Mechanisms of exchange bias with multiferroic BiFeO$_3$ epitaxial thin films

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We have combined neutron scattering and piezoresponse force microscopy to study the relation between the exchange bias observed in CoFeB/BiFeO$_3$ heterostructures and the multiferroic domain structure of the BiFeO$_3$ films. We show that the exchange field scales with the inverse of the ferroelectric and antiferromagnetic domain size, as expected from Malozemoff’s model of exchange bias extended to multiferroics. Accordingly, polarized neutron reflectometry reveals the presence of uncompensated spins in the BiFeO$_3$ film at the interface with the CoFeB. In view of these results we discuss possible strategies to switch the magnetization of a ferromagnet by an electric field using BiFeO$_3$.

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The Renaissance of Multiferroics [1, 2], i.e. materials in which at least two ferroic or antiferroic orders coexist, is motivated by fundamental aspects as well as their possible application in spintronics [3]. Such compounds are rare and the very few that possess simultaneously a finite magnetization and polarization usually order below about 100K [4, 5, 6, 7]. Ferroelectric antiferromagnets (FEAF) are less scarce, and some exhibit a coupling between their two order parameters. This magnetoelectric (ME) coupling allows the reversal of the ferroelectric (FE) polarization by a magnetic field [7] or the control of the magnetic order parameter by an electric field [8].

The practical interest of conventional antiferromagnets (AF) is mainly for exchange bias in spin-valve structures. The phenomenon of exchange bias (EB) [9] manifests itself by a shift in the hysteresis loop of a ferromagnet (FM) in contact with an AF and arises from the exchange coupling at the FM/AF interface [10, 11]. Combining this effect with the ME coupling in a FEAF/FM bilayer can allow the reversal of the FM magnetization via the application of an electric field through the FEAF, as reported recently at 2K in YMnO$_3$/NiFe structures [12].

To exploit these functionalities in devices one needs to resort to FEAF materials with high transition temperatures. BiFeO$_3$ (BFO) is a FE perovskite with a Curie temperature of 1043K [13] that orders antiferromagnetically below T$_N$=643K (T$_N$: Néel temperature) [14]. BFO thin films have a very low magnetization (~0.01 $\mu_B$/Fe) compatible with an AF order [15, 16], and remarkable FE properties with polarization values up to 100 $\mu$C.cm$^{-2}$ range [17]. Recently, we reported that BFO films can be used to induce an EB on adjacent CoFeB layers at room temperature [18]. This observation together with the demonstration of a coupling between the AF and FE domains [8] paves the way towards the room-temperature electrical control of magnetization with BFO. However, several questions remain before this can be achieved. Key issues concern the precise magnetic structure of BFO thin films, and the mechanisms of EB in BFO-based heterostructures.

In this Letter, we report on the determination of the magnetic structure of BFO films by means of neutron diffraction (ND), and the analysis of the EB effect in CoFeB/BFO heterostructures in terms of Malozemoff’s model [19]. Accordingly, we find a clear dependence of the amplitude of the exchange field $H_E$ with the size of the multiferroic domains, which provides a handle to control the magnetization of the CoFeB film by an electric field. The observation of EB and enhanced coercivity correlates with the presence of uncompensated spins at the interface between the FM and the AF, as detected by polarized neutron reflectometry (PNR).

BiFeO$_3$ films were grown by pulsed laser deposition [15], directly onto (001)- or (111)-oriented SrTiO$_3$ (STO) or (001)-oriented LaAlO$_3$ (LAO) substrates, or onto 10-25 nm-thick metallic buffers of La$_2$/3Sr$_1$/3MnO$_3$ (LSMO) or SrRuO$_3$ (SRO) [20]. 7.5 nm-thick CoFeB layers were sputtered in a separate chamber at 300K in a magnetic field of 200 Oe, after a short plasma cleaning. The samples were capped by 10-30 nm of Au. High resolution x-ray diffraction evidenced a cube-on-cube growth for all the perovskite layers onto the substrates. CoFeB was amorphous. While the (111)-oriented films were found to be rhombohedral as bulk BFO [21], (001)-oriented films were found tetragonal or monoclinic [22].

