Domain wall magnetism in thin films of orthorhombic manganites

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Thin films of orthorhombic TbMnO$_3$, as well as other orthorhombic manganites, epitaxially grown on cubic SrTiO$_3$ substrates display an induced magnetic moment that is absent in the bulk (antiferromagnetic) counterpart. Here we show that there is a clear correlation between the domain microstructure and the induced magnetic moment in TbMnO$_3$ films on SrTiO$_3$. In addition, the distinct dependence of the magnetization with the film thickness is not consistent with domain magnetism and indicates that the domain walls, rather than the domains, are the origin of the net magnetic moment. Since the orientation of the domain walls can be designed by the film-substrate relationship and its density can be tuned with the film thickness, these results represent a significant step forward towards the design of devices based on domain wall functionality.

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Magnetoelectric and multiferroic materials re-emerged about ten years ago [1,2] holding promise for novel devices and new physics [3–8]. Among these, the rare earth manganites (RMnO$_3$) are being intensively studied [9–12]. In these materials, the magnetic spin order can break inversion symmetry and directly induce ferroelectricity [13, 14]. Therefore, the cross-talking between the magnetic and electric degrees of freedom can be made very efficient [9].

Due to the crucial role that the structure plays determining the magnetic and ferroelectric order, it was naturally expected that the properties of multiferroics, and in particular manganites, could be greatly modified (an possibly improved) in thin films grown under epitaxial strain. Most multiferroics are ferroelectric antiferromagnets and present the limitation of lacking a net magnetization to be directly addressed by the electric or magnetic field. Remarkably, although the bulk materials are indeed antiferromagnetic, most existing reports on epitaxial manganite thin films coincide in a puzzling feature: the existence of an induced magnetic moment [15–21].

Recently, it has been proposed that the magnetic moment originates in the strain modification of the balance between the different magnetic exchange interactions [22], and that a canting of the Mn spins is induced [21, 23, 24]. Interestingly, the magnetic moment seems to be induced independently of the ground state magnetic structure of the bulk material: TbMnO$_3$ displays a cycloidal spin structure whereas YbMnO$_3$ and YMnO$_3$ have a collinear spin structure of E-type. In both types, the induced magnetization has been reported to follow a similar trend with the unit cell volume [24]. This opens the question if the magnetic moment arises from the modification of the bond lengths and bond angles, as expected, or if it originates from a more general feature of epitaxial orthorhombic manganites, such as the domain microstructure.

Indeed, it has been shown that orthorhombic manganites grown on cubic SrTiO$_3$ substrates show crystallographic twins [23]. Twinning is mainly determined by the symmetry relationships between the film and substrate materials but it is affected by the growth kinetics and it can differ depending on the growth conditions. TbMnO$_3$ thin films grown on (001)-SrTiO$_3$ by Daumont et al. with low deposition rates (approaching thermodynamic conditions) are reported to form four types of twin domains [23]. Despite the very large mismatch strain (+ 4.1% along [010]$_o$ and -5.7% along [010]$_o$), this microstructure allows the film to keep partial coherence with the substrate, either along the [100]$_o$ or the [010]$_c$ (substrate) directions and, importantly, it determines the evolution of the lattice parameters with increasing thickness: The partial coherence with the substrate and the crystal twinning are able to maintain the unit cell in-plane area constant, and thus the out-of-plane lattice parameter and the unit cell volume, basically unchanged for a large range of thicknesses from 5 to 70nm [23]. This domain/twin configuration relaxes the film by allowing $a_o$ and $b_o$ to change in opposite directions and by the same amounts. It can be rationalized that this is very efficient minimizing the elastic energy of the system [26]. In fact, similar twinning patterns have been observed in BiFeO$_3$ films grown on SrTiO$_3$ [27].

Here we investigate the possible relationship between the microstructure and the magnetic properties of epitaxial TbMnO$_3$ in order to learn about the origin of the ferromagnetic component observed in thin film manganites. It is worth to mention that the twin boundaries become antiferromagnetic domain boundaries below the magnetic ordering temperature and that it is reasonable to expect that the symmetry breaking that takes place at the domain walls could allow them to host net magnetic moment [25, 31]. Since the domain walls can be as small as a few nanometers,

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to directly image the magnetization at the domain walls is extremely challenging. The purpose of this Letter is to approach this problem using a more accessible alternative: investigating the thickness dependence of the magnetic response.

