Uncompensated magnetization and exchange-bias field in \( \text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3/\text{YMnO}_3 \) bilayers: The influence of the ferromagnetic layer

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We studied the magnetic behavior of bilayers of multiferroic and nominally antiferromagnetic \( \text{a-YMnO}_3 \) (375 nm thick) and ferromagnetic \( \text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3 \) and \( \text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3 \) (8...225 nm), in particular the vertical magnetization shift \( M_e \) and exchange-bias field \( H_E \) for different thickness and magnetic dilutions of the ferromagnetic layer at different temperatures and cooling fields. We have found very large \( M_e \) shifts equivalent to up to 100% of the saturation value of the \( \text{a-YMnO}_3 \) layer alone. The overall behavior, including XMCD magnetization shift measured at the Mn-L edge of the LSMO layer only, indicates that the properties of the ferromagnetic layer contribute substantially to the \( M_e \) shift and that this does not correlate straightforwardly with the measured exchange-bias field \( H_E \).

1. Introduction

In bilayers composed of antiferromagnetic (AFM) and ferromagnetic (FM) phases a “horizontal” shift in the field axis of the hysteresis loops is generally observed after cooling them in a field applied at temperatures between the Néel \( T_N \) and Curie \( T_C \) temperatures [1,2]. This “exchange-bias field” \( H_E \) has been studied in different systems due to its fundamental importance as well as its technological relevance in spin-valve sensors, actuators and in high-density recording media [3] and some details of the origin of \( H_E \) are still a matter of discussion [2].

Less studied is the shift in the magnetization axis, i.e. the “vertical” \( M_e \) shift in the hysteresis loop, probably because of its rather small relative values [4,5] and its dependence on the cooling field \( H_C \) [6,7]. Recently, a maximum shift of 16% of the saturation magnetization was found in \( \text{Fe}_2\text{Ni}_{1-x}\text{Fe}/\text{Co} \) bilayers, which appeared to have an exchange-bias field of its own [8]. It was proposed that \( M_e \) is related to uncompensated moments (UCM) at the AFM/FM interface and should have a direct correlation to \( H_E \) [8,9]. Element specific X-ray magnetic studies of \( \text{Fe}_2\text{Co} \) [10,11] and \( \text{Co}/\text{Fe} \) [12] layered structures confirmed the existence of this \( M_e \) shift and revealed its relation to specific UCM in the AFM material. Using polarized neutron reflectometry, Ref. [13] studied the magnetization depth profile and its pinned and unpinned components at the interface of the system \( \text{Co}/\text{Fe}_2\text{Co} \), revealing the existence of pinned moments in the FM layer and not just in the AFM layer, as commonly assumed.

Due to the limited number of studies on the \( M_e \) effect it is of general interest to find systems with larger magnetization shifts, not only because of its fundamental interest but also because this shift provides a new degree of freedom in the hysteresis loop that may be well have some applicability in future devices. In this work we studied the exchange-bias shifts \( H_E \) and \( M_e \) of the hysteresis loops as a function of temperature \( T \) and \( H_C \) for three AFM/FM bilayers having the same AFM layer but different thickness and dilution of the FM layer. Superconducting quantum interference device (SQUID) measurements indicate an unusually large uncompensated magnetization shift \( M_e \) that is not simply correlated with \( H_E \) and that does not originate only from the AFM layer but from the FM one. Soft X-ray magnetic circular dichroism measurements indicate also that the FM layer contributes to the magnetization shift.

2. Sample preparation details and X-ray characterization

We prepared bilayers composed of a FM \( \text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3 \) (LSMO) layer (selected for its weak anisotropy and small coercivity).

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covering an AFM orthorhombic o-YMnO₃ (o-YMO) layer grown on (100) SrTiO₃ substrates of area 5 × 5 mm² for samples A and B and 6 × 6 mm² for sample C. For the depositions a KrF excimer laser (wavelength 248 nm, pulse duration 25 ns) was used and the optimal parameters found for o-YMO were 1.7 J/cm² with 5 Hz repetition rate, 800 °C and 0.10 mbar for the substrate temperature and oxygen pressure during preparation. We have measured three bilayers, all of them with the same 375 nm thick o-YMO layer on STO substrates prepared always under the above-mentioned conditions. To check the reproducibility of the found effects we have prepared a fourth bilayer with identical thickness as in sample A but instead of the LSMO FM layer we used La₀.₆₇Ca₀.₃₃MnO₃ (LCMO) deposited on o-YMO and this last one on a (100) LSAT substrate.

