Magneto-electric coupling in antiferromagnet/ferroelectric Mn$_2$Au/BaTiO$_3$ interface

Evgeny Plekhano\textsuperscript{1}, Alessandro Stroppa,\textsuperscript{2} and Silvia Picozzi\textsuperscript{3}

\textsuperscript{1}King’s College London, Theory and Simulation of Condensed Matter (TSCM), The Strand, London WC2R 2LS, United Kingdom
\textsuperscript{2}Consiglio Nazionale delle Ricerche, Istituto SPIN, UOS CNR-SPIN L’Aquila, I-67100 L’Aquila, Italy
\textsuperscript{3}Consiglio Nazionale delle Ricerche, Istituto SPIN, UOS L’Aquila, Sede di lavoro CNR-SPIN c/o Univ. “G. D’Annunzio”, 66100 Chieti, Italy

Within the crucial issue of the electric field control of magnetism, the use of antiferromagnets coupled to ferroelectrics is much less explored than the ferromagnets counterpart, although the first choice might lead to better performances and larger stability with respect to external perturbations (such as magnetic fields). Here we explore the possibility to control the magnetic anisotropy of a Mn$_2$Au layer by reversing the ferroelectric polarization of BaTiO$_3$ in Mn$_2$Au/BaTiO$_3$ interfaces. By means of a thorough exploration of many possible geometry configurations, we identify the two most stable, corresponding to compressive and tensile strain at the interface. The first appears to be easy-axis while the second – easy-plane, with a large induced moment on the interface Ti atom. The reversal of ferroelectric polarization changes the anisotropy by approximately 50%, thus paving the way to the control of AFM properties with an electric field.

I. INTRODUCTION

The next generation of random access memory (RAM) devices will necessarily have to overcome the problem of high power consumption needed to maintain the written data, which amounts to approximately 99% of the total power consumed in current RAM. An innovative step in this direction might be taken by exploiting the so-called “magneto-electric coupling” (MEC), based on the interaction between the magnetic and ferroelectric order parameters, either in a single phase multiferroic\textsuperscript{1-4} or in a ferroelectric/ferromagnetic heterostructure\textsuperscript{5,6}. Thanks to the MEC, it could be possible to achieve a magnetic reading-process and electrical writing process of the information bits, therefore avoiding energy dissipation coming from significant currents on a small scale and allowing for higher bit density. In addition, the use of ferroelectric materials instead of dielectric ones in the Ferroelectric (FE) RAM (FERAM) dramatically increases the time during which the cell conserves its charge, hence reducing the power consumption. Ferromagnets, usually employed in devices based on MEC, are, however, subject to external magnetic fields. That is why it was recently proposed to use antiferromagnets (AFMs)\textsuperscript{7,8}, which have the advantage of being roughly insensitive to external magnetic fields, while keeping non-volatility. A number of candidate systems were proposed in the past for the electric control of antiferromagnetism: i) exchange-spring\textsuperscript{7-9} or field-cooling\textsuperscript{10} reversal of IrMn AFM magnetization, subsequently detectable by a change in tunneling current; ii) electric field switching of the IrMn magnetization through immersion in an ionic liquid\textsuperscript{11}; iii) BaTiO$_3$ polarization reversal which induces a FM-AFM switch in Fe\textsuperscript{12} or FeRh\textsuperscript{13} thin films.

Coupling ferroelectricity to the magneto-crystalline anisotropy (MCA) might represent an alternative way to electrically control the magnetic properties\textsuperscript{14-16}. For example, one might envisage controlling or even switching the difference in energy between easy and hard axis (i.e. the magnetic anisotropy energy, MAE) of the magnetic layer as a function of the direction of polarization in the underlying FE substrate. To our knowledge, this coupling between FE and AFM is rather unexplored in the literature, but could lead to significant advantages. Indeed, changing the orientation of the AFM quantization axis (e.g. from in-plane to out-of-plane and vice versa) is a serious technological challenge and would definitely benefit from a possible FE modulation of the MCA, thus facilitating the electrical writing process. Successively, the read could be accomplished e.g. via Tunneling Anisotropic Magneto-Resistance (TAMR)\textsuperscript{19}.