A first key information that is usually required to analyze EB is the magnetic structure of the AF. Bulk BFO is known to have a G-type AF order [14], with a superimposed cycloidal modulation [23]. In view of the strong strain sensitivity of the properties of FE and magnetic ox-
ides, one can anticipate that the magnetic order of BFO films might be different from that of the bulk. In order to determine their magnetic structure, selected (001)- and (111)-oriented BFO films were thus characterized by ND with the triple axis 4F1 spectrometer at the Orphée reactor of the Laboratoire Léon Brillouin (LLB) [21].

In a G-type AF, superstructure peaks are expected to appear at $\frac{1}{2} \frac{1}{2} \frac{1}{2}$-type reflections. In Fig. 1a and b, we show the diffracted intensity at the $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ reflection in BFO films grown on (001)- and (111)-oriented STO. Clearly an AF peak is present for both films. On the other hand, no intensity was measured at $0 0 \frac{1}{2}$-type or $\frac{1}{2} \frac{1}{2} 0$-type reflections, characteristic of A-type and C-type antiferromagnetism, respectively. These data thus show that both (001)- and (111)-oriented films are antiferromagnetic with a G-type order similar to that of the bulk. In other words, neither strain nor changes in the unit-cell symmetry modify the type of magnetic order, besides destroying the cycloidal modulation (see Ref. [22] for details on this aspect).

Within a simplistic model of EB, the exchange field $H_E$ depends on the interface coupling $J_{eb}=J_{ex} S_F S_{AF}/a^2$ ($J_{ex}$ is the exchange parameter, $S_F$ and $S_{AF}$ are the spin of the interfacial atoms in the ferromagnet and the AF, respectively, and $a$ is the unit cell parameter of the AF), on the magnetization and thickness of the ferromagnet $M_{FM}$ and $t_{FM}$, and on the anisotropy and the thickness of the AF $K_{AF}$ and $t_{AF}$ [11].

$$H_E = \frac{-J_{eb}}{\mu_0 M_{FM} t_{FM} a^2} \sqrt{1 - \frac{J_{eb}^2}{4K^2_{AF} t^2_{AF}}}$$

(1)

provided that $1/4R^2$ is smaller than 1 (otherwise $H_E$ is zero). If $t_{AF}$ is large, $R >> 1$ and thus $H_E \approx H_E^\infty$. In a na"ive picture of perfect surfaces and because the AF order is G-type in both (001) and (111) films, the (111) films are expected to have magnetically uncompensated surfaces, yielding $S_{AF}=5/2$, while the (001) films should have compensated surfaces, yielding in average $S_{AF}=0$. Therefore, a finite $H_E$ should be found for (111) films only. For (111) films, taking $J_{ex}=5 \times 10^{-22} J$ [24], $a=3.96\ \text{Å}$, $S_F=1/2$, $S_{AF}=5/2$, $M_{FM}=800\ \text{kA/m}$ and $t_{FM}=7.5\ \text{nm}$ one can estimate $J_{eb}=4\ \text{mJ/m}^2$ and the large value of $H_E=6.5\ \text{kOe}$.

Figure 1c and d show M(H) hysteresis loops measured at 300K for BFO(70nm)/CoFeB stacks grown on STO(001) and STO(111). The loops are shifted towards negative magnetic field values by an exchange field $H_E$ of -39 Oe for (001) films and -19 Oe for (111) films. Furthermore, the loops are enlarged by some tens of Oe compared to those measured on CoFeB single films [18]. From M(H) data for LSMO/BFO/CoFeB samples (see Fig. 1e and f), a symmetric (i.e. not showing EB) contribution from the LSMO films is visible (the Curie temperature of our LSMO films is about 330K) in addition to that coming from the CoFeB. For a given thickness, the exchange field experienced by the CoFeB is virtually the same irrespective of the presence of the LSMO buffer layer.

