Evidence of non-Dzyaloshinskii–Moriya ferromagnetism in epitaxial BiFeO$_3$ films

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X-ray diffraction analysis and high-resolution electron microscopy of BiFeO$_3$ films prepared by dc magnetron sputtering on single-crystal LaAlO$_3$ (001) substrates reveal that the films have a highly $c$-oriented orthorhombic crystalline structure. The magnetic properties of the BiFeO$_3$ films are typical of ensembles of interacting superparamagnetic clusters, rather than Dzyaloshinskii-Moriya weak ferromagnets. The appearance of extrinsic nanoscale superparamagnetic clusters is explained by an oxygen deficiency in certain regions of the film, where ferromagnetic ordering can be realized through a double-exchange Zener mechanism. © 2011 American Institute of Physics. [doi:10.1063/1.3555838]

I. INTRODUCTION

Multiferroics have attracted considerable attention because of their interesting fundamental properties, related to simultaneous ferroelectric and ferromagnetic ordering, and their potential for information storage applications, such as spintronic devices and sensors. The perovskite BiFeO$_3$ is a typical multiferroic compound with a ferroelectric transition temperature $T_{CN} \approx 1103$ K and antiferromagnetic (AFM) transition temperature $T_N \approx 643$ K. $^{1-3}$ The bulk single crystal has a rhombohedral crystal lattice with unit-cell parameters $a_R \approx 0.563$ nm and $c_R \approx 0.02$ nm. $^{4,5}$ In spite of its room-temperature multiferroicity, bulk BiFeO$_3$ is a canted $G$-type AFM with a weak ferromagnetic (FM) moment ($\sim 0.02$ $\mu_B$/Fe) $^6$ owing to antisymmetric Dzyaloshinskii-Moriya (DM) exchange. $^{7-9}$ At the same time, the enhancement of the FM response of BiFeO$_3$ is important because this increase can make this compound useful for practical applications. Recently, enhanced ferroelectric properties (including the FM magnetic moment) have been observed in BiFeO$_3$ thin films deposited on the single-crystal substrates. $^{5,10-12}$ The slight enhancement in the FM-like magnetic moment is attributed to oxygen deficiencies $^8$ and to lattice strains $^{12}$ accumulated during epitaxial film growth. The main explanation for this effect is suppression of the helical AFM order, which can lead to enhancement of the DM interaction and give rise to larger FM magnetic moments. However, other extrinsic factors can play an important role in the formation of the FM state in epitaxial BiFeO$_3$ films. $^{13}$

Here we report experiments on BiFeO$_3$ (BFO) films deposited on single-crystal LaAlO$_3$ (LAO) (001) substrates. The observed evidence of a non-DM-like FM response is discussed in detail.

II. EXPERIMENTAL TECHNIQUES

The films were prepared by dc magnetron sputtering at a substrate temperature of 650 °C. $^{14}$ To avoid the influence of lattice strain accumulated during deposition, all the films were annealed at 900 °C for 2 h in air. The thickness of the films was $d \approx 150$ nm. $\theta$-$2\theta$ x-ray diffraction (XRD) patterns were obtained using a Rigaku diffractometer with Cu $K_{\alpha}$ radiation. High-resolution electron-microscopy (HREM) was carried out using a Philips CM300UT-FEG microscope with a field emission gun operated at 300 kV. The point resolution of the microscope was on the order of 0.12 nm. All microstructure measurements were carried out at room temperature. The field-cooled (FC) and the zero-field-cooled (ZFC) magnetization curves were obtained with a Quantum Design SQUID magnetometer with an in-plane magnetic field orientation. To avoid the influence of the diamagnetic response from LAO, magnetization curves for the bare substrates were subtracted from the raw experimental curves.

III. MICROSTRUCTURE OF FILMS

Figure 1 shows (a) the XRD pattern and (b) the cross-sectional high-magnification HREM image taken from the [010] zone axis for BFO, including the film/substrate interface. The $\theta$-$2\theta$ XRD scan for the film displays only the fundamental Bragg peaks for the film and the substrate, indicating that deposition results in a highly $c$-oriented crystal structure. It can be seen that the film has an atomically clean and sharp interface without an amorphous intermediate layer or precipitates. The epitaxial relationship for the film and substrate was found to be [001] BFO/[001] LAO. This is confirmed by the corresponding fast Fourier transform (FFT) for the HREM image, shown in the inset to Fig. 1b, which
peaks for the film (BFO) and the substrate (LAO) can be seen. (b) High-
magnification cross-sectional HREM image taken at the BFO/LAO inter-
face. The dashed curve indicates the interface. The inset is an FFT of the
magnification cross-sectional HREM image taken at the BFO/LAO inter-
face. The inset is an FFT of the same HREM image.

