Unusual ferromagnetic YMnO$_3$ phase in $\text{YMnO}_3$/$\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ heterostructures

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Abstract
By means of first-principles density functional calculations, we study the structural, magnetic and electronic properties of $\text{YMnO}_3$/$\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ heterostructures. Although in the bulk the ground state of $\text{YMnO}_3$ is an antiferromagnet, the $\text{YMnO}_3$/$\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ heterostructure stabilizes the ferromagnetic (FM) phase in $\text{YMnO}_3$ in the interface region over a wide range of Coulomb repulsion parameters. The hypothetical FM phase of bulk $\text{YMnO}_3$ is dielectric and due to substantial differences between the lattice constants in the $ab$ plane, a strong magnetocrystalline anisotropy is present. This anisotropy produces a high coercivity of the unusual FM $\text{YMnO}_3$ that can explain the large vertical shift in the hysteresis loops observed in recent experiments (Paul et al 2014 J. Appl. Crystallogr. 47 1054). The correlation between weak exchange bias and the vertical shift is proposed, which calls for reinvestigation of various systems showing vertical shifts.

Keywords: magnetism, exchange bias, interfaces

1. Introduction

Heterostructures composed of competing magnetic and electric phases are often exploited as a source of novel physical phenomena and for their tailored new functionalities [1]. The interfaces between different materials offer the chance to manipulate the interplay between magnetic,
orbital, electronic and lattice degrees of freedom giving rise to behavior that can differ from the behavior of the bulk [2]. The interest for this research area points to the underlying fundamental physics as well as to develop new devices based on emergent phenomena at the interfaces of heterostructures. Particularly in oxide heterostructures, the magnetic, electronic and orbital interface reconstructions have got immense attention due to emerging novel electric and magnetic ground states [3–5]. Interfaces between ferroelectric oxides and collinear ferromagnets have presently drawn considerable attention [6–8] for the possibility to create artificial multiferroic materials at room temperature [9].

Exchange bias is one such outcome of interfacial coupling across two different magnetic states [10], usually antiferromagnetic (AFM) and ferromagnetic (FM) phases. In perovskite based heterostructures, magnetic interactions are particularly fascinating as they can show interface ferromagnetism between two antiferromagnets or between an antiferromagnet and a paramagnet [11]. Competing magnetic interactions, which give rise to proximity coupling such as exchange bias have found technological applications in magnetoresistive sensors, however its microscopic origin often raises debates particularly regarding the coupling configurations at the interface [10].

Orthorhombic YMnO₃ is a ferroelectric antiferromagnet with $T_{FE} \approx 30$ K and $T_N \approx 42$ K. The reported ferroelectric properties of YMnO₃ thin films indicate the occurrence of the coexistence of cycloidal and $E$-type AFM orderings [12] or of commensurate $E$-type AFM ordering at low temperatures [13]. Orthorhombic YMnO₃ is also energetically close to AFM $A$-type ordering [14]. Since the magnetic properties of YMnO₃ lie at the verge between different magnetic orderings, it is tempting to speculate that interfaces could modify this ordering as well the electronic and structural properties.

Magnetic heterostructures showing a horizontal shift of hysteresis loop along the field axis have been commonly observed for bilayer combinations [4, 15]. However, an uncommonly observed effect of exchange coupling across an AFM/FM interface is the shift along the magnetization axis or the vertical shift [16]. Element specific magnetic studies with x-rays of FeF₂/Co and CoO/Fe [17, 18] layered structures confirmed the existence of this vertical shift and revealed its relation to specific uncompensated moments in the antiferromagnet. The vertical shift is the irreversible magnetization of the non FM layer [19] and it was conjectured to be either correlated or not correlated to the bias field, but no convincing experiment could be made possible to identify due to the extremely small magnitude of the vertical shift. However, a recent study on heteroepitaxial interfaces involving YMnO₃ and the weak anisotropic ferromagnet La₀.₇Sr₀.₃MnO₃ (LSMO) showed an unusually large vertical shift. It was also shown that this vertical shift was correlated with the horizontal shift [8, 20]. Samples with a larger horizontal shift showed a smaller vertical shift and vice versa as in other systems [21]. In core/shell structured Fe nanoparticles, large exchange bias and vertical shifts were attributed to the frozen moments in a spin-glass like phase in the shell of the nanoparticles [22]. However the horizontal shift in YMnO₃/LSMO is negligible compared with the vertical shift. The vertical shift was found together with the horizontal shift [23, 24], but this system basically shows a pure vertical shift in the hysteresis loop. YMnO₃/La₂/₃Sr₁/₃MnO₃ heterostructure is the missing element in the phenomenology of the magnetic interface and can be a key point in the understanding of the magnetic interface phenomena. In this work we focus on the coupling between AFM YMnO₃ and FM La₂/₃Sr₁/₃MnO₃ to understand what is the specificity of this system to create a pure vertical shift.
The paper is organized as follows. In section 2, we describe the computational framework. In section 3, first principle calculations of structural, magnetic and electronic properties of YMnO$_3$/LSMO heterostructures are reported. In section 4 we compare the AFM and FM phases of bulk YMnO$_3$, while in section 5 we propose the microscopic mechanism to explain and the information necessary for interpreting the large vertical shift. Finally, in section 6 we present our summary and concluding remarks.