Malozemoff’s random field model [19] has been proposed to resolve the long-standing discrepancy between the model of Eq. (1) and the experimental data [10]. It considers that in the presence of some atomic-scale disorder that locally creates a net magnetization in the AF at the interface with the FM, the AF splits into domains, which decreases considerably the interface coupling that now writes:

$$J_{eb}=\frac{\zeta J_{ex} S_{AF} S_F}{aL}$$

(2)

L is the antiferromagnetic domain size and $\zeta$ a factor depending on the shape of the domains and on the averaged number of frustrated interaction paths for each uncompensated surface spin [19]. For hemispherical bubble domains, $\zeta \approx 2z/\pi$ and $z$ is of order unity [19]. From equations (1) and (2) and for large AF thickness ($R >> 1$) the exchange field should vary as $1/L$:

$$H_E = \frac{H_E^\infty}{1 - \frac{1}{4R^2}}$$

(3)

and indeed, a linear dependence of $H_E$ with $1/L$ was experimentally observed in several AF/FM systems [25, 26], providing strong support to the model.
In order to determine the domain size in antiferromagnets, a technique of choice is X-ray photoelectron emission microscopy [27, 28]. Alternatively, an estimation of the average domain size can be inferred from the width of the ND peaks that reflects the coherence length in the sample [29]. In some multiferroics like BFO, the FE and AF domains are coupled [8] so that it is possible to infer the size and distribution of the AF domains by imaging the FE domains, e.g. using piezoresponse force microscopy (PFM).

We have characterized the FE domains in two sets of BFO samples by combining in-plane and out-of-plane PFM measurements [30]. A first set consists of ~65 nm-thick BFO films grown on different buffers and substrates (see table I). A second set consists of BFO films with varying thickness (5 nm ≤ tAF ≤ 240 nm) grown on LSMO/STO(001). In BFO, since the polarization is oriented along the <111> directions there generally exist 8 possible polarization orientation variants. This leads to a large number of possible domain patterns and to several types of domain walls (DWs) depending on the angle between the polarization vectors in the adjacent domains (71, 109 or 180°). In principle only 71° and 109° FE DWs correspond to an AF DW [8]. In most of the samples considered in this study, the three types of DWs are present, with the density of 180° type DWs being negligible.

In the following we analyze the exchange field in terms of the average FE domain size LFE that we identify to half the FE domain periodicity, and the average AF domain size LAF that we identify to the coherence length in the ND experiments. Even in the case of a strict correspondence between the FE and AF domains, LFE is expected to be larger than LAF because it comprises both the domain and the DW widths while LAF mostly reflects the domain width.

**TABLE I: Experimental values of the exchange field and ferroelectric domain size for samples of the first set.**

| Substrate  | Buffer | tAF (nm) | H E  | LFE (nm) |
|-----------|--------|----------|------|----------|
| STO(001)  | LSMO   | 70       | -39  | 58       |
| STO(001)  | SRO    | 70       | -14.5| 98       |
| STO(111)  | LSMO   | 70       | -19  | 68       |
| STO(111)  | SRO    | 70       | -39  | 48       |
| LAO(001)  | LSMO   | 60       | 0    | 350      |
| LAO(001)  | SRO    | 60       | -29  | 55       |

Let us first compare the values of LAF and LFE for the samples of Fig. [I]. From Fig. [I], we calculate LAF = 42 nm while from PFM we find LFE = 58 nm for this sample. For the sample of Fig. [I], LAF = 56 nm and LFE = 98 nm. LFE is larger than LAF by some tens of nm that likely correspond to the DW width [31]. When LAF increases LFE increases also, as expected if the AF and FE domains are correlated, as found by Zhao et al [8].

**FIG. 2:** (a) Dependence of the exchange field on the inverse of the domain size for several ~65 nm thick BFO films. (b) Thickness dependence of the exchange field for CoFeB/BFO stacks grown on STO(001). The dotted lines are guides to the eye.

In figure 2, we plot the exchange field as a function of the inverse of the domain size for the first set of samples (constant thickness). A linear variation of H E with 1/L is observed, as expected from Eq. (3). Furthermore, there is an excellent quantitative agreement between the model and the data as illustrated by the similarity between the experimental points (solid symbols in Fig. 2a) and the values of H E calculated using the domain sizes (open symbols; the only free parameter is $\zeta$ that we set to 3.2).