Within this framework, in this manuscript we propose a new interface, i.e. [001]-oriented Mn$_2$Au/BaTiO$_3$, and explore theoretically the MCA modulation upon BaTiO$_3$ (BTO) polarization switch. As magnetic layer, we considered Mn$_2$Au, as it was recently shown to be an antiferromagnet with a strikingly high estimated Neel temperature (more than 1000K)\textsuperscript{17,18}. Owing to the strong spin-orbit in Au, it possesses also a sizable MCA, which results in a significant TAMR\textsuperscript{19-21}. We identify the most stable interface for each of the tensile and compressive mismatch types and show that the BTO polarization switch modulates the MCA energy barrier by approximately 50%, when going from the more to the less stable orientations of the sublattice magnetization.

The article is organized as follows: in Sec.II we analyze the magnetic and structural properties of a large number of theoretical Mn$_2$Au/BaTiO$_3$ interfaces, identifying among them the two most stable configurations. In Sec.III we study the MCA modulation upon polarization switch. Finally, the main results are summarized in Sec. IV.
II. SIMULATION RESULTS

Due to the large lattice mismatch between BTO and Mn$_2$Au, as discussed in detail in the following paragraph, we addressed the ultrathin limit of Mn$_2$Au films grown on BaTiO$_3$.

The stability range of BTO with respect to the in-plane lattice mismatch was found in Ref.\textsuperscript{22} to be $\pm 6\%$. The same range for Mn$_2$Au is difficult to estimate, although in Ref.\textsuperscript{20} it was shown that thin films of Mn$_2$Au/Fe were grown on MgO substrate. Assuming the MgO lattice parameter to be $a_{MgO} = 4.212 \, \text{Å}$ while the experimental\textsuperscript{23} $a_{Mn_2Au} = 3.328 \, \text{Å}$, we can estimate that in that case the lattice mismatch was either $-26.6\%$ (direct match) or $+10\%$ (45° rotated match). In the Mn$_2$Au/BTO case, considering the bulk thick layer of BTO with the in-plane lattice constant of the order of $4 \, \text{Å} \pm 6\%$, the direct and 45° rotated matches might be at the best $-12\%$ and $+10\%$ respectively. Given the high lattice mismatch, we only focus on the ultrathin limit of Mn$_2$Au films, i.e. half-unit-cell.

In order to find out the most stable configuration of the interface between Mn$_2$Au and BTO, we examine a large number of possible interfaces. We consider three unit cells of barium titanate (with the standard tetragonal distorted-perovskite cell) and a half-cell of Mn$_2$Au (HCMA). Mn$_2$Au crystallizes in the tetragonal $I4/mmm$ space group constituted by planes of Au alternated to Mn bilayers. From the magnetic point of view, the ground state shows planes of ferromagnetically aligned Mn atoms, with the adjacent planes coupled antiferromagnetically. On the barium titanate side we consider the TiO$_2$ termination, normally found as the most stable occurring at interfaces of BTO with metals\textsuperscript{12,24}. In order to explore all the possibilities, we consider three terminations of HCMA: i) Au; ii) Mn and iii) Mn$_2$. In addition, each HCMA termination has two possibilities to stack on the TiO$_2$ layer, e.g. for the Au termination, Au atoms can occupy either Ba or Ti position. Finally, we consider both direct and rotated by 45° match, i.e. corresponding to tensile and compressive strain. Summarizing, for each direction of BTO polarization (↑ and ↓, corresponding to polarization directed outwards or inwards with respect to the BTO layer), given three possible terminations on HCMA, two different stacking geometries and two different strain conditions, we consider $3 \times 2 \times 2 = 12$, which leads to a total of 24 simulated configurations (including polarization switching). The schematic view of the 12 configurations at fixed BTO polarization is shown in Fig.\textsuperscript{1}. In order to avoid the loss of ferroelectric (FE) polarization during the structural optimization (which might spuriously arise, due to the limited number of BTO unit cells), we used a sort of "constrained" atomic optimization: the farthest layer from the interface are forced to have the same structure as bulk BTO, whereas the layers closer to the junction are allowed to relax. We fix the in-plane BTO lattice constant to its experimental value $a = b = 3.991 \, \text{Å}$.

