

Evidence of non-Dzyaloshinskii–Moriya ferromagnetism in epitaxial BiFeO₃ films

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X-ray diffraction analysis and high-resolution electron microscopy of BiFeO₃ films prepared by dc magnetron sputtering on single-crystal LaAlO₃ (001) substrates reveal that the films have a highly *c*-oriented orthorhombic crystalline structure. The magnetic properties of the BiFeO₃ 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 BiFeO₃ is a typical multiferroic compound with a ferroelectric transition temperature $T_C \sim 1103$ K and antiferromagnetic (AFM) transition $T_N \sim 643$ K.^{1–3} The bulk single crystal has a rhombohedral crystal lattice with unit-cell parameters $a_R \sim 0.563$ nm and $\alpha_R \sim 59.4$.^{4,5} In spite of its room-temperature multiferroicity, bulk BiFeO₃ is a canted *G*-type AFM with a weak ferromagnetic (FM) moment ($\sim 0.02 \mu_B/\text{Fe}$)⁶ owing to antisymmetric Dzyaloshinskii–Moriya (DM) exchange.^{7–9} At the same time, the enhancement of the FM response of BiFeO₃ 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 BiFeO₃ thin films deposited on the single-crystal substrates.^{5,10–12} The slight enhancement in the FM-like magnetic moment is attributed to oxygen deficiencies⁵ and to lattice strains¹² 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 BiFeO₃ films.¹³

Here we report experiments on BiFeO₃ (BFO) films deposited on single-crystal LaAlO₃ (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 $d \sim 150$ nm. θ -2 θ x-ray diffraction (XRD) patterns were obtained using a Rigaku diffractometer with Cu K_α 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 θ -2 θ 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

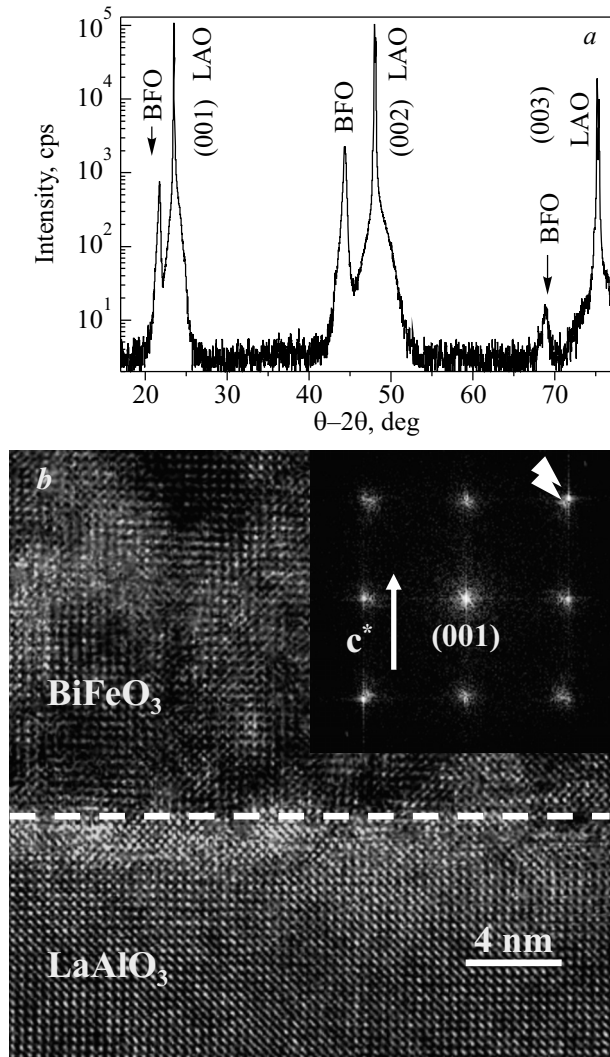


FIG. 1. (a) XRD scan for BFO/LAO film. Only the fundamental Bragg peaks for the film (BFO) and the substrate (LAO) can be seen. (b) High-magnification cross-sectional HREM image taken at the BFO/LAO interface. The dashed curve indicates the interface. The inset is an FFT of the same HREM image.

