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Magnetoelectric coupling at biferroic interface studied from first principles

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Abstract. We present an *ab initio* study of a prospective composite multiferroic $L\text{-Fe}_2/\text{PbTiO}_3(001)$, with a Fe-film thickness of $L \leq 4$ monolayers. The change in magnetization induced by the electric polarization reversal is discussed. Our calculations imply a strong magnetoelectric coupling for $L=1$ and a dramatic change of the magnetic order with increasing the Fe-film thickness between $1 \leq L \leq 3$.

In the absence of space-inversion and time-reversal symmetry, the occurrence of ferroelectricity and magnetism in the same phase of a so called multiferroic (MF) material [1] permits both a switchable electric polarization, \vec{P} , and a switchable magnetization, \vec{M} . This phenomenon, in principle, allows to store information in nanometer-sized memories with four logic states [2]. Although some MFs, such as BiFeO_3 and $R\text{MnO}_3$ (R rare earths), were known since mid of the seventies, the search for novel multiferroics is not finished yet. In multiferroics, an applied electric field, \vec{E} , displacing the magnetic ions, affects the magnetic exchange coupling or, vice versa, the external magnetic field, \vec{H} , induces the electric polarization: $P_i \sim \alpha_{ij}H_j$, where α is the magnetoelectric tensor and $(i, j = x, y, z)$. According to Landau theory, the linear magnetoelectric (ME) contribution to the Gibbs free energy is $E_i\alpha_{ij}H_j$. It should be kept in mind that magnetoelectricity is a volume effect for which the induction of \vec{M} depends linearly on \vec{E} . In a single-phase MF, \vec{P} and \vec{M} interact weakly and, therefore, α is marginal there. Besides, all single-phase MFs possess a hierarchy of phase transformations [3], in which ferromagnetism disappears far below room temperature.

Ab initio calculations based on density functional theory (DFT) predict that a more robust scenario of magnetoelectricity occurs in epitaxially grown composite MF [4] where the ME effect is mediated by strain across the ferroelectric/ferromagnet interface. Obviously, the quest for fundamentally new MF requires a better understanding of the mechanisms which mediate the ME coupling. In this work, we perform the DFT calculations of the electronic and ferroic properties of $L\text{-Fe}_2/\text{PbTiO}_3(001)$, with Fe film thickness, L , ranging between one and four monolayers (ML). This is a prototype system of composite MF. Its PbTiO_3 (PTO) substrate is highly polar, with a spontaneous polarization of $75\mu\text{C}/\text{cm}^2$. Besides, the body-centered cubic Fe and PTO(001) have a good match of their in-plane lattice constant when the bcc-Fe [110] axis is aligned to the [100] axis of PTO. The mismatch of $<3\%$ allows epitaxial growth. This has been recently demonstrated for another composite MF, BaTiO_3/Fe [5]. All calculations were performed by the Vienna *Ab initio* Simulation Package (VASP) [6], using the projector-augmented wave pseudopotentials and a planewave basis cutoff energy of 650 eV. The relaxation

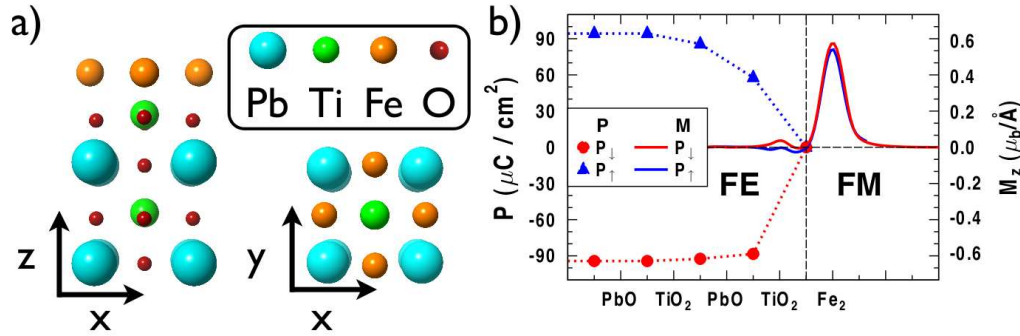


Figure 1. (a): The side- and top view of the TiO-terminated PbTiO₃(001) substrate covered by a single Fe layer. (b): The ferroic properties of 1-ML Fe on PTO are plotted near the interface along [001]: P_{\uparrow} (blue dotted), P_{\downarrow} (red dotted) and the corresponding z -projected magnetization densities $M_z^{P_{\uparrow}}$ (blue solid) and $M_z^{P_{\downarrow}}$ (red solid). The largest change in M_z induced by the P -reversal comes from interfacial Ti.

in a slab geometry and further calculation of the ferroic properties were performed within the local spin-density approximation to DFT.