2. Computational details

We have performed first-principles density functional calculations by using the VASP [25] package based on plane wave basis set and projector augmented wave method [26]. A plane-wave energy cut-off of 400 eV has been used. For the treatment of exchange-correlation, Perdew–Burke–Ernzerhof [27] generalized gradient approximation (GGA) has been considered. In order to include strong electron correlations, we have considered a Hubbard $U$ approach [28], commonly used to describe the electronic structures of correlated oxides. For bulk parts of LSMO, we have considered the $U$ value of 3 eV for Mn-d orbitals, following the recommendations in published articles [29]. For bulk YMnO$_3$, we find that electronic polarization is well described for $U$ larger than 2 eV while the magnetic properties are in agreement with experiment for $U$ below 4 eV.

In our simulations, the heterostructures were constructed using a lateral supercell $a \times 2b$ with the lattice parameters of YMnO$_3$. We denote $U_{\text{INN}}$ as the Coulomb repulsion parameter of YMnO$_3$ in the inner layers of the heterostructure. This value is tuned between 2 and 4 eV because in this range we are able to reproduce the magnetic and electronic properties of bulk YMnO$_3$. The layer between YMnO$_3$ and LSMO is termed as ‘interface layer’. For simplicity, we have considered a sharp interface in this study. As the appropriate value of the Coulomb parameter $U_{\text{INT}}$ is unknown for the interface part, we have varied it for interface Mn atoms between 1 and 8 eV and have examined the possible magnetic structures. In all calculations, the Hund parameter $J_H$ was kept as 0.7 eV. A $6 \times 4 \times 1$ $k$-points set was used for Brillouin zone integrations in the Monkhorst–Pack scheme for the heterostructures. For the bulk calculations of YMnO$_3$, we have used a $6 \times 6 \times 6$ $k$-points mesh for geometry optimization and a $8 \times 8 \times 8$ $k$-points mesh for the calculations of density of states (DOS). The geometries were relaxed until the forces on all atoms were reduced to 5 meV Å$^{-1}$.

Bulk phases of LSMO were studied and our results are in agreement with the literature [30]. We find that bulk LSMO is a FM metal with a pseudocubic symmetry. However LSMO will adapt to the orthorhombic YMnO$_3$ substrate in the supercell.

To extract the character of the electronic bands at low energies, we used the Slater–Koster interpolation [31] scheme based on the Wannier functions [32, 33]. Such an approach is applied to determine the real space Hamiltonian matrix elements in the $e_g$-like Wannier function basis for bulk YMnO$_3$. After obtaining the Bloch bands in density functional theory, the Wannier functions are constructed using the WANNIER90 code [34]. Starting from an initial projection of atomic $d$ basis functions belonging to the $e_g$ manifold and centered on Mn sites, we get the two $e_g$-like Wannier functions.
3. First principles calculations of heterostructures

First, we study the case of a heterostructure with two YMnO₃ layers, two LSMO layers and two interface layers from structural and magnetic point of view. Further, using the results of this heterostructure, we analyze in more detail the properties of a larger supercell with five YMnO₃ layers.

3.1. Superlattice: structural properties

We have used the experimental values [13] of YMnO₃ for the in-plane lattice parameters of the supercell. For the c axis, the bulk value has been chosen and at the interface, the average out-of-plane separation between YMnO₃ and LSMO has been used to get the total c value of the supercell. The following notations will be used for the heterostructure, we define L₀ as the interface layer and L₁ as the first neighbor layer. In the supercell with five YMnO₃ layers, the second and third neighbor layers of the interface are denoted as L₂ and L₃ respectively, as shown in figure 1.

First of all, we study the smaller supercell with two YMnO₃ layers. In our interface model, we have a layer of YO, a layer of MnO₂ and another layer of La₋₁₋₁SrₓO that close the cage around the MnO₆ octahedra. However, the exact stoichiometry of the La₋₁₋₁SrₓO layer at the interface is unknown. We have calculated the energies for different magnetic phases and different Coulomb repulsion parameters U_{INT}. The most stable configuration is with LaO layers and SrO layers in agreement with similar results for other kinds of supercells [29, 30] and the
interface with only La atoms has always the lowest energy. Therefore, at the interface, we have MnO₆ octahedra enclosed in a cage with Y on one side and La on the other side. Probably, the La atoms are energetically favored because of their atomic radii being very similar to the Y radii. As Y and La are electronically equivalent, there is no charge doping or double exchange at the interface. Thus the interface layer can be metallic or insulator depending on the magnetic phase. On the other hand, the inner layers of LSMO will be always metallic because of the presence of Sr that produces a charge doping.

Assuming the LaO layer at the interface, we report the results for the supercell with five YMnO₃ layers at $U_{\text{INT}} = 2 \text{ eV}$ and $U_{\text{NN}} = 3 \text{ eV}$ with the magnetic ground state reported in figure 1. The magnetic ground state, discussed in the next subsection, is composed of FM layers at the interface (L₀) and the first layer of YMnO₃ (L₁). We find that the structural properties of the interface layer L₀ are intermediate between YMnO₃ and LSMO. All the Mn–O bonds are inequivalent and there are long (l) and short (s) bonds due to Jahn–Teller effect (JT). In the bulk AFM phase the JT distortion gives $(l-s)/(l+s) = 0.077$. The Mn–O long bonds at the interface are 2.08 and 2.15 Å while the Mn short bonds are 1.93 and 1.98 Å, reducing the $(l-s)/(l+s)$ factor to 0.039. Along the c-axis, the Mn–O bond is 1.89 Å between the Mn and the O atoms of the LaO plane, while it is 1.93 Å between the Mn and the O atoms of the YO plane as in the AFM YMnO₃ bulk. At the L₁ layer, JT yields $(l-s)/(l+s) = 0.070$ with the long bonds of 2.21 Å and the short ones of 1.92 Å.

