First principles calculation of uniaxial magnetic anisotropy and magnetostriction in strained CMR films

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We performed first-principles relativistic full-potential linearized augmented plane wave calculations for strained tetragonal ferromagnetic La(Ba)MnO$_3$ with an assumed experimental structure of thin strained tetragonal La$_{0.67}$Ca$_{0.33}$MnO$_3$ (LCMO) films grown on SrTiO$_3$[001] and LaAlO$_3$[001] substrates. The calculated uniaxial magnetic anisotropy energy (MAE) values, are in good quantitative agreement with experiment for LCMO films on SrTiO$_3$ substrate. We also analyze the applicability of linear magnetoelastic theory for describing the strain dependence of MAE, and estimate magnetostriction coefficient $\lambda_{001}$.

I. INTRODUCTION

Magnetic multilayers based on “colossal” magnetoresistive (CMR) materials are important for many magnetic applications including recording media and magnetoresistive sensors. The particular class of CMR materials, La$_{1-x}$A$_x$MnO$_3$ (A=Sr,Ca,Ba), is particularly interesting because they share the same basic perovskite crystal structure with many dielectrics, superconductors, and ferroelectrics. This structural similarity opens interesting possibilities for the epitaxial growth of CMR magnetic heterostructures for device applications.

Magnetic anisotropy energy (MAE) and magnetostriction in magnetic CMR heterostructures is significantly different from the MAE in bulk manganites [1]. Uniaxial magnetic anisotropy in thin La$_{0.67}$Ca$_{0.33}$MnO$_3$ (LCMO) films grown on SrTiO$_3$[001] (STO) substrate has been measured and interpreted to be due to the strain arising from a film/substrate lattice mismatch [1]. The possibility of producing strained LCMO films grown on a LaAlO$_3$ (LAO) substrate with the easy magnetization axis along film normal has been proposed.

In order to tackle the origin of the uniaxial MAE in strained CMR films we performed first-principles calculations of MAE for the strained tetragonal ferromagnetic La(Ba)MnO$_3$ (L(B)MO) with an assumed experimental structure of strained LCMO-films grown on STO and LAO substrates. We also analyze the applicability of linear magnetoelastic theory for describing the strain dependence of MAE, and estimate magnetostriction in LCMO-films.

II. COMPUTATIONAL METHOD

The experimental data of the MAE and magnetostriction in LCMO films have been obtained from magnetization curve measurements [1]. The 58 nm thick films were grown on [001] oriented STO substrate using atomic layer by layer molecular-beam epitaxy [2]. X-ray diffraction data showed that the films have a tetragonal unit cell with in-plane lattice constant 7.3696 a.u. which is consistent with STO substrate lattice constant and perpendicular lattice constant of 7.2373 a.u. This is fully consistent with the so-called “coherent” regime of the film strain in the “elastic” approximation [3]: film in-plane lattice constant matches with substrate in-plane lattice constant that results in perpendicular tetragonal strain determined by film Poisson ratio. As a result there are no misfit dislocations and no thickness dependence of the perpendicular strain.

An anisotropic energy density of a tetragonal ferromagnetic film on non-magnetic substrate can be written as [4]:

$$E/V = -K_1^s m_x^2 - K_2^s m_y^4 - K_3^s m_x^2m_y^2 - \frac{2}{t}(K_1^v m_z^2 + K_2^v m_y^4 + K_3^v m_x^2m_y^2)$$  

(1)

where, $K^v$ terms are 2nd and 4th-order volume-type anisotropy constants, $K^s$ terms are surface/interface-type 2nd and 4th-order anisotropy constants, $m_{x,y,z}$ are magnetization cosines with respect to the crystal axes, and $t$ is a thickness of magnetic film. For the particular case of LCMO films considered here $t$ is $\approx 150$ ML and surface term in Eq.(1) can be safely neglected. Therefore, as a computational model for LCMO film grown on STO and LAO substrates we used strained tetragonal bulk La(Ba)MnO$_3$ with the crystal structure parameters chosen in accordance with experiment [5]. We also assume that the 4th-order terms in Eq.(1) are significantly smaller (as usual) than 2nd-order uniaxial anisotropy constant $K_1^s$, and did not consider them.