1. Results and Summary

To model the (001) surface of PTO, we used the 5-unit-cell (~ 2 -nm) thick supercell, with a vacuum spacer of 2 nm in the [001] direction. The lattice parameters were set to the equilibrium values of tetragonal PTO [7]. The Ti/O displacements cause the direction of \mathbf{P} along [001]. When \mathbf{P} is antiparallel to the surface normal (P_{\downarrow}), oxygen is placed above the cations in each ML, and *vice versa*, the configuration P_{\uparrow} means that all intralayer displacements $\delta = z_{\text{O}} - z_{\text{cation}} < 0$. Since PTO(001) is TiO₂ terminated [7] for both directions of \mathbf{P} , we calculated, first, Fe₂/TiO₂/PTO(001) where the Fe atoms find their relaxed positions atop oxygen, as shown in Fig. 1(a). This is in agreement with previous *ab initio* calculations [4]. We relaxed the three top PTO layers and Fe layers until the forces are less than 5 meV/Å.

In Fig. 1b, we plot the layer-resolved electric polarization of 1-Fe₂/PTO(001), which was calculated as $P_i = \delta_i \cdot q_{\text{Born}}$, where q_{Born} is the Born effective charge. P_{\downarrow} approaches its bulk value within the first PTO unit cell whereas the state P_{\uparrow} needs the thickness two times larger than that of P_{\downarrow} . For each P , its magnitude vanishes at the interface. As the result, the two z -projected magnetization densities, which are plotted in Fig. 1b, show no significant difference above the interface. Nevertheless, the total change in magnetization: $\Delta M = M(P_{\downarrow}) - M(P_{\uparrow})$ for this system is about $1\mu_B$. This effect can be explained by a detailed analysis of the electronic density of states. The hybridization between the d -minority states of Fe and Ti d -states leads to an induced magnetic moment on the Ti site, which is oriented opposite to m_{Fe} . This is shown in detail in Fig. 2a for P_{\uparrow} and P_{\downarrow} . For P_{\uparrow} , the Fe-Ti distance is shorter and, therefore, the corresponding m_{Ti} is larger than that of the P_{\downarrow} state. The induced and antiferromagnetically oriented magnetic moment of interfacial Ti contributes significantly to the $1\mu_B$ -value of ΔM .

We suggest that the magnetic structure may change from strongly ferromagnetic to nearly zero- M ferrimagnetic when a second Fe layer is added (see, Fig. 2b). In the second layer, one Fe sits atop the Ti site of PTO while another Fe atom finds its relaxed position above Pb. For $L=2$, the magnetic moments of interfacial Fe are suppressed while the two environmentally different Fe sites of the surface layer, which show rather significant moments of $2.3\mu_B$ and $2.1\mu_B$, are ordered antiferromagnetically to each other. This is mostly due to a relatively short separation of 1 Å between the Fe layers. The surface Fe atom atop Ti obeys the largest magnetic moment

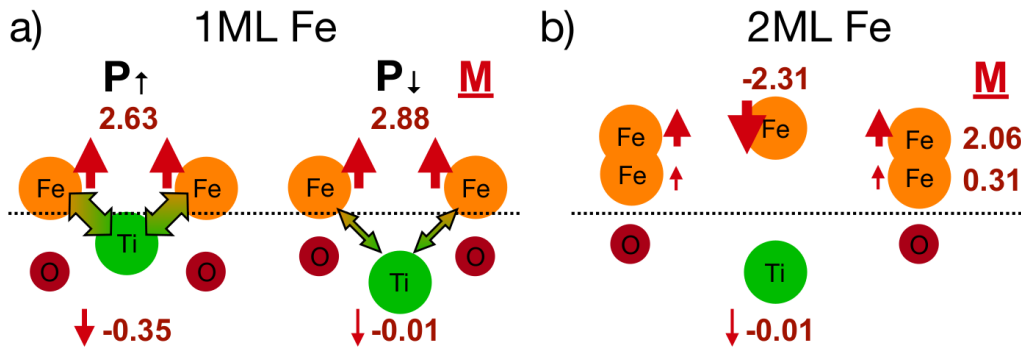


Figure 2. (a): Magnetic structure of dually polar 1-Fe₂/PTO(001) is shown as the side view. Here, the numbers indicate the Fe and Ti magnetic moments while their directions are shown by arrows. (b): Nearly zero-*M* and ferrimagnetically ordered structure of 2-Fe₂/PTO(001) is sketched for P_↓ only.

for this configuration. This Fe atom and underlying Ti are most affected to the polarization reversal. Regarding the 2-ML Fe film, the issue of reduced atomic volume of interfacial Fe and its suppressed magnetic moment as well as the antiferromagnetic ordering in the topmost Fe layer were discussed in the literature [8]. Ferromagnetic order is restored for thicker Fe films but with significantly reduced magnetization as compared to Fe bulk.