The Mn–O–Mn bond angle is a very important parameter for manganite perovskites. The in-plane Mn–O–Mn bond angle is 159.7–165.0° for LSMO layer, while it is 148.8–150.2° at the interface L₀ layer. More crucial is the result for the YMnO₃ region (L₁, L₂ and L₃ layer). Figure 2(a) shows the two different bond angles in the $ab$ plane for the P2₁ nm space group for the AFM layers in the bulk phase and in the heterostructure.

As YMnO₃ becomes FM at the interface, it is interesting to examine the bulk FM phase of YMnO₃. Remarkably, in the FM bulk YMnO₃ the bond angles become equal due to the change of the symmetry that becomes $Pbnm$. Because the polarization comes from the difference...
between the two bond angles \([35]\), the compound does not show ferroelectricity at zero temperature in its FM phase. We will refer to this phase as dielectric.

Our calculations yield \(\alpha_1^{\text{AFM}} = 143.3^\circ\) and \(\alpha_2^{\text{AFM}} = 144.7^\circ\) in the AFM bulk phase and \(\alpha_{\text{FM}} = 144.2^\circ\) in the FM bulk phase. Similar results are obtained in the AFM L2 layer with \(\alpha_1^{L2} = 142.9^\circ\) and \(\alpha_2^{L2} = 144.2^\circ\), while for the more inner AFM layer L3, we have \(\alpha_1^{L3} = 142.7^\circ\) and \(\alpha_2^{L3} = 144.1^\circ\). For these AFM layers the polarization is along the \(a\) axis as in the bulk system. Instead, we found different results for the FM layer L1 near the interface. The tilt of the the octahedra pushes two O atoms above and two O atoms below the Mn atoms plane, and due to the strong asymmetry between \(z\) and \(-z\) directions, we again have two independent couples of Mn–O–Mn bond angles as shown in figure 2(b). However, the geometrical configuration of the two couples of angles is rotated by \(90^\circ\) with respect to the AFM case as well the possible polarization that is now expected along the \(b\) axis. The two bond angles are \(\beta_1^{L1} = 143.3^\circ\) and \(\beta_2^{L1} = 144.0^\circ\). Moreover, another component of polarization is possible along the \(c\) axis due to the breaking of inversion symmetry at the interface, but no polarization will be present along the \(a\) axis. Basically, the interface induces a shift of the transition metals along the \(c\) axis reducing the symmetry of \(\text{YMnO}_3\) as already demonstrated at the interfaces of other perovskite heterostructures [36].

While the origin of the polarization is magnetic in bulk \(\text{YMnO}_3\), the origin of the polarization is structural in the L1 layer due to the asymmetry induced by the interface. The reduction of the polarization along the \(a\) axis might be an easy experimental check to confirm our prediction about the creation of FM \(\text{YMnO}_3\) layers at the interface of the \(\text{YMnO}_3/\text{LSMO}\) heterostructures.

### 3.2. Superlattice: magnetic properties

Besides the most stable magnetic phases, \(G\)-type, \(A\)-type and \(E\)-type magnetic phases were also studied at the interface. The spin configuration is \(3d^{4\uparrow}\) according to Hund’s rule both for the interface and \(\text{YMnO}_3\) inner layers independently from the magnetic phase, while it is \(3d^{3.5\uparrow}\) in the \(\text{LSMO}\) due to the charge doping. We report the energy as function of \(U_{\text{INT}}\) in figure 3 for different magnetic phases. The four following magnetic phases are close to the ground state:

1. A fully FM phase (FM–FM)
2. An AFM \(E\)-type in \(\text{YMnO}_3\) and FM phase in \(\text{LSMO}\) and interface (AFM–FM)
3. A FM phase with spin up in \(\text{YMnO}_3\) and a FM with spin down in \(\text{LSMO}\) and interface (FM\(u\)–FM\(d\))
4. An AFM \(E\)-type in \(\text{YMnO}_3\) and an AFM \(A\)-type in \(\text{LSMO}\) and interface (AFM–AFM)

We find that in the range of typical \(U_{\text{INT}}\) for this system (between 1.8 and 4.1 eV) the heterostructure is completely FM also in \(\text{YMnO}_3\). Above 4.1 eV, we find an \(E\)-type solution in \(\text{YMnO}_3\) and an \(A\)-type solution in \(\text{LSMO}\). We remember that the heterostructure is orthorhombic. Instead, the \(\text{LSMO}\) bulk system is pseudocubic and does not present any instability towards the \(A\)-type magnetic order. Finally, at very low values of \(U_{\text{INT}}\), we have the FM \(\text{YMnO}_3\) with opposite moments with respect to the FM \(\text{LSMO}\) and interface. Remarkably, AFM \(E\)-type in \(\text{YMnO}_3\) and FM \(\text{LSMO}\) and interface is the sum of the two bulk ground states, however is never the ground state. Although \(U_{\text{INT}}\) is a local property of the interface layer, we can see that it influences the properties of the whole heterostructure determining a change of the
magnetic properties. A small variation of $U_{\text{INT}}$ can also have long range effects on the magnetic properties.

