Emergence of ferromagnetism in antiferromagnetic TbMnO$_3$

by epitaxial strain

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We show that in oxide thin films of spiral antiferromagnetic orthorhombic TbMnO$_3$, ferromagnetism emerges resulting from epitaxially induced strain. The unit cell volume can be tuned (contracting up to a 2%) by varying thickness and deposition conditions; it is found that the ferromagnetic response correlates with the unit cell deformation. Such effect of strain on the magnetic properties turns out to be similar to that occurring in collinear orthorhombic antiferromagnets such as YMnO$_3$. Owing to the intimate relationship between magnetic order and ferroelectricity in TbMnO$_3$, these results may provide a new route to induce magnetoelastic coupling and tailor their ferroelectric response.

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The coupling of ferroelectricity and ferromagnetism in a single material or heterostructure attracts much attention due to its promising applications in sensor and data storage technologies. The scarcity of materials which individually display this feature triggered the development of varied strategies where, for instance, the coupling is mediated by elastic or exchange-bias effects. Particularly relevant is the discovery that ferroelectricity can be obtained subsequent to magnetic ordering. Antiferromagnetic orthorhombic rare earth manganites (RMnO$_3$) probably constitute the best known example of such materials. Either if the magnetic structure is collinear (E-type as in YMnO$_3$ (YMO) (Ref. 4) or (HoMnO$_3$) (Ref. 5) or noncollinear [spiral as in TbMnO$_3$ (TMO)]$^6$, magnetic interactions give rise to atomic displacements destroying the center of symmetry and thus allowing an electrical polarization.$^7$ Due to this intimate link between magnetic structure and ferroelectricity, changes in the electrical polarization upon applied magnetic fields are to be expected. Indeed, it was the early experimental observation of such effects in bulk TMO (Ref. 8) that triggered intensive theoretical research and exploration of epitaxial thin films. However, investigation of magnetic properties on RMnO$_3$ films (Refs. 9–17) revealed the unexpected existence of a ferromagnetic response in otherwise bulk antiferromagnetic materials. Whereas in the case of E-type spin-ordered structures, its origin has been attributed to strain-induced deformation of the unit cell and subsequent unbalancing of magnetic interactions,$^9$–$^12,17$ it also has been proposed domain walls boundaries to be relevant in the case of the spiral TbMnO$_3$.$^{16}$ However, it turns out that the signatures of ferromagnetism reported$^3,9$–$^17$ are in all cases intriguingly similar. Whether the origin of the ferromagnetism in both compounds is the same irrespective of their bulk magnetic structure is a critical open issue that we aim to disentangle in this paper.

We report here on the magnetic properties of epitaxial TMO thin films. Data shows that the ferromagnetic response can be selected at wish by tuning the unit cell volume ($V_c$) through the film thickness and deposition conditions. Of relevance here is that the obtained $V_c$ versus ferromagnetism correlation clearly resembles that reported for orthorhombic YMO thin films indicating that its origin does not depend on the bulk magnetic structure and it is strongly related to the unit cell distortion.

Thin films were deposited by pulsed laser deposition using a KrF excimer laser focused on a stoichiometric TbMnO$_3$ target with the fluence and the repetition rate set to 1.5 J/cm$^2$ and 5 Hz, respectively. Films were grown on (001)-oriented SrTiO$_3$ (STO) substrates, heated at 785 °C and placed at 5 cm from the target. A set of samples was grown at 0.1, 0.2, 0.3, and 0.4 mbar oxygen pressure; the laser pulses were adjusted to obtain films with thickness around 40 nm. This set of samples was completed with three thicker films grown at fixed pressure (0.3 mbar) and being 95, 137, and 140 nm thick. Crystal structure was investigated using four-circle x-ray diffractometer. Magnetic data were recorded using a superconducting quantum interference device with the magnetic field applied parallel to the sample surface.