We perform density functional theory (DFT) simulations using the Vienna Ab initio Simulation Package (VASP)\textsuperscript{25} and the Generalized Gradient Approximation (GGA)\textsuperscript{26} in the Perdew-Burke-Ernzerhof (PBE) formalism for the exchange-correlation potential. We use an energy cutoff for the plane wave basis of 500\,eV and a $12 \times 12 \times 1$ Monkhorst-Pack $k$-point mesh\textsuperscript{27}, while the structural optimization is accomplished until the ionic forces become less than 0.01\,eV/Å. In order to evaluate the magneto-crystalline anisotropy, the relativistic spin-orbit coupling (SOC) is self-consistently taken into account in the usual perturbative way. Simulations are done by resorting to the slab geometry, with 20 Å of vacuum added along the $z$-axis in order to avoid the self-interaction through the periodic boundary conditions. In addition, since the BTO layer has a net dipole moment oriented along the $z$ axis, the dipole corrections, as implemented in VASP, were used, so as to make any possible electric field in the vacuum region far from the slab to vanish.

As mentioned, by construction all the interfaces can be divided into two groups, when referring to the strain state: compressive and tensile. The absolute values of the lattice mismatch in both cases are comparable, although the number of Mn$_2$Au atoms is different in the two strain cases (cfr Fig. 2 below). Therefore, we identify the lowest energy configuration within each group for each direction of polarization $P_{\text{BTO}(i)}$. The comparison of the interface properties is summarized in Tabs.\textsuperscript{I,III}. Here, the interfaces 1–3 and 7–9 are under tensile strain, while the junctions 4 – 6 and 10 – 12 are under compressive strain. It can be seen from Tab.I that the properties of the system crucially depend on the HCMA termination. Remarkably, interface 3, IF-3, the most stable in the tensile group -
Table I. Relevant properties of the interfaces with $P_{BTO}$ (collinear calculations without SOC, dipole corrections included). The energy difference $\Delta E_{\text{tot}}$ (in eV per unit cell, second column) is measured relative to the lowest energy configurations in each group (IF-3 and IF-5 respectively, highlighted in bold). The magnetic moment $\mu$ is shown for interface Ti and Mn atoms (third and fourth column, respectively) and measured in units of $\mu_B$. The interplanar distance between Ti and planar O-atoms (in Å, fifth column).