When we analyze the bigger supercell with five YMnO$_3$ layers we have qualitatively similar results. To investigate how the ferromagnetism goes deep in the YMnO$_3$ region, we analyze the magnetic properties as function of $U_{\text{INN}}$ in figure 4. Two FM layers for $U_{\text{INN}} = 2–3$ eV are present in the ground state. These two FM layers correspond to the two L1 layers in figure 1. When $U_{\text{INN}} = 4$ eV all the five YMnO$_3$ layers become FM. In summary, we found in two different supercells and in the typical range of Coulomb repulsion for this system that the first neighbor layer of the interface is FM. This is in agreement with recently observed few nanometers of FM layer at the interface of YMnO$_3$/LSMO [20]. The YMnO$_3$ develops an interface-induced ferromagnetism as in other perovskite systems at the borderline between

**Figure 3.** Total energies of the magnetic phases of YMnO$_3$/LSMO with six layers as a function of Coulomb repulsion at the interface. We report the difference between one magnetic phase and the fully ferromagnetic solution. The fully ferromagnetic solution is the ground state between 1.8 and 4.1 eV.

**Figure 4.** Total energy as a function of the number of ferromagnetic YMnO$_3$ layers for the heterostructure with five YMnO$_3$ layers. The energy of the ground state is set to zero. In the configuration with no FM layers, we have five $E$-type AFM layers. In the configuration with two FM layers, we have two ferromagnetic L1 layers. In the configuration with five FM layers, the heterostructure is fully ferromagnetic.
different magnetic orders [4, 37]. We also calculate the superexchange parameters for the supercell with five YMnO$_3$ layer and we get $J_{\text{INT\_LSMO}} = -39$ meV, therefore there is a strong coupling between the interface and LSMO. Instead, the coupling $J_{\text{INT\_YMO}}$ between L0 and L1 is just $-1.2$ meV. Moreover, we propose the following argument to additionally support our conclusions. We will show that the YMnO$_3$ FM phase has larger bandwidth compared to the AFM phase. LSMO also has a large bandwidth and can hybridize with YMnO$_3$ increasing its bandwidth and favoring its FM phase.

3.3. Superlattice: electronic properties

We calculated the DOS for the heterostructure shown in figure 5. As expected, the LSMO region shows a metallic behavior (figure 5(a)). In the L0 layer we have three electrons in the $t_{2g}$ manifold and one occupied electron in the $e_g$. There are two $e_g$ metallic bands at the Fermi level in the L0 layer (figure 5(b)). Remarkably, the most occupied $e_g$ orbital is $x^2-y^2$ as shown in figure 6 though the layer is metallic and also the $3z^2-r^2$ orbital gives us a strong contribution to the DOS at the Fermi level. However, this is completely different from YMnO$_3$ where the most occupied orbital has $3r^2-r^2$ character in the bulk and heterostructure in both FM and AFM phases. The interface layer is half metallic while both the FM and AFM YMnO$_3$ layers are insulators as observed in the local DOS of these atoms respectively in figures 5(c) and (d). Ferromagnetism brings metallicity and therefore the electronic polarization is zero at the interface layer. Electrons on atoms with spin majority down are more localized and the bandwidth is narrower in the DOS.

![Figure 5. Layer-resolved DOS of the superlattice with five YMnO$_3$ layers. The Fermi energy is set to zero. Spin up (down) contributions are shown in the positive (negative) y-axis. The (a), (b), (c) and (d) panels show respectively the local DOS of Mn atoms in the LSMO, L0, L1 and L2 layer. The DOS of the L3 layer is very similar to L2. The entire system shows a half-metallic behavior. Solid red (dashed blue) line represents the DOS of the Mn atoms where the spin majority is up (down). We indicate in the figure the region where the main orbital contribution to the DOS for the majority spin is $t_{2g}$ (green dashed line) and $e_g$ (pink dotted line).](image-url)
4. Bulk YMnO$_3$

We have reported an unusual FM phase in YMnO$_3$ in the previous section. To understand more about this new phase, we study and compare the FM and AFM phases at the experimental volume. We calculate the properties of YMnO$_3$ on the basis of the experimentally refined coordinates of the ferroelectric crystal at 21 K [13] with lattice constant $a = 5.246$, $b = 5.830$ and $c = 7.330$ Å for the AFM phase. For the FM phase we performed the relaxation of the atomic positions because this phase is not observed in the bulk. Let us consider three pseudocubic axes along the Mn–Mn directions for YMnO$_3$. There are three inequivalent directions for YMnO$_3$, which are called 1, 2 and c. Along the direction 1, the coupling is FM while along the directions 2 and c, it is AFM as shown in figure 2(a).

4.1. Magnetic and structural phases

We can map our YMnO$_3$ system in a Ising model where $\sigma_i = \{-1, +1\}$ respectively for spin down and spin up:

$$ H = \sum_{\langle i,j \rangle} J_{ij} \sigma_i \sigma_j, $$

(1)

where the sum is over pairs of adjacent spins. We report in figure 7 the values of magnetic superexchange $J_{ij}$ as function of $U$ and with a fixed ratio between the Hund coupling and Coulomb repulsion $J_H/U = 0.15$. Depending on the $U$ value, we have three magnetic phases:
The results are in agreement with [38]. The experimental magnetic phase is reproduced for $U < 4$ eV.