Since the measured films are ferromagnetic at low temperature for $x = 0.33$ Ca concentration, we considered the only ferromagnetic phase. We also used end-point ferromagnetic LaMnO$_3$ and BaMnO$_3$ instead of actual LCMO in spite of the fact that both LMO and BMO have an antiferromagnetic ground state. The use of ferromagnetic LMO and BMO to approximate ferromagnetic LCMO films allows us to calculate the possible range of values for the uniaxial anisotropy in real LCMO films and to analyze the effect of electron concentration (changing Mn-site d-occupation) on MAE.
We used a relativistic version of the full-potential linearized augmented plane wave method to obtain the self-consistent solutions of Kohn-Sham-Dirac equations and ground state charge and spin densities for the magnetization directed along [001]-axis. For both strained LMO and BMO we used the special k-point method for the Brillouin zone (BZ) integrations. 348 k-points mesh in the 1/8th irreducible part of the BZ is employed for the self-consistent calculations and a Gaussian broadening ($\sigma = 0.0014 \, \text{Ry}$) is used for the eigenstates weighting. Lattice harmonics with angular momentum $l$ up to 8 are used to expand the charge and spin densities and wavefunctions within the muffin-tin sphere. More than 100 plane waves per atom/spin are used as the first variational basis set to solve the scalar-relativistic Kohn-Sham equations; all occupied and empty states up to 2 Ry above $E_F$ are used as a second variational basis set to calculate spin-orbit coupling matrix elements. Self-consistency is achieved to within 1 $\times 10^{-5}$ Ry for all-electron total energy.

The spin and orbital magnetic moments for magnetization along the [001] axis for strained LMO and BMO for STO and LAO substrates are shown in Table I. The orbital magnetic moments are antiparallel to spin moments, which is consistent with the atomic Hund’s rule for the case of less than half-filled d-shell. There is a decrease of spin moment and an increase of absolute value of the orbital moment with substitution of La by Ba due to decrease of Mn d-occupation. Assuming single-site approximation for the magnetic moment we can estimate LCMO spin moment to be 2.85 $\mu_B$ and orbital moment -0.011 $\mu_B$ for the STO substrate and 2.77 and -0.014 $\mu_B$ respectively for LAO substrate.

The MAE is then obtained by applying the force theorem to the spin - axis rotation: from the self-consistent ground state charge and spin density obtained for the [001] spin axis, a calculation of the band structure for [100] spin axis orientation is performed; difference of the single particle eigenvalue sums is then taken to be the MAE. For the MAE calculations we used special k-points mesh which was chosen with respect to the magnetic symmetry for the [100] spin axis. Since the local force theorem was used, the symmetry of eigenvalues rather than Hamiltonian was considered: for the tetragonal symmetry and magnetization directed along [100] it leads to exclusion of fourfold rotations with respect to [001] axis and leaves only eight space group symmetry operations (mmm space group) which are used to generate a set of irreducible k-points in 1/8th of BZ (different from those for self-consistent calculations).

To achieve convergent results for the MAE, we have increased the number of the BZ k-points and have done the band calculation for both the [001] and [100] spin axes using the ground state charge and spin densities. The MAE dependence on the number of k-points for the LMO(STO) is shown in Fig. 1. Surprisingly good convergence (less than 1 $\mu eV$) was achieved for 1000 k-points in 1/8th of BZ (8000 in full BZ). This set of k-points was then used for all MAE calculations.

### III. RESULTS AND DISCUSSION

The calculated uniaxial MAE for all four cases (L(B)MO(STO) and L(B)MO(LAO)) are shown in Table II. The calculated MAE values are in very good agreement with experiment for LCMO films ($-56 \mu eV$) on a STO substrate. This is direct numerical evidence of the magnetoelastic origin of the uniaxial MAE in strained LCMO films and supports quantitatively an interpretation of experiment given in Ref. [1]. For LMO(LAO) and BMO(LAO) we calculated the MAE to be positive. It is in qualitative agreement with very recent experiments for La$_0.5$Ca$_0.5$MnO$_3$ films grown on LAO substrate [12].

In addition to calculated magnetocrystalline MAE caused by spin-orbit interaction we have to take into account demagnetization energy (DE) which is due to “classic” magnetic dipole-dipole interaction. For the ferromagnetic film the DE can be evaluated numerically [3]. We calculated the DE using the results of Ref. [13] and taking into account that magnetic moment in L(B)MO is located at Mn-site (cf. Table I).

The values of DE for all four cases (L(B)MO(STO) and L(B)MO(LAO)) are shown in Table II. (We took into account the only in-plane dipole-dipole interaction between Mn-sites.) For the case of L(B)MO(STO) both MAE and DE keep magnetization in the film plane. For the case of LMO(STO) the sum of MAE and DE is negative ($-28 \mu eV$) and magnetization is in the film plane. For the BMO(STO) the total uniaxial MAE is positive ($42 \mu eV$) and magnetization is directed along the film normal.

Assuming single-site approximation for the magnetic anisotropy we can estimate total uniaxial MAE $\approx -7 \mu eV$ per cell for LCMO film on LAO substrate. It means that the absolute value of the magnetoelastic MAE is very close to the absolute value of the demagnetization field for LCMO film on LAO substrate.

To check the applicability of linear magnetoelastic theory we map our results onto the usual anisotropic magnetoelastic energy dependence on strain:

$$E = B_1 (e_z - e_0) m_z^2 + \text{const} ,$$

where $e_0$ is a biaxial (in-plane) strain due to the film/substrate lattice mismatch, $e_z$ is a uniaxial (along [001]) strain, $B_1$ is a magnetoelastic coefficient, and $m_z$ is a magnetization cosine with respect to the z([001])-axis.