For the FM layer we used LSMO deposited immediately on the o-YMO layer with the following parameters: 10 Hz repetition rate and 0.35 (0.38) mbar oxygen pressure, 8 (30) nm thickness and at the same laser fluency and substrate temperature, for sample A (B). In order to corroborate the contribution of the FM layer in the \( M_s \)-shift we have decreased further the oxygen concentration to deposit the LSMO film in sample C (oxygen pressure 0.10 mbar) with a larger thickness of 225 nm decreasing in this way its coercivity. For the fourth LCMO/YMO bilayer the YMO layer was grown under similar conditions as before but the LCMO layer under an oxygen pressure of 0.55 mbar; all other conditions as for the LSMO layers.

The epitaxial growth in the 0 0 1 direction for the o-YMO and 1 0 0 for LSMO phases was confirmed by X-ray diffraction using Cu – Kα line. As an example we show in Fig. 1 the X-ray spectrum of the single o-YMO layer on STO. The preferential growth of the (0 0 1) planes of the orthorhombic phase YMO is clearly seen. Within the experimental resolution no maxima due to the hexagonal phase are observed. Fig. 2 shows the X-ray spectrum obtained for sample B. The main diffraction peaks from the LSMO layer are observed as a weak shoulder near the STO main maxima. Magnetization measurements were performed with a SQUID from Quantum Design in the temperature range between 5 and 350 K. The SQUID measurements were done at different applied fields and different field sweep conditions taking into account the particular purpose of the measurement. For example, to obtain the transition temperatures we measured at remanence or at relatively low fields (Figs. 4 and 8(a)) or in ZFC-FC states (Fig. 3). Furthermore, because both exchange-bias effects depend on the magnitude of the field applied on cooling \( H_{\text{FC}} \) from a temperature above the \( T_N \) of the AFM layer, hysteresis loop measurements were performed at different \( H_{\text{FC}} \)’s.

In addition, we performed soft X-ray absorption and circular dichroism measurements using the bending magnet beamline

![Fig. 1. X-ray spectrum of the single YMO AFM layer on STO substrate.](image1)

![Fig. 2. X-ray spectrum of the bilayer sample B. The labels indicate the corresponding main diffraction peaks.](image2)

![Fig. 3. (a) Hysteresis loop of the magnetization at 5 K for the 375 nm thick YMO layer on STO. The error bars indicate the maximum error due to the SQUID and geometry measurements. (b) Temperature dependence of the magnetic moment of a single YMO layer on STO in ZFC and FC states at an applied field of 0.05 T. An error bar of ± 0.3 μemu is the expected maximum error from our SQUID measurements.](image3)
6.3.1 at the Advanced Light Source in Berkeley, CA (USA) and the elliptical undulator beamline 13.1 at the Stanford Synchrotron Radiation Lightsource, Stanford, CA (USA). For these measurements the sample was mounted between the poles of an electromagnet so that the X-rays are incident on the sample under a grazing angle of 30° parallel to the direction of the applied magnetic field. The X-ray absorption intensity was monitored using the electron yield method. Hysteresis loops were acquired by sweeping the external field while monitoring the electron yield at the Mn $L_3$ and $L_2$ absorption resonance ($\approx 640$ eV). This approach is surface sensitive and in general it yields information only on the first $\sim 5$ nm of the sample. Assuming an exponential escape depth of 2.5 nm, then 95% of the signal comes from the top 6 nm of the sample. This is essentially our probing depth. For a more detailed description of the technique see Refs. [10,11].

3. Results

3.1. Single YMnO$_3$ Layers

According to the literature [14,15] the $\alpha$-YMO phase is AFM with Néel temperature $T_N = 42 \pm 2$ K and with a ferroelectric transition at $\sim 31$ K. In spite of its low $T_N$ this material has several advantages for exchange-bias studies. It belongs to the family of the perovskite manganite RMnO$_3$ and the magnetic and electrical properties can be changed by cation substitution keeping similar lattice constants and therefore without drastic changes in its structural properties. On the other hand, $\alpha$-YMO is a phase that was not thoroughly studied yet and the influence of its ferroelectric behavior, in spite of the low temperature, might be used as a paradigm for potential applications in magnetoelectric devices [16].