We also perform relaxation of atomic positions in the FM phase, and we calculate again the $J_{ij}$’s using the formula (1). We find that the magnetic couplings are qualitatively the same, but the FM region is greater as reported in figure 8. The FM phase of YMnO$_3$ is reported in table 1 and it has the same group symmetry of the dielectric phase. In this new phase, we recover the inversion symmetry.

**Figure 7.** Effective superexchange for YMnO$_3$ at experimental positions as function of $U$. We have three independent values of $J$. If $J$ is negative we have FM coupling, if $J$ is positive we have AFM coupling. When $J_1$ is negative and the others are positive we have the $E$-type magnetism. When $J_1$ and $J_2$ are negative and $J_c$ is positive we have the $A$-type magnetism. Finally, when they are all negative we have the FM phase.

**Figure 8.** Effective superexchange for YMnO$_3$ at predicted position of ferromagnetic phase as function of $U$. We have three independent values of $J$. If $J$ is negative we have FM coupling, if $J$ is positive we have AFM coupling. When $J_1$ is negative and the others are positive we have the $E$-type magnetism. When $J_1$ and $J_2$ are negative and $J_c$ is positive we have the $A$-type magnetism. Finally, when they are all negative we have the FM phase. Because of the predicted position of ferromagnetic phase, the FM region is wider with respect to the previous case.

$E$-type at low $U$, $A$-type at intermediate $U$ and FM at high $U$. The results are in agreement with [38]. The experimental magnetic phase is reproduced for $U < 4$ eV.
Electrons are more localized in the AFM E-type phase than in the FM phase. JT is reduced in the FM phase and \((l-s)/(l+s)\) goes from 0.077 in the E-type to 0.067 in the FM phase. The orbital order is \(3l^2-r^2\) in both magnetic phases and also hopping parameters are not modified.

The mechanism of polarization proposed for AFM E-type materials is based on the \(3l^2-r^2\) orbital order and asymmetric hopping in the \(P2_{1}nm\) phase [35], while in the FM \(Pbnm\) phase the hoppings are equal by symmetry and the polarization is zero.

### 4.2. Hopping parameters

The low-energy physics of YMnO₃ can be captured by \(e_g\) states. We calculate the hopping parameters for the low energy band structure in the basis of \(e_g\)-like Wannier functions. We report the band structure of nonmagnetic YMnO₃ using GGA in figure 9. In the nonmagnetic phase we have the \(t_{2g}\) orbital between \(-1\) and \(+0.5\) eV above the Fermi level. The bandwidth of the \(3d\) \(e_g\) orbital is 2.5 eV and is between 1 and 3.5 eV above the Fermi level. The hopping parameters of the nonmagnetic phase for the \(e_g\) manifold are reported in table 2. The hopping in the \(ab\) plane are almost similar, small differences rise from different bond angles and Mn–Mn distances. In a perfect tetragonal symmetry, we should find \(|t_{1,2}^{pq}|\) along the direction 1 equal to \(|t_{1,2}^{q,p}|\) along the direction 2. We find a large hopping \(|t_{1,2}^{pq}| \approx -243\) meV between \(x^2-y^2\)-like Wannier function in the \(ab\) plane, and we have a hopping between \(3z^2-r^2\)-like Wannier function along the \(c\) direction that is \(-307\) meV. These values of hoppings are in good agreement with

| a(Å) | b(Å) | c(Å) | Wyckoff | x   | y    | z    |
|------|------|------|---------|-----|------|------|
| 5.2456 | 5.8298 | 7.3295 | Y(4c)  | 0.01922 | -0.08437 | 0.25000 |
|       |      |       | Mn(4b) | 0.50000 | 0.00000 | 0.00000 |
|       |      |       | O(8d)  | 0.20026 | 0.17625 | 0.05314 |
|       |      |       | O(4c)  | 0.61256 | 0.03692 | 0.25000 |

**Table 1.** Calculated structural parameters of ferromagnetic YMnO₃ (space group \(Pbnm\) (no. 62)) phase within GGA (\(U = 0\)) at the experimental volume. \(a, b\) and \(c\) are the lattice constants in Å.

**Figure 9.** GGA band structure (red) and \(e_g\) bands (green) obtained using the Wannier functions for the nonmagnetic phase of YMnO₃. The Fermi level is set to zero. The path in the band structure is the same as in [38].
values for other Mn-perovskites. We observe that the second neighbor hopping are strongly asymmetric along the two directions $a$ and $b$. It was shown that the orbital order is $3l^2-r^2$ and $l^2-r^2$ and considering the larger value of $b$, the charge of the Mn atoms points towards the direction $b$. This is the main reason why the hopping parameters are bigger along the $b$ axis creating a large anisotropy in the plane.

We repeat the calculation for the FM positions and the hopping parameters of the nonmagnetic phase for the $e_g$ manifold are reported in table 3. Although there are no dramatic change in the hopping parameters of the FM phase, the change of the symmetry makes the hopping similar along the directions 1 and 2. Assuming the microscopic mechanism for ferroelectricity due to the asymmetry between hopping parameters [35], the new symmetry destroys the electric polarization making a dielectric system. The strong anisotropy between $a$ and $b$ is present also in the FM phase.