As illustrated by Fig. 2b, this model also accounts for the thickness dependence of the exchange field. Below a critical BFO thickness of about 10 nm, there is no exchange bias but at larger thickness, H E increases abruptly and takes values of about 40 Oe for tAF ≥ 35 nm. A similar thickness dependence was reported for other AF/FM systems such as FeMn/NiFe [32] and is expected from Eq. (3). Combining Eq. (1) and Eq. (2), and using the measured domain sizes one can calculate H E for these films. The only free parameters are $\zeta$ and KAF. As shown by the open symbols in Fig. 2b, a rather good agreement with the data is obtained for $\zeta$=3.2 (as before) and KAF=6.8 kJ/m³. We note that this value of KAF is lower than the value inferred for the bulk from electron spin resonance experiments [24] by about one order of magnitude. This can be due to the low thickness of the BFO films and possibly to strain effects, or reflect modified magnetic properties at the BFO/CoFeB interface, as will be discussed in the following.

To validate the analysis of our data with Malozemoff’s model, we have attempted to detect the presence of a net magnetization in BFO close to the interface with CoFeB using PNR. The PNR measurements were carried out with the PRISM instrument of the LLB at room temperature. Spin-up and spin-down reflectivities ($R_{++}$ and $R_{--}$) were collected and the data were corrected for the polarization efficiency. The
least square fittings were made using the Simul-Reflec software. The structural parameters of the layers were first determined by fitting X-ray reflectometry data (not shown). In the following we discuss the results for a Au(30nm)/CoFeB(7.5nm)/BFO(18nm)//STO(001) sample displaying an EB of 18 Oe and in which the CoFeB/BFO interface has a roughness of only 0.5 nm, yielding high quality reflectivity data.

Figure 3 shows the PNR results and the corresponding fits using two different sample models. In the first sample model (Fig. 3a) we only consider the presence of three layers, i.e. Au, CoFeB and BFO. The best fit is obtained for the structure Au(30.0±0.5nm)/CoFeB(7.0±0.5nm)/BFO(18±0.5nm) with zero magnetization in the BFO and Au layers, and a magnetization of 1±0.05 \( \mu_B/\text{f.u.} \) for the CoFeB. As can be appreciated, the fit is good but not perfect (see arrows). The fit quality is significantly improved, especially at high \( \theta \), by using a four-layer model, i.e. splitting the BFO layer in two. The best fit is then obtained if a 2±0.5nm layer carrying a magnetic moment of 1±0.5\( \mu_B/\text{f.u.} \) is present in the BFO, at the interface with the CoFeB. This ultrathin magnetic layer inside the BFO accounts for the presence of a large density of uncompensated spins within Malozemoff’s model (see Fig. 1). This observation suggests that two different, yet possibly related and complementary, strategies are possible to tune the magnetic switching fields of the ferromagnet electrically. One would rely on the manipulation of the pinned uncompensated spins to modify the exchange field \( H_E \), e.g. by changing the domain size that should be controllable by ad-hoc electrical writing procedures. The other could consist in controlling the unpinned uncompensated spins in order to alter the coercive field \( H_C \). This might be achieved by modifying the effective surface anisotropy of the AF, for instance by playing with the ferroelastic energy of the domains, which would change the magnetoelastic contribution to the anisotropy.

In summary, we analyzed the exchange bias in the CoFeB/BiFeO\(_3\) system and found that the exchange field does not correlate with the type of magnetic surface of the antiferromagnet - compensated or uncompensated. Rather, the exchange field scales with the inverse of the ferroelectric and antiferromagnetic domain size in the multiferroic BiFeO\(_3\) film, as expected from Malozemoff’s model that we extend for the first time to the case of ferroelectric antiferromagnets. Polarized neutron reflectometry measurements reveal the presence of a net magnetic moment within a ~2 nm slab in the BFO at the interface with the CoFeB, reflecting the presence of uncompensated spins in the BiFeO\(_3\), consistent with the observation of exchange bias and enhanced coercivity. As the ferroelectric domain structure can be easily controlled by an electric field, our results strongly suggest that the electrical manipulation of magnetization should be feasible at room temperature in BFO-based exchange-bias heterostructures.

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