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 microstructure 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 substrate show a nonlinear behavior with a distinct increase in the magnetic moment in the low-temperature range. This ex-

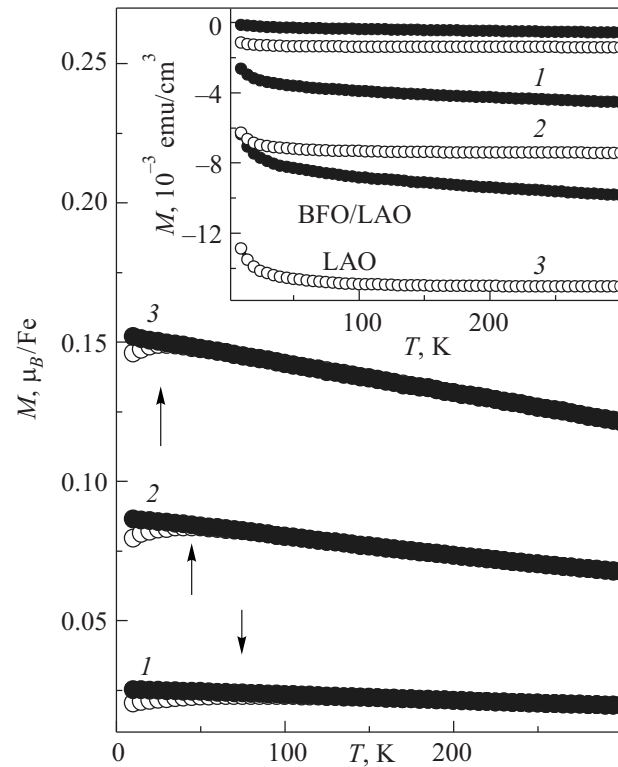


FIG. 2. Temperature dependences of the in-plane ZFC (open symbols) and FC (solid symbols) magnetic moments of BFO films (after subtraction of the substrate response), measured in applied magnetic fields of 0.1 (1), 0.5 (2), and 1.0 T (3). The arrows indicate the temperature for ZFC/FC $M(T)$ splitting. The inset shows the raw in-plane FC $M(T)$ curves for the film and substrate (BFO/LAO, solid symbols) and for the bare substrate (LAO, open symbols), measured at the same magnetic fields.

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 interpretation 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 confirmed 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

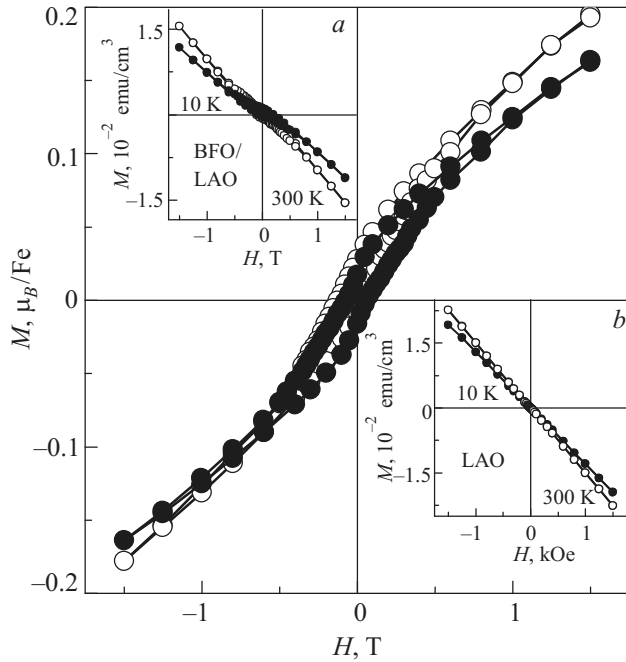


FIG. 3. In-plane magnetic hysteresis loops for a BFO film (after subtraction of the substrate response), taken at room temperature (solid symbols) and 10 K (open symbols). The curves are only nominal fits. Insets *a* and *b* show the raw in-plane magnetic hysteresis loops for the film with a substrate (BFO/LAO) and for the bare substrate (LAO), respectively, measured at the same temperatures.