### 4.3. Polarization and electronic properties

We investigate the electronic properties of the AFM and FM phases of bulk YMnO$_3$. We show the influence of the Jahn–Teller effect and the change of symmetry on the DOS in the FM phase. Both magnetic phases show insulating behavior (see figure 10). In the AFM case we have the $t_{2g}$ at 1 eV below the Fermi level, while in the FM case is as 2 eV below the Fermi level. Instead of the classical $e_g$ orbital, we have a linear combination of them. In both magnetic phases, we have the orbitals $3l^2-r^2$ just below the Fermi level and the $s^2-z^2$ just above the Fermi level as already known [35] for the AFM phase. In the FM case, the bandwidth is larger because electrons are more delocalized.

The value of polarization within GGA is $1.4 \mu C cm^{-2}$ along the direction $-a$ and decreases with increasing $U$, which is in good agreement with the results in literature [13].

| $e_p$, $e_q$, $\Delta^1$, $\Delta^2$ | $\epsilon_p$ | $\epsilon_q$ | $\Delta^1$ | $\Delta^2$ |
|-------------------------------------|--------|--------|--------|--------|
| First neighbor                      | 1591   | 2019   | 438    | 438    |
| Direction                           | $t^{1,2}_{p,p}$ | $t^{1,2}_{p,q}$ | $t^{1,2}_{q,p}$ | $t^{1,2}_{q,q}$ |
| 1                                   | $-243$ | 203    | 137    | $-109$ |
| 2                                   | $-244$ | $-138$ | $-203$ | $-112$ |
| c                                   | $-53$  | $-79$  | $-79$  | $-307$ |
| Second neighbor                     | $t^{1,2}_{p,p}$ | $t^{1,2}_{p,q}$ | $t^{1,2}_{q,p}$ | $t^{1,2}_{q,q}$ |
| a                                   | 16     | 6      | 5      | $-6$   |
| b                                   | 59     | 3      | 4      | $-28$  |

Table 2. Hopping parameters in YMnO$_3$ in the $e_g$-like basis at experimental positions. The basis is composed by $lx^2-y^2$, $1$, $lx^2-y^2$, $2$, $13z^2-r^2$, $1$, and $13z^2-r^2$, $2$. Hopping integrals $t^{1,2}_{j,j'}$ are from a site $i$ with orbital $j$ to neighboring site $i'$ with orbital $j'$. The connecting vector is $T = lx + my + nz$ where the vectors $x$, $y$ and $z$ connect two first-neighbor Mn atoms first-neighbor; the hopping integrals are tabulated up to the first-neighbor. $\epsilon_j$ is the energy on site for the orbital $j$ on the site $i$ and $\Delta^i$ is the on-site interorbital hopping of the atom $i$. We denote $p$ and $q$ respectively the orbitals $x^2-y^2$ and $3z^2-r^2$ in the hopping notation. We also report second neighbor hopping parameters along the two strongly different $a$ and $b$ axes. All energies are in meV.
Experimental value of polarization is between 0.25 and 0.5 μC cm⁻² and it is reasonably reproduced for $U$ greater than 2 eV. For instance, at $U = 4$ eV and $J_H = 0.6$ eV our calculated polarization is 0.36 μC cm⁻² which has a better agreement with the experimental value and the HSE calculation. The polarization is zero for the FM phase. Choosing a Coulomb repulsion parameter between 2 and 4 eV, we can reproduce the magnetic and electric properties with a ground state close to the $A$-type phase as shown in figure 7 and in experiment [14].

**Table 3.** Hopping parameters in YMnO₃ in the $e_g$-like basis in the predicted positions of the FM phase. The basis is composed by $|lx^2 − y^2, 1⟩$, $|lx^2 − y^2, 2⟩$, $|3z^2 − r^2, 1⟩$ and $|3z^2 − r^2, 2⟩$. Hopping integrals $t^{1,2}_{jj'}$ are from a site $i$ with orbital $j$ to neighboring site $i'$ with orbital $j'$. The connecting vector is $\mathbf{T} = l\mathbf{x} + m\mathbf{y} + n\mathbf{z}$ where the vectors $\mathbf{x}$, $\mathbf{y}$ and $\mathbf{z}$ connect two first-neighbor Mn atoms first-neighbor; the hopping integrals are tabulated up to the first-neighbor. $\epsilon_j$ is the energy on site for the orbital $j$ on the site $i$ and $\Delta_i$ is the on-site inter-orbital hopping of the atom $i$. We denote $p$ and $q$ respectively the orbitals $x^2 − y^2$ and $3z^2 − r^2$ in the hopping notation. We also report second neighbor hopping parameters along the two strongly different $a$ and $b$ axes. All energies are in meV.

| Direction | $t^{1,2}_{pp,i}$ | $t^{1,2}_{pq,i}$ | $t^{1,2}_{qp,i}$ | $t^{1,2}_{qq,i}$ |
|-----------|------------------|------------------|------------------|------------------|
| First neighbor | 1604 | 2033 | 427 | 427 |
| 1 | -238 | 183 | 126 | -97 |
| 2 | -238 | -126 | -183 | -97 |
| c | -33 | -70 | -70 | -322 |
| Second neighbor | | | | |
| a | 17 | 1 | 1 | -7 |
| b | 46 | -4 | -4 | -13 |