Figure 1(a) shows the $\theta/2\theta$ scan of a selected TMO sample (38 nm thick, 0.3 mbar). Only reflections corresponding to the substrate and to the TMO(001) planes are observed indicating that the films are c-textured and the $Pbnm$ settings is used.$^{18}$ $\phi$-scans around the (111) reflections of the substrate and the film are shown in Fig. 1(b). Four narrow substrate STO(111) peaks, 90° in-plane spaced, are visible in Fig. 1(b), together with four o-TMO(111) reflections, located at 45° from each STO(111) reflection; this indicates that the in-plane axes (a, b) of the film are 45° in-plane rotated with respect to the [100] direction of the substrate. The broadening of the TMO(111) peaks results from the existence of 90° in-plane twinning, as we have exhaustively analyzed for o-YMO(001)/STO(001) films.$^{19}$ Reciprocal space maps around the TMO(208) and TMO(028) reflections are shown in Figs. 1(c) and 1(d), respectively. The crossing of the dashed lines in these plots signals the location for the corre-
the inverse susceptibility versus temperature leads to a Curie-Weiss behavior, but no well-defined antiferromagnetic up-turn at low temperatures. In agreement with bulk measurements, the extrapolation of the linear regime of the susceptibility curves to lower temperatures reveals that the magnetic moment of the sample is fully relaxed. In contrast, data in Fig. 1 shows that the zero-field cooled (ZFC) and field cooled (FC) magnetic fields for a selected TMO sample (140 nm thick, 0.3 mbar). The extrapolation of the linear regime of susceptibility curves to lower temperatures reveals that the magnetic moment \( \mu_{\text{eff}} = 12 \mu_B \) which is in agreement with the contribution from Tb\(^{3+}\) and Mn\(^{3+}\) ions, \( [\mu_{\text{eff}}(\text{Tb})+\mu_{\text{eff}}(\text{Mn})]=11 \mu_B \). Magnetic moment \( \mu_{\text{eff}}(\text{Tb}) = 9.72 \mu_B \) and \( \mu_{\text{eff}}(\text{Mn}) = 4.90 \mu_B \).

Figures 3(a)–3(c) show the zero-field cooled (ZFC) and the FC (ZFC-FC) magnetization curves for a selected TMO sample with distinct VC values. A clear splitting of both curves is well visible revealing a net magnetization. The FC curves for the complete set of samples. All measurements have been performed at 500 Oe applied in-plane of the sample.
behavior is found in all films as shown in Fig. 3(d), where only FC curves are included for the sake of clarity. Note that data clearly resembles the behavior reported for YMO films\textsuperscript{11} and Y\textsuperscript{3+} is a nonmagnetic atom. Owing to this similarity and the fact that the net magnetic moment is observed well above the expected Tb\textsuperscript{3+} ions ferromagnetic ordering, it turns out plausible that the ZFC-FC splitting is caused only by the Mn sublattice.

Following the criteria we already used for YMO films,\textsuperscript{11} we plot in Fig. 4 the dependence of $\chi(T=25$ K) on $V_c$ aiming to quantitatively evaluate how epitaxial strain is inducing the weak ferromagnetism. In contrast to our early work on YMO,\textsuperscript{11} we used $V_c$ instead of the strain along [010] to correlate the magnetic response because the observed trend is identical but $V_c$ includes all structural distortions. We have subtracted the paramagnetic contribution of Tb\textsuperscript{3+} ions to evaluate the contribution of the magnetically ordered Mn\textsuperscript{3+}O\textsubscript{2} sublattice: this allows comparing the strain-induced magnetization to that reported for YMO films in Ref. 11. Data in Fig. 4 collects the main finding here, that is the ferromagnetic response of the TMO films is determined by the unit cell contraction and its behavior mimics that reported for YMO films.\textsuperscript{11} It thus follows that the magnetic structure of the pristine bulk material, that is its spiral or collinear orders are not relevant to the magnetic response of strained YMO or TMO films. Indeed, the evident similarity between magnetic properties in strained YMO and TMO films suggest that the magnetic structure could be similar in both strained films thus vanishing the boundary between E-type (YMO) (Ref. 4) and spiral (TMO) (Ref. 6) magnetic orderings existing in bulk orthorhombic rare earth manganites. As suggested in Ref. 16, a possible scenario could be that epitaxial strain primarily suppresses the spiral order in TbMnO\textsubscript{3} in favor of the E-type as found in YMnO\textsubscript{3}. Subsequent strain-unbalanced magnetic interactions may lead to the observed weak ferromagnetic response as found in YMnO\textsubscript{3}.\textsuperscript{11}

In summary, we have shown that by gradually contracting the unit cell of epitaxial TMO(001) thin films a ferromagnetic response gradually emerges. The present work shows that despite the fact that the bulk magnetic ground structure of TbMnO\textsubscript{3} is spiral, the changes in the magnetic structure upon epitaxial strain follow the same pattern as observed in the strained YMO films having a collinear (E-type) ground magnetic structure. Therefore, it follows that in TbMnO\textsubscript{3} can be made (weak) ferromagnetic under strain. Although it remains to be seen that the ferroelectric character is preserved, recent results\textsuperscript{23} on the closely related YMnO\textsubscript{3} strongly suggest that strained TbMnO\textsubscript{3} films may become a new member of the reduced family of biferroic: ferromagnetic and ferroelectric, materials.

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