(solid symbols) after subtraction of the AFM linear term. The insets show the same dependences more on magnified scales. 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

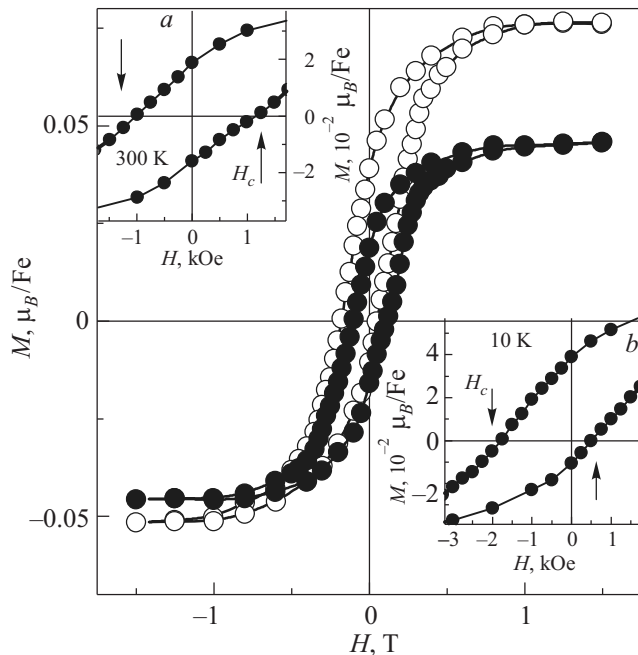


FIG. 4. The FM component of the in-plane magnetic hysteresis loops for the BFO film (after subtraction of the linear AFM response), taken at room temperature (solid symbols) and 10 K (open symbols). Insets *a* and *b* show the same curves on magnified scales. The arrows indicate the coercive magnetic field. The curves are nominal fits.

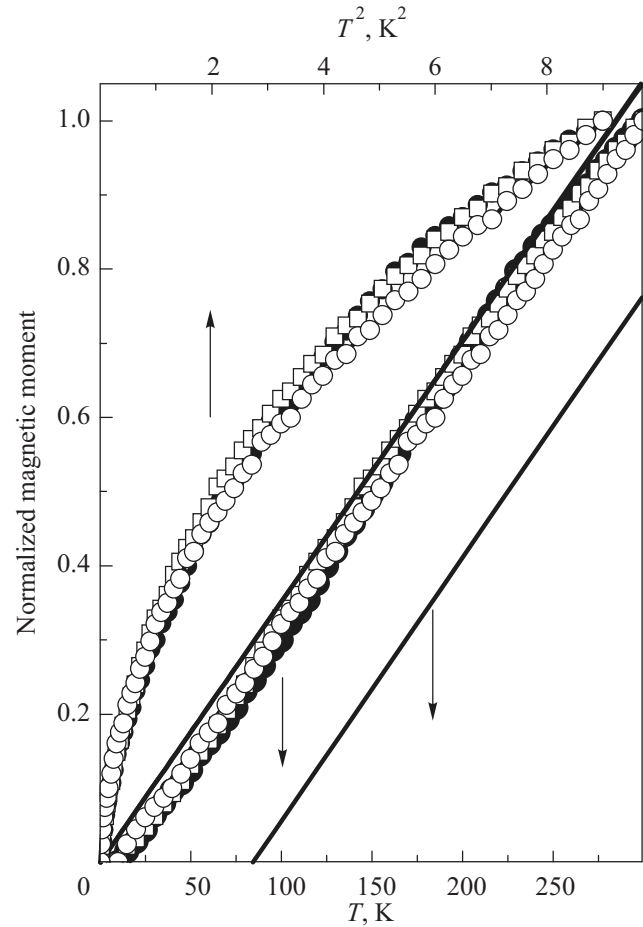


FIG. 5. Temperature-dependent normalized magnetic moment of a BFO film, measured at different applied magnetic fields: $H=0.1$ (solid circles), 0.5 (open squares), and 1.0 T (open circles). The solid curve is theoretical, obtained using the SPM approach (described in text).