**Figure 10.** Total DOS per formula unit for YMnO₃ in the $E$-type (red solid line) and FM (blue dashed line) phase. The Fermi level is set to zero. Majority (minority) spin contributions are shown in the positive (negative) $y$-axis. We indicate in the figure the main orbital contribution to the DOS for the majority spin of the FM phase.
4.4. Magnetocrystalline anisotropy

As the magnetic field in the experimental case is applied in the ab plane, we are interested to study the anisotropy for the same situation. For the FM Pbnm phase, the formula for the anisotropy energy $E_A$ in the $ab$ plane for this system is

$$ E_A(\phi) = K_2 \cos^2 \phi + K_4 \cos^4 \phi, \quad (2) $$

where $\phi$ is the angle between the $a$-axis and the magnetization in the $ab$ plane. As the hard axis is along the $c$-axis, we can neglect it in the expression (2) for anisotropy energy. Our calculated ab initio value of the magnetocrystalline anisotropy in the FM phase is $K_2 = 0.561$ meV [20] per formula unit for the leading term. The higher order anisotropy term $K_4$ is also reported in table 4 and is found to be negligible. As the value of $K_2$ is positive, the easy axis is along the $b$ axis when $\phi = 90^\circ$. Our calculated value of $K_2$ is quite big in comparison to the values found in the literature [39] and is also two orders of magnitude greater than usual magnetocrystalline constants. This large value originates from a significant anisotropy $b/a = 1.111$ between the lattice parameters combined with the $3f^2-r^2$ orbital order.

To simulate the hysteresis we need to take into account the interaction of the magnetic system with the external magnetic field. The effect of the magnetic field on the energy is represented by the Zeeman energy $E_H$, which is expressed as:

$$ E_H(\phi) = -MH \cos (\phi - \phi_F), \quad (3) $$

where $\phi_F$ is the direction of the external magnetic field $H$ and $\phi - \phi_F$ is the angle between the magnetic field and the magnetic moment $M$. Here, we do not take into account interface and shape anisotropies. Our calculated total magnetic moment $M = M_{\text{spin}} + M_{\text{orbital}}$ has module $M = 3.62 \mu_B$ per Mn atom. Adding the equations (2) and (3), we get the expression for the total energy as

$$ E(\phi) = K_2 \cos^2 \phi - MH \cos (\phi - \phi_F). \quad (4) $$

For $\phi_F=90^\circ$, there is only one stable solution for $H > H_C = 2K_2/M$ that is the coercive field in this limit case. In this simple model, this critical magnetic field coincides with the magnetic anisotropy field, that is the magnetic field needed to saturate the magnetization along the hard axis. Using the total energy (4) we calculate the hysteresis for YMnO$_3$. It is found that the coercive field $H_C$ is of the order of $2 - 5 \times 10^4$ Oe, while in the experiment about YMnO$_3$/LSMO heterostructure [8] the magnetic field was up to $0.5 \times 10^4$ Oe. In our study, the magnetic anisotropy field is $5.4 \times 10^4$ Oe.

In LSMO, the expression for the magnetocrystalline anisotropy is

$$ E(\theta) = K_2^{LSMO} \sin^2 \theta, \quad (5) $$

\begin{table}[h]
\centering
\caption{Magnetocrystalline anisotropy constants for YMnO$_3$ in a fully ferromagnetic bulk phase.}
\begin{tabular}{|c|c|c|}
\hline
 & $K_2$ & $K_4$ \\
\hline
meV/(formula unit) & 0.561 & 0.008 \\
$10^4$ J m$^{-3}$ = $10^5$ erg cm$^{-3}$ & 160 & 2 \\
\hline
\end{tabular}
\end{table}
where \( \theta \) is the angle between the direction of the magnetization and the [001] direction. A very small anisotropy \( K_{\text{LSMO}}^2 = 0.18 \times 10^4 \text{Jm}^{-3} \) was measured in LSMO [40]. Following equation (5), the easy axis is along the \( c \) axis and the hard axes are in the \( ab \) plane. However at the interface we have an orthorhombic structure of LSMO and hence we expect a small magnetocrystalline anisotropy with a different easy axis. However, we neglect this effect and consider the easy axes plane as the \( ab \) plane as suggested by the experiments.

5. Hysteresis loops for two independent FM phases

In [8], a vertical shift \( m_{\text{shift}} \) in YMnO\(_3\)/LSMO heterostructures at 10 K was found experimentally and this vertical shift is attributed to the properties of the diluted AFM state in a magnetic field. However, the properties of the diluted AFM state disappears at low temperature in bulk YMnO\(_3\) and an \( E \)-type AFM phase take place [13]. Instead, the nature of the large vertical shift might be found in the interdiffused FM layer at the interface composed also by an unusual YMnO\(_3\) FM phase. We have shown that the YMnO\(_3\) L1 layer near the interface becomes FM. Therefore, the \( m_{\text{shift}} \) effect can be explained with the large coercivity of FM YMnO\(_3\). The magnetic field used to reverse the spin in FM LSMO is too small to reverse the spin in FM YMnO\(_3\). More clearly, the FM layer of YMnO\(_3\) is a hard ferromagnet and weakly ferromagnetically coupled to the interface and LSMO. The region composed by the interface and LSMO is a soft ferromagnet. Let us assume that the FM YMnO\(_3\) is magnetically decoupled from the interface. The total energy of the system can be written in the following way:

\[
E(\phi_S, \phi_H) = n_S(K_S^2 \cos^2 \phi_S - M_S^2 H \cos(\phi_S - \phi_F)) + n_H(K_H^2 \cos^2 \phi_H - M_H^2 H \cos(\phi_H - \phi_F)),
\]