(001)-oriented TbMnO$_3$ (TMO) thin films were deposited on (001)-SrTiO$_3$ substrates using Pulsed Laser Deposition (PLD) with a KrF excimer laser while monitoring the growth using RHEED. The films were grown under an oxygen pressure of 0.9 mbar, at a temperature of 750°C, energy density of 2 J.cm$^{-2}$ and a repetition rate of 1Hz. The thickness of the films was varied from 15nm to 80nm. The structure was analyzed by x-ray diffraction using synchrotron (W1 at HASYLAB and BM28 (XmaS CRG) at ESRF) and lab sources. The details are reported elsewhere.

The microstructure of the films was studied using transmission electron microscopy (TEM) in plane-view. The magnetization of the films has been measured on 5mm x 5mm samples of different thicknesses using a SQUID magnetometer, both under zero-field-cooled (ZFC) and field-cooled (FC) conditions. The field applied during the field-cooled runs was 2.5kOe. The measurements are performed during heating under a applied magnetic field of 1kOe. All the measurements presented here have been corrected by subtracting the diamagnetic contribution of the SrTiO$_3$ substrate and were measured with the field perpendicular to the surface of the films.

Figure 1 shows the total observed magnetic moment as a function of temperature for films with the same surface area but different thicknesses ranging from 15nm to 80nm under zero-field-cooled (ZFC) and field-cooled (FC) conditions. All the films show a splitting between the ZFC and FC curves, indicative of an induced net magnetic moment, absent in the bulk material and similar to the one observed in YbMnO$_3$, HoMnO$_3$, YMnO$_3$ and TbMnO$_3$ films on SrTiO$_3$ substrates. The splitting appears close to the bulk ordering temperature of around 40K, where the Mn$^{3+}$ spins order in an incommensurate sinusoidal fashion. This indicates that the induced magnetic moment is related to the ordering of Mn$^{3+}$ spins rather than to the ordering of the Tb$^{3+}$ spins, which takes place at about 7K in the bulk.

We have shown that the films are single phase and stoichiometric so that the induced magnetic moment cannot be related to the double-exchange mechanism, which can give rise to a ferromagnetic metal, as in the case of Sr or Ca-doped LaMnO$_3$, via electron hopping between Mn$^{3+}$ and Mn$^{4+}$. Surface ferromagnetism seems unlikely because the thicker, rougher, films that show the largest surface area, display the smallest magnetic moment. Moreover, neutron reflectometry has shown that the induced magnetization is not a surface effect.

Figure 2 displays the value of the FC-ZFC splitting in units of magnetization (normalizing by the film volume), at 15 K (this temperature is chosen to avoid the effect of Tb ordering), for the films discussed in Figure 1. Films with thicknesses above 70nm differ from the fully strained thinner samples and present two structures: a relaxed part with bulk lattice parameters and a strained part. These relaxed films are indicated by a hatched region in Fig. 2. It can be seen that the magnitude of the induced magnetization does scale linearly with the inverse of the thickness (1/d) for the strained films, whereas the dependence departs from the linearity for the relaxed films.

Using the lattice parameters of the films, the orthorhombic distortion angle $\gamma$ could be calculated using $\gamma=\cos (\sqrt{a_o^2+b_o^2}/a_o+b_o^2)$ and is shown in Fig. 3. The orthorhombic distortion, and thus $90^\circ-\gamma$, increases with increasing thickness, towards the bulk value. In the relaxed part of the thicker film, the angle $\gamma$ reaches the bulk value (symbol with a star). $\gamma$ shows a linear dependence with the inverse of the thickness, similar to that of the induced magnetization. This indicates that the induced magnetic moment is, indeed, related to the amount of strain in the film, as it was recently reported. However, we show next that the effect of strain is indirect and that the net moments do not
result from the modification of the exchange interactions in the strained unit cells.