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 $H_c \sim \pm 1100$ 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 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.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 $\Delta M(T) = [M(0)$

$-M(T))/[M(0)-M(300\text{ K})]$ was used in this analysis. Therefore, the observed FM response in our BFO film can not be regarded as the result of the DM interaction alone. 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,¹⁶ $L(\alpha) = \coth(\alpha) - \alpha^{-1}$, where $\alpha = \mu_{\text{eff}}H/k_B T$, μ_{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 $\Delta M(T) = [M(0) - M(0)L(\alpha)]/[M(0) - M(300\text{ K})]$. Figure 5 shows that the experimental curves are fit very well by a Langevin function with μ_{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 μ_{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 for the FM/AFM magnetically coupled system and is referred to as an “exchange bias” (EB) interaction. It is generally accepted that the EB owing to the exchange anisotropy at the FM/AFM interface, is produced by a coupling between the FM layer and the uncompensated interfacial spins in the AFM layer, the number of which determines the magnitude of the exchange field (H_{EB}).¹⁹ Thus, for the EB effect to occur, the FM and AFM phases must be separated from each other by an interface that does not exist in a classical DM-like ferromagnet, because in this case the FM state is an *intrinsic* property of the *G*-type AFM state. On the other hand, exchange bias has been observed in multiferroic epitaxial heterostructures^{20,21} and bilayers^{22,23} with common FM layers, although the *G*-type AFM state is compensated in BFO.²⁴

The insets in Fig. 4 show that the magnitude of the exchange field $H_{\text{EB}} \sim 0$ at room temperature while $H_{\text{EB}} \sim 1000\text{ Oe}$ at 10 K . This is explained by an effective transition of SPM clusters to the blocking state with decreasing temperature. Above a certain blocking temperature (T_B), the magnetic moments of the SPM particles move freely owing to thermal fluctuations, while they undergo a transition to a blocked state (and can be recognized as the FM phase) when $T \leq T_B$. The main evidence for this transition is a substantial ZFC/FC $M(T)$ splitting which does not disappear even for applied magnetic fields exceeding the coercive field. The blocked-unblocked transition shows up more clearly in Fig. 6

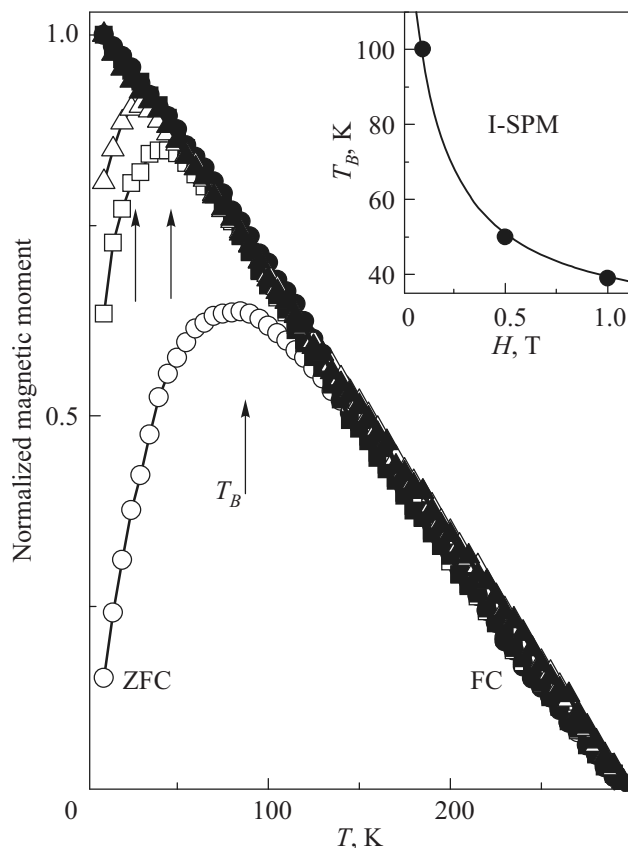


FIG. 6. Temperature dependence of the in-plane ZFC (open symbols) and FC (solid symbols) normalized magnetic moment for the BFO film, measured in applied magnetic fields of 0.1 (circles), 0.5 (squares), and 1.0 T (triangles). The arrows indicate the blocking temperature. The curves are nominal fits. 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).

(the arrows indicate T_B). The inset shows the magnetic field dependence of the blocking temperature, which can be described by a semi-empirical expression of the form $T_B(H) = T_B(0)/(1 + \beta H)$, where $T_B(0)$ is the blocking temperature at $H = 0$, $\beta \sim M_s^2(0)/k_B T$, and $M_s(0)$ is a saturation magnetic moment at $H = 0$ (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 deficiency⁵ 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 $\text{Fe}^{3+}-\text{O}^{2-}-\text{Fe}^{2+}$ 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

BiFeO₃ films have been prepared by dc magnetron sputtering on LaAlO₃ (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 interacting SPM clusters. 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.²⁷

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