(6)
as the sum of the energy of a soft ferromagnet (S) and a hard ferromagnet (H). \( n_S \) and \( n_H \) represent respectively the numbers of atoms in the soft and hard FM regions. When a relatively small magnetic field is applied, the hard ferromagnet does not reverse when the magnetic field is applied in the opposite direction, determining a shift of the magnetization. The magnetic configuration coming from equation (6) is shown in figure 11. The \( m_{\text{shift}} \) is the magnetization of the pinned magnetic moment in the AFM region. If we compare our results with the experimental values of the vertical shift, we observe that the FM phase of heterostructure should be composed of few interface layers of YMnO\(_3\) within the approximation of a sharp interface. What seems to be important in the determination of \( m_{\text{shift}} \) is the roughness of the interface, which is not considered in this work. A large roughness give us a large FM interdiffused layer and therefore a large \( m_{\text{shift}} \) as experimentally observed [8]. Another important condition is the weak coupling between the L0 and L1 layers (see figure 1), that permits the L0 layer to rotate avoiding to influence the L1 layer.

The peculiarity of this system is the weak exchange bias. The reduced horizontal shift arising from weak exchange bias can be attributed to the weak coupling between the rotating FM phase (L0) and the AFM phase (L2). Indeed, the exchange bias is proportional to the magnetic coupling between these phases [41]. However this is a second neighbor exchange interaction and hence, leads to a weak exchange bias. A large vertical shift comes from a large value of pinned magnetic moment in the AFM region and hence, the magnetic coupling
between AFM and FM is weak. Large vertical shift is associated to a small exchange bias when the creation of the pinned magnetic moments destroys the AFM order. To have the simultaneous presence of large magnetic moment and large exchange bias, we need a net magnetic moment in the AFM phase and an AFM phase strongly coupled to the FM phase. This is observed in other systems where the net magnetic moment is provided by non-collinear magnetic structures in AFM phase or in a ferrimagnetic one [23, 24].

This phenomenon of pure vertical shift is realized mainly due to three conditions. First, we need a FM layer in the AFM side of the interface. Second, this FM layer should have to be magnetically weakly coupled to the FM side of the interface. Finally, we need a large magnetocrystalline anisotropy of the FM layer relative to the FM side of the interface. The first two conditions are possible just when we have the $A$-type and the FM phases energetically close to the ground state as in the case of YMnO$_3$ (shown in figures 7 and 8). The third condition, that we need, is a strongly anisotropic system described above.

6. Conclusions

In conclusion, by means of first-principles density functional theory, we determined the structural, electronic and magnetic properties of YMnO$_3$/LSMO heterostructures. We find that the most stable structural configuration has a LaO layer in the LSMO side of the heterostructure. The interface layer shows half-metallic FM behavior with the LSMO region of the superlattice and its DOS exhibiting a $x^2$-$y^2$ character at the Fermi level. Remarkably, it is found that this interface stabilizes an unusual insulating FM phase in the layer closer to the interface in the
YMnO$_3$ side. This unusual phase is only present at the interface of these two dissimilar oxides and is not found experimentally in the bulk.

The FM phase of bulk YMnO$_3$ is insulating with a smaller band gap. It has a different space group ($Pbnm$) and a reduced Jahn–Teller effect compared to the usual bulk AFM phase. This different symmetry destroys the polarization along the $a$ axis in the FM layers and hence, a reduced polarization is observed in the YMnO$_3$/LSMO heterostructures. Moreover, our calculated hopping parameters in the $ab$ plane are distinctly different along the $a$ and the $b$ axes yielding a strongly anisotropic ferromagnet with a large coercivity in the $ab$ plane. Therefore, we have found a strongly anisotropic ferromagnet at the interface between an isotropic ferromagnet LSMO and a strongly anisotropic antiferromagnet YMnO$_3$. We show that the magnetization within this FM YMnO$_3$ layer is responsible for the large vertical shift observed in YMnO$_3$/LSMO heterostructures [20]. Indeed, a relatively small magnetic field applied to the entire heterostructure can rotate the moments in the LSMO part while the moments in YMnO$_3$ are pinned due to large coercivity. This pinned magnetic moment in YMnO$_3$ causes the vertical shift $m_{\text{shift}}$ in the hysteresis loop. A simple check of this picture is the measure of the polarization. Indeed, the calculated electronic polarization is reduced in the heterostructure compared to bulk YMnO$_3$. Hence, one can conclude that the vertical shift is due to the net magnetization of the AFM layers.

The small value of the exchange bias in YMnO$_3$/LSMO is due to the magnetic profile where there is no first neighbor magnetic interaction between the rotating LSMO FM region and the AFM inner layer region that produces the exchange bias. The existing weak second neighbor exchange interaction is too weak to produce any significant exchange bias effects. Our conclusions support the idea that horizontal and vertical shifts observed in the hysteresis loops are correlated and tend to exclude each other if the creation of the pinned magnetic moments destroys the AFM order. Thus our study, in general, would instigate revisits on various other systems showing such pure vertical shifts.

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