magnetic intensity. In addition, the energy necessary for a reversal of contributing domains is not sufficient in this case. Here the ratio of domains corresponding to the ICM and CM order remains unaffected at all applied fields.

IV. DISCUSSION

In Fig. 3 we plot the volume fraction of the CM E -type magnetic domains in strained TbMnO_3 thin films as a function of external magnetic field. For both $H||a$ and $H||b$ the volume fraction of the CM domains accounts for about 25–30% in zero field and increases rapidly with field. The population of CM domains becomes already dominant at moderate magnetic fields below about $\mu_0 H \sim 1.5$ T, corresponding to a rather small energy of about 0.18 meV. The energy scale of the coupling of the magnetic field to the Mn spins is thus significantly smaller than the exchange interaction parameters, which are about 1 to 3.5 meV and define the stable magnetic ground state in o-RMnO_3 .

We explain the field and field direction dependent intensities with a field driven reorientation of the Mn spins. The application of an external magnetic field along the a direction tends to flip the antiferromagnetic spins normal to the a direction into the bc plane, which reduces the effective exchange energy. Experimentally, the population of the IC domains decreases rapidly during this reorientation process and this

implies that the Mn sublattice magnetization possesses a large a -axis component m_a^{IC} in the ICM ordered state.

The incommensurate magnetic state can arise from an amplitude modulated spin density wave (SDW) or a spiral spin state. In insulating systems, the local moments are unlikely to be modulated and a SDW state has never been observed in bulk RMnO_3 . This conjecture is further supported by a representation analysis as described in Refs. [13,14]. For crystals of $Pbnm$ symmetry the incommensurate order with $q = (0, q_k = 0.485, 0)$ is either collinear or a spin spiral. The existence of ferroelectric ordering, however, rules out the collinear magnetic state. All experimental observations are consistent with an ab -spiral magnetic ground state as predicted elsewhere [5,10].

We want to point out that the large P values $\sim 1 \mu\text{C}/\text{cm}^2$ at $T = 37.5$ K) observed in thin strained TbMnO_3 films originate from a combined effect of symmetric ($S \cdot S$)-type exchange striction for E -type CM order and an antisymmetric ($S \times S$)-type Dzyaloshinskii-Moriya interaction of the ab -spiral ICM order. Similar contributions to the FE polarization are observed in bulk $\text{Eu}_{1-x}\text{Y}_x\text{MnO}_3$ and $\text{Y}_{1-y}\text{Lu}_y\text{MnO}_3$ [11].

Based on our results we propose the following scenario: At zero field, the IC ferroelectric phase is described by coexisting domains of an ICM ab spiral and CM E -type order. These domains are spatially separated in real space as shown schematically in Fig. 4. For simplicity and to emphasize the mixed state the spin structure of the E -type order is depicted with the dominant sublattice magnetization component along the b axis, whereas the ab spiral of the ICM order is drawn with comparable components along the a and b axis. The length scale of the magnetic domains is arbitrary and the phase between the magnetization components and the chirality of the spiral order is not known. The application of a magnetic field enhances the density or the population of CM domains at the expense of the ICM domains.

To explain the origin of the coexisting magnetic phases, we discuss the proposed microscopic mechanism based on Monte Carlo simulations, which support such a unique behavior in o-RMnO_3 spin-driven multiferroics [4]. Depending on the antiferromagnetic exchange interaction parameter J_b , a first order transition along the b axis from an ICM spiral to a CM E -type phase is expected to occur at a finite thermal energy ($k_B T \neq 0$). For $1.4 \text{ meV} < J_b < 2.5 \text{ meV}$ and keeping other parameters fixed an ICM state deeply localized within the E -type phase can occupy a local energy minimum although the system favors the E -type order as the lowest energy state. As a consequence, the trapped ICM state will become part of a coexisting ICM/CM mixed state. The present experimental result therefore implies that the proposed coexisting state can be understood within such a spin model framework [4]. Supporting arguments for this scenario are the higher J_b -values for strained TbMnO_3 films, which were argued to be responsible for the observed tuning of the multiferroic ground state from an ICM bc -spiral in bulk to the E -type state [5]. We propose a scenario in which the large strain ($\sim 1.7\%$) along the b axis enhances the exchange interaction parameter J_b . This favors the spiral state (~ 1 meV) and stabilizes the coexisting state below $T_N \sim 41$ K. On cooling below $T_{\text{lock}} \sim 31$ K, the system locks to the E -type state and this leads to a further increase of J_b (> 2.5 meV).

FIG. 4. Cartoon showing the proposed magnetic spin structure of the mixed state in real space when projected in the ab plane. Mn d orbitals are staggered and the oxygen ion is represented by green circles.

Finally, we would like to comment on the theoretical prediction of a first order transition between the incommensurate spiral phase and the commensurate E -type state. Capacitance measurements along the a axis in o-HoMnO_3 films by Shimamoto *et al.* find a small thermal hysteresis indicative of a first order nature of the FE transition [15]. Strong thermal hysteresis effects are also present in field cooled and zero field cooled magnetization measurements of o-RMnO_3 films [16]. An example is shown for a TbMnO_3 thin film in Fig. S4. Both findings support the theoretical description of the coexisting ICM/CM phase.

Although the proposed theoretical model captures the gross experimental features, some differences remain. The magnetic ordering vector of the predicted ICM state is slightly lower ($q_{\text{ICM}}^{\text{cal}} \sim 0.458$) compared to the observed value ($q_{\text{ICM}}^{\text{exp}} \sim 0.485$). Calculations of the spin-correlation function in momentum space predict the ICM state to have a collinear ordering of the Mn spins, which cannot explain the observed finite sublattice magnetization components within the ab plane. A collinear spin ordering with canted moments is also ruled out by symmetry. Such a spin state would result in an effective ferromagnetic magnetization, which is not observed in magnetic susceptibility measurement [6].

It is important to note that the magnetic field induced properties of the magnetic state observed in strained TbMnO_3 thin films are significantly different from the behavior observed in bulk samples. In bulk TbMnO_3 , the application of a magnetic field along the b axis causes a flipping of the spin cycloid from the bc to the ab plane in the multiferroic state [1,17]. This is accompanied by a switching of the ferroelectric polarization from $P||c$ to $P||a$. A very different behavior is observed in our strained films. There, the application of a magnetic field transforms the spin spiral state into an E -type ordered state. This experimental finding strongly supports the proposed model of an ICM state occupying local energy minima within the E -type ordered CM state. The effect of the

magnetic field is to drive the ICM domains towards the more favorable CM order.

V. CONCLUSION

In summary, we investigated the high temperature ferroelectric ICM phase in thin epitaxially strained (010) TbMnO_3 films, which precedes the CM E -type phase ground state. Magnetic neutron diffraction confirms the depiction of the ferroelectric ICM phase by a unique coexistence of E -type and ab -spiral domains with the proposed ab -spiral spin structure of the ICM order. An external magnetic field favors the CM order as shown by the increase of the density of CM domains at the expense of ICM domains. These experiments also indicate why strained o-RMnO_3 thin films are nominal ICM but electrically behave like a commensurate E -type showing a large electrical polarization. The present work highlights the ability of epitaxial strain to stabilize unique mixed magnetic states. We further demonstrate that strain engineering in thin film systems is a good tuning parameter and tool to develop the physics of magnetic states in multiferroic materials.

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