For all $L \leq 4$, the total energies of both the ferromagnetic (FM) and antiferromagnetic (AFM) configurations of L -Fe₂/PTO(001) were calculated for each P . The energy difference, $\Delta E \equiv E_{AFM} - E_{FM}$, is plotted in the left panel of Fig. 3. When $L=1$ the system is always ferromagnetic whereas the reversal of P shows minor effect. For $L=2$, the AFM order is energetically preferable. In this case, however, we detected some sort of ferrimagnetic structure with nearly zero- M , which is shown in Fig. 2b. When $L \geq 3$ we obtained $E_{FM} < E_{AFM}$ for both polarization directions that means that ferromagnetism is restored.

Fig. 3b shows the magnetization of L -Fe₂/PTO(001) as a function of L . It was calculated for

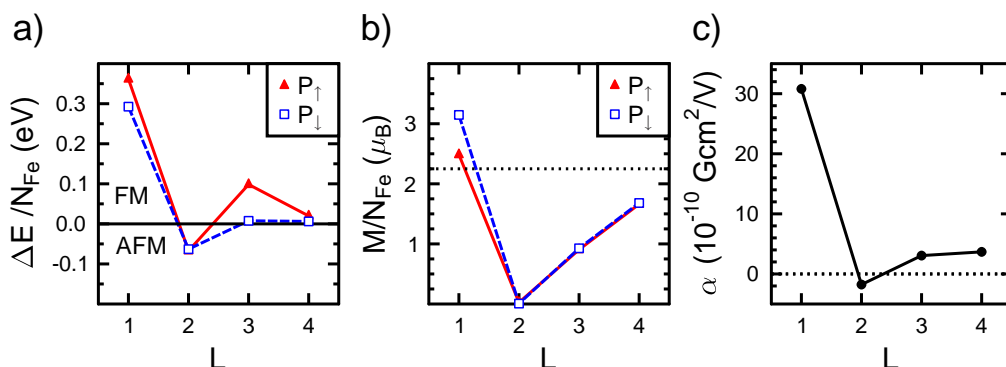


Figure 3. Magnetism and magnetoelectricity of L -Fe₂/PTO(001) versus the Fe-film thickness, L . (a): the total-energy difference $\Delta E \equiv E_{AFM} - E_{FM}$ between the antiferromagnetic (AFM) and ferromagnetic (FM) configurations. ΔE is normalized with respect to the number N_{Fe} of Fe atoms in the supercell. (b): the magnetization per Fe atom for the lowest-energy configuration. Here, the dotted line indicates the magnetic moment of Fe bulk. (c): The magnetoelectric coupling coefficient α is plotted versus L .

each P and energetically favorable magnetic solution, which is always ferromagnetic except $L=2$. The M is normalized to the number of Fe atoms in the supercell to allow a comparison between the different Fe thicknesses. The two curves in Fig. 3b correspond to dually polar substrate, and their difference is the change in magnetization, ΔM , with respect to the P reversal. For $L=1$, the large $m_{Fe} \approx 3 \mu_B$ enables the large value of M while the $1 \mu_B - \Delta M$ is due to the Ti-moment variation induced by a strong magnetoelectric coupling. For $L=2$, when the system becomes magnetically soft, M drops down to almost zero as shown in Fig. 3b. Then, with increasing the Fe film thickness $L > 3$, M gradually approaches the bulk Fe magnetization. In Fig. 3c, we plot the interface ME coupling coefficient α versus L . It was defined as $\alpha = \Delta M / (E_c \cdot A)$, where A is the surface area and E_c is the coercive field needed to switch the polarization. Here, the experimental $E_c = 33$ kV/cm of PTO was used. In fact, α quickly decays with increasing L . This is obvious since the ME effect in composite multiferroic is confined to its interface.

In summary, we computed from first-principles the ferroic properties of L -Fe₂/PbTiO₃(001) near its ferromagnet/ferroelectric interface. We find the interface ME coupling rather strong in this prototype MF. The change in magnetic order seen between $1 \leq L \leq 3$, is understood in terms of hybridization of the electronic states. Our preliminary calculations suggest also that intrinsic oxidation [9] of composite MF may not significantly damage their magnetoelectricity.

2. Acknowledgment

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