In order to release the strain imposed by the substrate, a material can form domains/domain walls, which reduce the stored elastic energy. Four types of domains are present in sufficiently thin films of orthorhombic TbMnO$_3$ grown on (001)-SrTiO$_3$ whereas other types of domains are formed for other orientations [23, 34]. Using the plane-view TEM images of TMO films with different thicknesses [26], the number of domain walls for a given area was calculated. Fig. 2 shows the number of domain walls per unit area ($\sigma$) as a function of the inverse thickness of the films. As for the induced magnetization, the data shows that $\sigma$ scales linearly with the inverse of the thickness, for the strained films. Moreover, the relaxed film, containing strained and relaxed sublayers and displaying well-developed grains with clear boundaries, deviates from this linear behavior. This $\sigma(d)$ dependence is not unexpected because the size of the domains, $D$, is determined by the balance between the total elastic energy of the film and the domain wall formation energy. Although for elastic domains a quadratic dependence $D \propto d^{1/2}$ is commonly observed [36, 37], it can be shown that for $D$ of the same order as $d$, the dependence is linear [38, 39].

Thus, both the orthorhombic distortion and the density of domain walls scale like the induced magnetization as a function of film thickness, $d$. To learn which of the two is responsible for the observed behavior is most relevant because it will help designing novel multiferroics with addressable magnetic moments. We show next that our data clearly point towards the second rather than the first mechanism, that is, to the induced magnetic moment residing at the domain walls.

If the magnetic moment resides exclusively at the domain walls, given the $\sigma(d) \propto d^{-1}$ dependence of Fig. 2(a), the total induced magnetic moment, $m_T$, should be thickness independent [see Fig. 2(d)], as it is indeed observed in Fig. 1 by the similar FC-ZFC splitting shown for all thicknesses. For the same reason, the magnetization, $M_T$, should scale as the inverse thickness, as observed in Figure 2(a). The observed behavior is not consistent with a net magnetic moment per formula unit in the domains, which should show a thickness independent $M_T$ [see Fig. 2(c)].

With the observed induced magnetic moments of ($m_T(1kOe)= 5 \times 10^{-6}$ emu) in Fig. 1, and the TEM images to estimate the number of domain walls, one can use the expression in Fig. 2d to estimate the domain wall satura-
tion magnetization as $M_{S,DW} \simeq 0.7 \mu_B/f.u.$ and $M_{S,DW} \simeq 3.5 \mu_B/f.u.$, for domain wall thicknesses of 5 nm and 1 nm, respectively.\cite{40}

First, we point out that domain walls should have their own physical properties, different from the properties of the domains, simply because the symmetry at the wall position is different from the symmetry of the crystal. The size of the domains in the thinner (17nm) films is as small as around $20 \times 4 \text{ nm}^2$\cite{26} and therefore a considerable volume fraction of the film has domain wall character. The thin films, thus, will clearly reveal any salient properties of the domain walls. Second, we note that the process of domain wall formation is common to all orthorhombic perovskites epitaxially grown on cubic substrates and thus, it makes sense that the different manganites, with very different spin structures in bulk, still produce similar induced magnetization. Third, our observations are supported by symmetry arguments showing that ferromagnetism can exist in the domain walls of magnetoelectric antiferromagnets\cite{29,30}.

This behavior should thus not be restricted to orthorhombic manganites and could also explain the observed correlation between the length of the $109^\circ$ walls and the exchange bias in thin films of BiFeO$_3$\cite{41}. Earlier on, Fiebig and co-workers reported that the ferroelectric domain walls of multiferroic hexagonal (bulk) manganites can have a net magnetization at their center\cite{42} as well as enhanced magnetoelectric coupling\cite{43}. During the preparation of this manuscript we have become aware of the recent work of Ueland et al. reporting neutron scattering experiments on single crystals of HoMnO$_3$ that are also consistent with the presence of a net magnetization at the antiferromagnetic domain walls\cite{44}. Another possibility to explain the observed domain wall magnetism is the, postulated long ago\cite{45} and recently observed\cite{32}, existence of uncompensated spins at antiferromagnetic domains walls.

The concept of using domain walls as functional objects\cite{31,46,47} is creating a new field of research. Epitaxial thin films are ideal candidates to work with because in these materials domain walls can be engineered to appear in large amounts. Moreover, their orientation and density can be controlled by both the substrate material and the film thickness. This letter shows that there is a great opportunity for utilizing the distinct properties of the domain walls to create novel multiferroic and magnetoelectric materials.

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