Fig. 3(a) shows the magnetization loop of single $\alpha$-YMO layer. The hysteresis loop indicates a magnetization at saturation of 1.8 emu/cm$^3$ at 5 K and at applied fields $\mu_0H > 0.5$ T in agreement with reported values [17]. Fig. 3(b) shows the magnetic moment of a single $\alpha$-YMO layer (6 x 6 x 0.375 mm$^3$) on STO measured as a function of temperature in ZFC and FC states at an applied field of 0.05 T. A clear increase in $m(T)$ decreasing temperature is observed at $T \approx 42$ K. An hysteresis between ZFC and FC is observed already below $T \sim 60$ K. As was shown in earlier studies on YMO we may expect to have persistent spin waves at temperatures above $T_N$ [18].

From the hysteresis loop shown in Fig. 3(a) one may speculate that the YMO film behaves as a ferro- or ferrimagnet and not, as expected, as an antiferromagnet. In fact, a recent study suggests a change of the usual bulk antiferromagnetic state to a strain-dependent non-collinear magnetic one in thinner (≤ 120 nm) $\alpha$-YMO films [19]. Taking into account that our YMO layers are much thicker and show a different $m(T)$ behavior as those reported in Ref. [19], i.e. at ZFC and low applied fields the measured $m(T)$ of our YMO films alone resembles practically the usual $T$-dependence found for antiferromagnets, the magnetic behavior of our $\alpha$-YMO layers may correspond to the one observed in diluted antiferromagnets in external magnetic field (DAFF). It is well known that DAFF develop a domain state when cooled below $T_N$ (sometimes with a spin-glass-like behavior) and this leads to a net magnetization, which couples to the external field, see e.g. Refs. [4,7,20–22].

From the measured temperature dependence of the magnetic moment and the observed scaling of the exchange-bias field $H_E$ with the inverse of the thickness of the LSMO layer for samples A and B, see Section 3.2, and the quantitative agreement of the obtained $H_E$ and $M_E$ shifts for the fourth sample (similar to sample A but with LCMO instead of LSMO) we may conclude that YMO behaves as an AFM or DAFF layer for the exchange-bias effects. Whatever the real magnetic equilibrium state of our $\alpha$-YMO films is, we may expect to see exchange-bias effects when these films are coupled to a ferromagnet. Further examples for exchange-bias effects in heterostructures with different ferro- or ferrimagnets can be seen in Refs. [23,24] and $H_E$ effects, positive as well as negative, has been also observed in ferrimagnetic based bilayers [25].

3.2. $\text{La}_0.7\text{Sr}_0.3\text{MnO}_3/\text{YMnO}_3$ bilayers

Fig. 4 shows the remanent moment for samples A and B measured increasing temperature at zero field, after cooling them to 5 K in a field of 0.1 T applied in-plane, i.e. $a$ or $b$ direction. Changes in slope of the remanence moment are observed near the Néel temperature onset $T_N \sim 50$ K of the $\alpha$-YMO layer. This increase of $\sim 8$ K in $T_N$ might be related to the an exchange-bias [26,27] or strain [28] effect. An anomaly is also observed at $T \sim 20$ K, as shown in Fig. 3(b), and already reported in the literature [14,29]. The temperature dependence of the remanence measured in sample B shows a clear change of slope near the Curie temperature of the LSMO layer. In contrast, due to the smaller LSMO thickness the remanent moment of sample A does not show a clear anomaly at $T_C$; similarly for sample C (not shown). For sample C we show in Fig. 4 the field cooled (FC) curve at 0.1 T; the absence of a marked anomaly at $T_C$ and the smooth decrease of the magnetic moment with $T$ demonstrates the expected strong magnetic dilution of the LSMO film. The existence of the FM state in this layer was confirmed through hysteresis loop measurements up to its ferromagnetic onset at $T_C \sim 300$ K. The FC results presented below were obtained always after cooling the samples from $T > T_C$ at zero field and after applying an in-plane field $H_{E,C}$ at 100 K $> T_N$.

Fig. 5(a) and (b) shows the hysteresis loops for ZFC and FC measurements at 5 K for samples A and B. A remarkable $M_E$ shift of the same order of the saturation magnetic moment $m_s$ is observed for sample A after FC from 100 K at $\mu_0H_{E,C} = 0.5$ T. For sample B the $M_E$ shift is also clearer measured but it is smaller relative to $m_s$. The sign of the $M_E$-shift changes when the direction of $H_{E,C}$ changes, i.e. it has the same sign as that of $H_{E,C}$. This indicates that the effective UCM layer is pinned in the direction of the cooling field, which means a ferromagnetic coupling.