reveals an almost rectangular pattern containing only the fundamental Bragg spots. The slight splitting of Bragg spots (indicated by two short arrows) is related to the difference between the film and substrate crystal lattices. The micro-
structure analysis shows that the prepared films have an orthorhombic crystal structure with lattice parameters \( a \sim b \sim 0.3997 \) nm, \( c \sim 0.4045 \) nm, and an angle between atomic rows of \( \theta \sim 89.4^\circ \) that is consistent with published data.5,10–12

IV. MAGNETIC PROPERTIES

Figure 2 shows the in-plane FC (solid symbols) and ZFC (open symbols) temperature dependences of the magnetic moment, \( M(T) \), for different applied magnetic fields, after subtraction of the diamagnetic response of the substrate. For comparison, the inset shows the raw FC \( M(T) \) curves for the substrate with (solid symbols) and without (open symbols) a deposited film. In both cases, the LAO size was the same, \( 0.5 \times 0.5 \times 0.5 \) mm. The \( M(T) \) curves for the bare LAO sub-
strate show a nonlinear behavior with a distinct increase in the magnetic moment in the low-temperature range. This ex-
ponential rise of \( M(T) \) with decreasing temperature can be explained by the presence of paramagnetic impurities in the LAO substrate. Therefore, additional \( M(T) \) measurements of the bare substrate are very important for correct interpreta-
tion of the magnetic properties of the BFO film.

The \( M(T) \) curve in Fig. 2 is typical for a multiphase magnetic system, involving an AFM matrix with \( T_N \) higher than room temperature and the FM component. This is con-
firmed by the linear field dependence of the magnetic moment at 300 K, which can be expressed by the empirical relation \( M(300 \, \text{K}, H) = M(300 \, \text{K}, 0) + \chi(300 \, \text{K})H \), where \( M(300 \, \text{K}, 0) = 0.009 \mu_B/\text{Fe} \) is the magnetic moment without an applied magnetic field and \( \chi(300 \, \text{K}) = 0.113 \mu_B/\text{Fe} \cdot \text{T}^{-1} \) is the magnetic susceptibility. The presence of FM phase shows up in the ZFC/FC \( M(T) \) splitting, which is indicated by the arrows.

Figure 3 illustrates the magnetic hysteresis loops, \( M(H) \), for the BFO film at 10 K (open symbols) and 300 K (solid symbols) after subtraction of the diamagnetic response of the substrate. Insets a and b show the corresponding raw \( M(H) \) curves for the BFO film with the substrate and for the bare LAO substrate, respectively. The \( M(H) \) curves can be treated as a superposition of AFM (linear term) and FM (hysteresis term with a saturation) contributions, and indicate, as do the \( M(T) \) curves, that two different magnetic phases exist in the BFO film.

Figure 4 shows the FM contribution to the hysteresis loops for the BFO film at 10 K (open symbols) and 300 K
10 K, respectively, in good agreement with published data. Analysis of the hysteresis loops reveals that the saturation magnetic moment is \( M_s \sim 0.045 \) and 0.064 \( \mu_B/\text{Fe} \) at 300 and 10 K, respectively, in good agreement with published data for thin films.\(^5,6,15\) At the same time, the hysteresis loop has an almost symmetric shape (within the experimental error) with a coercive field of \( H_c \sim \pm 1100 \text{ Oe} \), and a remanent magnetic moment \( M_r \sim \pm 0.016 \mu_B/\text{Fe} \) at a room temperature; it becomes highly asymmetric with decreasing temperature: \( H_c \sim +500 \) and \( -2500 \text{ Oe} \), and \( M_r \sim +0.039 \) and \( -0.011 \mu_B/\text{Fe} \) at 10 K. Therefore, the low-temperature hysteresis loop exhibits an exchange bias field and vertical asymmetry that was observed early on in nanoscale BFO powders.\(^\text{11}\) It is worth noting that the hysteresis loops were measured after cooling without an applied magnetic field (ZFC regime).