Using Eq.(2), the values of strain [14] and MAE, we calculate the values of $B_1$ for L(B)MO for STO and LAO substrates (cf. Tab. II). There is quite pronounced variation of $B_1$ for LMO for the different substrates. It means that for LMO there is significant deviation from linear MAE dependence on strain (Eq.(2)), and linear theory is rather qualitative. For the case...
of BMO the variation of $B_1$ is smaller, therefore linear theory is more reliable. Note, that calculated values of magnetoelastic coefficient $B_1$ are in very reasonable agreement with the experimentally derived value $-6.7 \times 10^7 \text{ erg/cm}^3$ (−2.44 meV per cell) for LCMO films on STO substrate.

In spite of the fact that linear theory gives the only a semi-quantitative description of uniaxial MAE dependence on strain, our calculations show that one can still use it for estimation of the sign and order of magnitude of the magnetostriction coefficient $\lambda_{001}$. To determine $\lambda_{001}$ one has to minimize the sum of Eq. (3) and elastic energy (3):

$$E_{\text{elastic}} = \frac{1}{2} c_{11} e_z^2 + 2c_{12} e_z e_0 + \text{const},$$

where, $c_{11}$ and $c_{12}$ are elastic moduli, with respect to $e_z$, with $e_0$ fixed by substrate. It leads to the following expression for the magnetostriction constant $\lambda_{001}$ (see for details Ref. [3]):

$$\lambda_{001} = -\frac{2}{3} \frac{B_1}{c_{11}}$$

Assuming $c_{11} = 2 \times 10^{12} \text{ erg/cm}^3$ [3] and using calculated values of $B_1$ (cf. Tab. II) we calculate $\lambda_{001}$ for L(BO)MO films on STO and LAO substrates (cf. Table III). Our calculated values of $\lambda_{001}$ agree in sign and order of magnitude with the experimentally derived value $7 \times 10^{-5}$. However, we have to note that it is unclear what definition for $\lambda_{001}$ in terms of $B_1$ and $c_{11}$ was used in Ref. [3]: using the data of Ref. [3] and Eq. (3) we calculated $\lambda_{001} = 2.23 \times 10^{-5}$ in very good agreement with our results.

IV. CONCLUSION

To summarize, we have shown quantitatively that the observed uniaxial anisotropy in LCMO films grown on STO substrate is caused by strain arising from film/substrate lattice constant mismatch. It is also shown that the magnetoelastic MAE is positive for LCMO films on LAO substrate and absolute value of MAE is close to the absolute value of demagnetization energy. By varying the strain arising from a film/substrate lattice constant mismatch one can control the uniaxial anisotropy for LCMO films in order to overcome the demagnetization energy and provide [001] spontaneous magnetization direction.

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TABLE I. Experimental lattice constant (a, in a.u.) and c/a ratio for tetragonal strained LCMO films on STO and LAO substrates; spin ($M_s$) and orbital ($M_l$) magnetic moments for LMO and BMO for the [001] spin direction.

| Substrate: | STO   | LAO   |
|------------|-------|-------|
| a=b        | 7.3697| 7.1618|
| c/a        | 0.982 | 1.047 |

| Film:      | LMO   | BMO   | LMO   | BMO   |
|------------|-------|-------|-------|-------|
| $M_s$ (Mn) | 2.996 | 2.563 | 2.880 | 2.542 |
| $M_s$ (Total)| 3.145 | 2.727 | 3.022 | 2.712 |
| $M_l$ (Mn) | -0.004| -0.023| -0.007| -0.023|
| $M_l$ (Total)| -0.002| -0.021| -0.006| -0.024|

TABLE II. Biaxial ($e_0$) and uniaxial ($e_z$) strains, uniaxial MAE ($\mu$eV), demagnetization energy (DE) ($\mu$eV), $B_1$ (meV) for LMO and BMO films on STO and LAO substrates.

| Substrate: | STO   | LAO   |
|------------|-------|-------|
| $e_0$      | 0.008 | -0.021|
| $e_z$      | -0.0101| 0.0258|

| Film:      | LMO   | BMO   | LMO   | BMO   |
|------------|-------|-------|-------|-------|
| MAE        | -40.9 | -53.3 | 37.7  | 100.2 |
| DE         | -65.7 | -48.7 | -66.1 | -58.3 |
| $B_1$      | -2.259| -2.944| -0.806| -2.141|

TABLE III. $\lambda_{001} \times 10^5$ for LMO and BMO films on STO and LAO substrates.

| Substrate: | STO   | LAO   |
|------------|-------|-------|
| $\lambda_{001}$ | 2.1   | 2.74  |

FIG. 1. The calculated uniaxial MAE dependence on k-points number in 1/8th irreducible part of the BZ.