In the determination of the $M_E$ and $H_{E,C}$ shifts we took special care to rule out effects due to minor hysteresis loops [30]. Studying the behavior of the loops at different $H_{E,C}$ we conclude that no minor loops and a clear saturation behavior of the
and $m_0^-$ are the saturation moments at positive and negative fields. The shift in the field axis is defined as $H_k = (H_c^+ + H_c^-)/2$, where $H_c^+$ and $H_c^-$ are the coercive fields in upward and descending loop branches, respectively. We note that the $H_k$ values were obtained only after centering the hysteresis loop, subtracting the upward $M_c$ shift.

Fig. 6 shows the coercivity $H_k$ (a), the exchange-bias $H_E$ (b) and the vertical shift in magnetic moment $m_{shift}$ (c) as a function of $T \leq 80$ K for sample B, measured after $\mu_0H_{HC}=0.3$ T, as an example. A similar behavior is observed for samples A and C. Both $H_c$ and $H_k$ show an anomaly at $T \approx 20$ K, in agreement with the behavior found in the remanence curve, see Fig. 4, suggesting that the transition at that temperature influences the exchange interaction. At $T \approx 35$ K $H_k$ crosses zero and changes to positive. This sign change of $H_k$ from negative to positive increasing temperature was observed also in Co/Cu bilayers[21] and suggests a change from direct ($J_{interface} > 0$) to indirect ($J_{interface} < 0$) interface interaction. As expected, $H_E(T)$ as well as $m_{shift}$ vanish at $T \geq T_N$. In contrast to $H_E(T)$ no anomalous behavior is observed in $m_{shift}(T)$ at $T < T_N$, with exception of the slope change at $T \approx 20$ K, see Fig. 6(c).

Fig. 7 shows the $H_{HC}$-dependence of $H_k$, $m_{shift}$ and $H_E$ for the three samples measured at 5 K. The decrease of $H_k$ from samples A to B agrees with the expected inverse proportionality of $H_k$ with the thickness of the FM layer. According to this thickness dependence sample C should show nearly one order of magnitude smaller $H_k$ than for sample B, in clear disagreement with the obtained result, see Fig. 7(c), suggesting that the magnetic dilution of this sample is responsible for the large observed $H_k$ field. This interesting and original behavior is in agreement with the theoretical study published recently by Usadel and Stamps[31] where they consider the influence on $H_k$ of the dilution of the FM layer alone. These authors found theoretically that an increase in the moment...
It is known that unexpected phenomena can occur at oxide interfaces. A recent study, for example, found an excess magnetization produced at the interface between STO and an AFM La$_{1/2}$Ca$_{2/3}$MnO$_3$ layer [32], which origin remains unclear. In our case the large $m_{\text{shift}}$ values—actually a giant $M_e$ effect—indicate that a large contribution should come from the FM layer. Taking into account the saturation moments of the LSMO layers alone, we estimate for example that a thickness of the LSMO layer of less than 1.3 nm for sample B and < 10 nm for sample C should be enough to produce the observed $m_{\text{shift}}$ at $H_{\text{FC}} = 0.5$ T.

### 3.3. La$_{0.65}$Ca$_{0.35}$MnO$_3$/YMnO$_3$ bilayer

Further evidences for the reproducibility and robustness of the effects observed in the three LSMO/YSM bilayers reported in the last section are provided by the results of a LCMO/YSM bilayer with similar geometry and preparation conditions as sample A. Fig. 8(a) shows the remanent magnetic moment of this bilayer after cooling the sample at 1 T applied field. The transition at the Néel temperature of the YSM layer is clearly seen as well as the change of slope at $\sim 20$ K. In Fig. 8(b) the hysteresis loops for three field cooled states at fields $H_{\text{FC}} = \pm 1$ T and 2 T are shown. At low $H_{\text{FC}}$ fields both exchange-bias effects are clearly observed.

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**Fig. 7.** Dependence of the coercive field $H_c$ (a), shift in magnetic moment $m_{\text{shift}}$ (b) and exchange-bias field $H_B$ (c) on the cooling field $H_{\text{FC}}$ for the three measured bilayers at 5 K. In (b) we plot $m_{\text{shift}}$ normalized by the maximum saturation moment $m_{\text{YMO}}$ of the YMO layer, i.e. $m_{\text{YMO}} = 17$ µemu for samples A and B and 24.5 µemu for sample C. Note that the values of $m_{\text{shift}} \sim 0$ at $H_{\text{FC}} = 0$ were obtained using maximum fields between 0.3 and 0.5 T for the hysteresis loops. For all the other points the maximum field of the loops coincides with $H_{\text{FC}}$.