**V. DISCUSSION**

As a rule, the weak FM response in BFO is treated as an intrinsic property of the AFM state with a specific symmetry, which originates in the non-collinearity of the magnetic sublattices (or a spin canting) owing to the DM relativistic interaction. In this case the temperature dependence of the reduced magnetic moment for the DM-like weak FM state follows \( \Delta M(T)/M(0) \propto T^2 \), where \( \Delta M(T) = M(0) - M(T) \), instead of the Bloch law \( \propto T^{3/2} \) typical of common FMs.\(^9\) However, Fig. 5 shows that the experimental \( \Delta M(T) \) curves are linear rather than parabolic. For the sake of convenience, the normalized magnetic moment \( \Delta M(T) = [M(0) - M(T)]/M(0) \)
The linear $\Delta M(T)$ dependence can be explained by assuming that an additional FM phase forms the separated FM clusters, which can then be treated as an ensemble of superparamagnetic (SPM) particles. Given that the SPM state is customarily described by a Langevin function, $L(\alpha) = \coth(\alpha) - \alpha^{-1}$, where $\alpha = \mu_\text{eff} / k_B T$, $\mu_\text{eff}$ is the average effective magnetic moment of the SPM particle and $k_B$ is the Boltzmann constant, the normalized magnetic moment can be written in the form $\Delta M(T) = [M(0) - M(300 \text{ K})] / [M(0) - M(300 \text{ K})]$. Figure 5 shows that the experimental curves fit very well by a Langevin function with $\mu_\text{eff}$ as the only fitting parameter. For clarity, the theoretical $\Delta M(T)$ curve for $H = 0.1 \text{ T}$ (solid curve) is shifted along the temperature axis. This fit to the experimental $\Delta M(T)$ curves reveals that the effective magnetic moments of the SPM clusters are $\mu_\text{eff} \sim 1.86 \cdot 10^4$, $3.88 \cdot 10^3$ and $2.05 \cdot 10^3 \mu_B$ for applied magnetic fields $H = 0.1$, 0.5 and 1.0 T, respectively. The observed magnetic field dependence of $\mu_\text{eff}$ is governed by a possible dipolar interaction between SPM clusters.\(^{17,18}\) Taking the magnetic moment of Fe$^{3+}$ to be $\sim 6 \mu_B / \text{Fe}$ and assuming a spherical shape for the SPM clusters with a volume of $\pi D^3 / 6$, their average diameter is estimated to be $D \sim 7.3$, 4.33 and 3.5 nm for magnetic fields of 0.1, 0.5 and 1.0 T, respectively. In principle, these values are quite reasonable and indicate that an additional FM phase exists in the film in the form of SPM clusters.

Another peculiarity of the magnetic properties of these films, which confirms the foregoing assumption, is related to the asymmetric hysteresis loop observed at low temperature. A shift of the hysteresis loop along the field axis is typical of the asymmetric hysteresis loop observed at low temperature. Films, which confirms the foregoing assumption, is related to the asymmetric hysteresis loop observed at low temperature. The inset shows the blocking temperature. The curves are nominal fits. The inset shows the magnetic field dependence of the blocking temperature. The smooth curve is theoretical, based on a model of interacting SPM clusters (described in the text).

(\text{the arrows indicate } T_B). \text{ The inset shows the magnetic field dependence of the blocking temperature, which can be described by a semi-empirical expression of the form } T_B(H) = T_B(0) / (1 + \beta H), \text{ where } T_B(0) \text{ is the blocking temperature at } H = 0, \beta \sim M_s^2(0) / k_B T, \text{ and } M_s(0) \text{ is a saturation magnetic moment at } H = 0 \text{ (for spontaneous magnetization). This expression was obtained for an interacting SPM phase, which includes a strong dipolar interaction among SPM clusters.}^{17,18,25,26}\)

Based on an analysis of the $M(T)$ and $M(H)$ dependences, one can, therefore, conclude that these BFO films can be regarded as a magnetic phase separated system consisting of a G-type AFM matrix and FM inclusions of non-DM-like origin. These inclusions are formed because of an oxygen deficiency, which appears in certain local regions of the film owing to crystal lattice imperfection or overstrain. A changing oxygen stoichiometry leads to the conversion of Fe$^{3+}$ to Fe$^{2+}$, which causes the formation of a carrier-mediated local FM order across the Fe$^{3+}$--O$^{2-}$--Fe$^{2+}$ bonds, similar to that observed in the electron- or hole-doped manganites.\(^{27}\) Consequently, besides the intrinsic DM-like weak FM state, extrinsic nanoscale FM clusters may exist in BFO films, which have magnetic behavior typical of interacting SPMs.
VI. CONCLUSIONS

BiFeO$_3$ films have been prepared by dc magnetron sputtering on LaAlO$_3$ (001) single-crystalline substrate. XRD and HREM analysis reveal that the deposition results in a highly $c$-oriented orthorhombic crystal structure. Their unusual (for typical DM-like ferromagnets) magnetic properties, such as a linear $M(T)$ dependence, significant ZFC/FC $M(T)$ splitting in applied magnetic fields greater than the coercive field, and the exchange-bias effect observed at low temperatures, testify to the existence of an additional extrinsic FM phase in the film. The magnetic behavior of this phase is well described by a phenomenological model of the FM phase in the film. We argue that extrinsic FM clusters form as the result of oxygen deficiencies in certain regions of the film where the FM ordering caused by a double-exchange Zener mechanism.

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