<table>
<thead>
<tr>
<th>IF</th>
<th>$\Delta E_{\text{tot}}$ (eV)</th>
<th>$\mu$ (Ti$_1$ &amp; Ti$_2$)</th>
<th>$\mu$ (Mn$_1$)</th>
<th>Ti-O displ. (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.800</td>
<td>-0.07, -0.17</td>
<td>-4.07, 4.02</td>
<td>-0.12, 0.00</td>
</tr>
<tr>
<td>2</td>
<td>1.865</td>
<td>0.08, 0.14</td>
<td>-4.07, 4.09</td>
<td>-0.14, 0.01</td>
</tr>
<tr>
<td>3</td>
<td>0.000</td>
<td>0.59, 0.35</td>
<td>-3.89, 3.93</td>
<td>-0.14, -0.01</td>
</tr>
<tr>
<td>4</td>
<td>2.177</td>
<td>0.15, 0.20</td>
<td>3.60, -3.56</td>
<td>-3.25, 3.38</td>
</tr>
<tr>
<td>5</td>
<td>0.000</td>
<td>-0.09, -0.02</td>
<td>3.23, -3.12</td>
<td>-2.32, 2.83</td>
</tr>
<tr>
<td>6</td>
<td>1.086</td>
<td>0.00, 0.00</td>
<td>3.26, -3.26</td>
<td>-3.74, 3.74</td>
</tr>
<tr>
<td>7</td>
<td>1.822</td>
<td>-0.04, -0.02</td>
<td>-4.07, 4.07</td>
<td>-0.08, 0.04</td>
</tr>
<tr>
<td>8</td>
<td>0.166</td>
<td>-0.61, -0.41</td>
<td>-4.05, 4.02</td>
<td>-0.20, -0.02</td>
</tr>
<tr>
<td>9</td>
<td>1.926</td>
<td>0.06, 0.22</td>
<td>-3.94, 3.90</td>
<td>-0.16, 0.00</td>
</tr>
<tr>
<td>10</td>
<td>2.330</td>
<td>0.02, 0.00</td>
<td>3.54, -3.51</td>
<td>-3.30, 3.35</td>
</tr>
<tr>
<td>11</td>
<td>1.887</td>
<td>-0.21, -0.01</td>
<td>2.58, -2.76</td>
<td>-0.04, 3.79</td>
</tr>
<tr>
<td>12</td>
<td>2.855</td>
<td>-0.52, -0.34</td>
<td>4.00, -3.77</td>
<td>-3.76, 3.81</td>
</tr>
</tbody>
</table>

Table II. Relevant properties of the interfaces with $P_{BTO}$ for the most stable configurations, i.e. IF-3 and IF-5 (collinear calculations without SOC, dipole corrections included). For the $P_{BTO}$ values see rows in bold, as reported Tab. I. The magnetic moment $\mu$ is shown for interface Ti and Mn atoms (third and fourth column, respectively) and measured in units of $\mu_B$. The interplanar distance between Ti and planar O-atoms (in Å, fifth column).

<table>
<thead>
<tr>
<th>IF</th>
<th>$\mu$ (Ti$_1$ &amp; Ti$_2$)</th>
<th>$\mu$ (Mn$_1$)</th>
<th>Ti-O displ. (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.30, 0.02</td>
<td>-3.94, 3.94</td>
<td>-0.24, -0.21</td>
</tr>
<tr>
<td>5</td>
<td>0.01, 0.00</td>
<td>-3.27, -3.09</td>
<td>-2.54, 3.03</td>
</tr>
</tbody>
</table>

III. DISCUSSION

A. Magneto-electric coupling

As was mentioned above, compressive and tensile interfaces show very different magnetic properties. Namely, in their respective ground-state configurations, the interface Ti atom in IF-3 bears a large induced magnetic moment, while in IF-5 it is almost non-magnetic. The moment of Ti is caused by the hybridization with surrounding Mn moments, and it is the positions and orientations of these Mn atoms that the magnitude of the Ti moment depends on. In IF-3, the Ti-Mn distance is somewhat larger than in the IF-5 (3.13 Å vs 2.77 Å), however, in the IF-3, the most stable magnetic configuration has the nearest-
Table III. Total energies obtained by changing the spin quantization axis for the most stable interfaces in the compressive and tensile strain (IF-3 and IF-5) as a function of polarization switching. The arrows in the second and fourth columns are related to the orientation of Mn moment and have the following meaning: ↑- perpendicular to the interface; →- parallel to the interface along the α-axis; ↗- parallel to the interface and diagonal in the a – b plane. The total energy difference ∆$E_{tot}$ is measured relative to the lowest energy configuration (highlighted in bold), for each of the strain and polarization conditions.