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**Fig. 8.** (a) Temperature dependence of the zero field remanent magnetic moment measured after field cooled at 1 T of a bilayer La$_{0.65}$Ca$_{0.35}$MnO$_3$ (8 nm)/YMnO$_3$ (375 nm), similar to sample A, but the YMO layer first deposited on a (100)LSAT substrate. (b) Hysteresis loops at 5 K measured for the same sample after field cooled (FC) at the fields shown in the figure.
4. Discussion and conclusion

To further corroborate our conclusion that the observed vertical shift is mainly due to the FM and its interface region with the AFM layer we show the hysteresis loops acquired using X-ray magnetic circular dichroism in Fig. 10. For sample A we find a shift of 5% using the surface sensitive approach measuring the response of the Mn ions within the LSMO FM layer only. That one observes a vertical shift in the dichroism signal coming from the FM layer, whatever its magnitude, is a clear indication that this FM layer is contributing to the effect and that the magnetization shift is not confined to the bulk or at the interface of the AFM layer only. Because 95% of the secondary electrons detected in our XMCD experiment originates from the top 6 nm [10,11], just 2 nm below the interface region (sample A has 8 nm thin LSMO layer on top of the YMO layer), we can conclude that the interfacial region of the FM/AFM layer should contribute significantly more to the shift compared to the rest layers of the FM. This result agrees with the estimates from the bulk SQUID measurements, i.e. one needs about 1 nm thick FM layer (e.g. for sample A) to account for the observed shift.

Note that our XMCD measurements have been performed at 15 K, hence it is expected that the XMCD results should show lower values compared with those from the SQUID measurements performed at 5 K. In fact, if the coercive field is 0.4 T, a reduction of 15% is observed in the shift at 15 K respect to the 5 K measurement for sample A. For sample B a similar behavior is observed (see Fig. 6), being this reduction 20% for Hc = 0.3 T.

Taking into account the previous statement that it is highly unlikely that the entire AFM bulk contributes to the shift we can conclude that the excess magnetization is produced predominantly at the FM interface during the field cooling process due to interfacial exchange coupling between the AFM and the FM as shown previously for the case of CoFe2O4 [11].

Using similar arguments on the importance of the magnetic dilution of the AFM layer [20], we argue that in our system the dilution of the FM layer may play a major role in the shift in the other words, the robust AFM layer influences the magnetic behavior of the FM one, within a certain thickness from the interface. Recently, a magnetization shift was reported for ferrimagnetic very-thin hard/soft (3 nm/12 nm) DyFe2/YFe2 heterostructures [23]. We note...
however that in that work the $M_t$ effect is in the opposite direction to that of the applied $H_{BC}$, in clear contrast to our observations.

Furthermore, a comparison between the overall behavior obtained for $m_{main}(H_{BC})$ and $H_{y}(H_{BC})$ indicates that there is no simple correlation between the two exchange-bias effects. Note that $H_y$ decreases strongly from sample A to B, whereas $m_{main}$ increases. Although element selective X-ray magnetic measurements would help to determine the penetration depth of the UCM in each of the layers, it is clear from our SQUID measurements that the o-YMO layer alone cannot be the reason for the observed giant $M_t$ effect, this is the main message of our work.

In conclusion, our studies on LSMO/o-YMO bilayers and on a single LCMO/o-YMO bilayer found large uncompensated $M_t$ shifts, whose sign correlates with the direction of the cooling field $H_{BC}$. Both, the exchange-bias $H_y$ and $M_t$ effects, vanish near $T_N$ of the YMO layer. The large $m_{main}$ values indicate that the AFM layer cannot be the only responsible but a certain thickness of the FM layer near the interface. This behavior can be actually understood taking similar arguments as those used for the AFM layer in the domain state exchange-bias model of Refs. [9,20]. Tuning the thickness and magnetic dilution of the FM layer one should be able to obtain large $M_t$ shifts making it an effect worth to study in systems with $T_N > 300$ K. The different behaviors of $H_y$ and $M_t$ with temperature, cooling field and FM layer thickness indicate that these two phenomena are not correlated in a simple way.

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References


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