<table>
<thead>
<tr>
<th>$P_{BTO}$</th>
<th>$\Delta E_{tot}$(meV)</th>
<th>$\Delta E_{tot}$(meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{\uparrow}$</td>
<td>IF-3↑ 0.86 IF-5↑ 0.00</td>
<td>IF-3→ 0.11 IF-3↗ 2.36</td>
</tr>
<tr>
<td>$P_{\downarrow}$</td>
<td>IF-3↑ 2.55 IF-3→ 0.00</td>
<td>IF-3↗ 0.02 IF-5↗ 2.17</td>
</tr>
</tbody>
</table>

where $\Delta M$ is the increment of the magnetic moment (per 1 BTO unit cell) and $E_c$ is the BTO coercive field. Being BTO in common between Ref. 28 and the present work and being $\Delta M$ comparable when BTO is interface with Fe or Mn$_2$Au, the surface magneto-electric coefficient appears to be of the same order of magnitude. This is a rather unexpected result: an interface coupling between a ferroelectric and an antiferromagnet can generate a sizable magneto-electric coupling with a net interface magnetization.

B. Magnetic anisotropy

The results obtained when considering different spin-quantization axes, aimed at evaluating the MCA and its dependence on the direction of BTO ferroelectric polarization, are reported in Tab.III. As evident, IF-3 shows an easy-plane anisotropy, while the IF-5 is characterized by an easy-axis. Upon switching the BTO polarization, the MCA properties of the IF-3 and IF-5 are sizeably affected: for the IF-3 the easy-plane anisotropy changes from 2.6 meV at $P_{BTO\uparrow}$ to 0.8 meV at $P_{BTO\downarrow}$, while for the IF-5 the easy-axis anisotropy varies from 2.2 meV at $P_{BTO\downarrow}$ to 1.4 meV at $P_{BTO\uparrow}$. It follows that the MCA changes by almost 50% upon polarization switch. It is important to note that in both interfaces the $P_{BTO\uparrow}$ polarization corresponds to lower MCA and that these MCA energies, if measured per formula unit of Mn$_2$Au, are comparable to the MCA of the bulk Mn$_2$Au (1.22 meV).

IV. CONCLUSIONS

In this manuscript, we have presented an investigation of the Mn$_2$Au/BTO interface by considering a large number of interface structural configurations and identifying the most stable junctions under compressive and tensile strain. By a thorough study of their magnetic and ferroelectric properties we show an example (i.e. in the IF-3 interface) of a FE-AFM coupling which generates a net FM magnetization at the interface tuned by the FE polarization switch. The FE polarization also modulates the magneto-crystalline anisotropy within the range of approximately 50%. Interestingly, this is an example of an interface containing an AFM ingredient which generates a net magnetic moment in the layer close to the junction. This interface magnetization is strongly affected by the direction of $P_{BTO}$, i.e. with a change of 100%. The magnetic anisotropy of HCMA is also modulated by the $P_{BTO}$ switch, with a change of approximately 50%. Different interfaces (under compressive and tensile strain conditions) could be realised by changing the growth conditions of Mn$_2$Au on BTO, i.e. by varying the lattice spacing of BTO using different substrates.

The physical mechanism, responsible for the MEC presented here, has to be ascribed to a sizable Mn-Ti hybridization, which leads to a significant transfer of magnetic moment on Ti atoms. The switch of FE polarization implies a change of Mn-Ti distance and, hence, of the magnetic moment transfer, thereby reversing a very subtle balance of total energies, leading to magneto-crystalline anisotropy. The MEC studied in this manuscript is a surface effect. As such, we expect it to be most efficient for thin films of Mn$_2$Au. It should be noted, however, that experimentally, it is quite difficult to control the growth of Mn$_2$Au thin films, and that due to the richness of intermetallic phases formed by manganese and gold, the result might have a different stoichiometry: e.g. MnAu$_2$ or MnAu. The study of these possibilities goes beyond the scope of the present manuscript, although, thanks to the fact that both MnAu$_2$ or MnAu are antiferromagnets with interesting properties, once interfaced with BTO, they might well exhibit peculiar magneto-electric effects.

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