Predicted Magnetoelectric Effect in $\mathrm{Fe/BaTiO_3}$ Multilayers: Ferroelectric Control of Magnetism

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An unexplored physical mechanism which produces a magnetoelectric effect in ferroelectric-ferromagnetic multilayers is studied based on first-principles calculations. Its origin is a change in bonding at the ferroelectric-ferromagnet interface that alters the interface magnetization when the electric polarization reverses. Using $\mathrm{Fe/BaTiO_3}$ multilayers as a representative model, we show a sizable difference in magnetic moments of Fe and Ti atoms at the two interfaces dissimilar by the orientation of the local electric dipole moments. The predicted magnetoelectric effect opens a new direction to control magnetic properties of thin-film layered structures by electric fields.

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Multiferroic materials are of great scientific and technological interest due to their magnetoelectric properties, originating from the coupling between ferroelectric and ferromagnetic order parameters [1–4]. The interplay between ferroelectricity and magnetism allows a magnetic control of ferroelectric properties [5] and an electric control of magnetic properties [6] and could yield new device concepts, such as ferroelectric and multiferroic tunnel junctions [7,8]. Recently, it became possible to fabricate composite multiferroics by artificially making ferroelectrics and ferromagnets in nanoscale heterostructures. The two-phase multiferroics may play an important role in future magnetoelectric devices, because none of the existing single-phase multiferroics combine large and robust electric and magnetic polarizations at room temperature [4]. In a thin-film geometry, such composites can be created in two extreme forms: a multilayer consisting of alternating layers of the ferroelectric and ferro(ferri)magnetic phases or a vertically aligned columnar nanostructure. When the magnetoelectric coupling is caused exclusively by elastic interactions, the effect in a multilayer structure is expected to be negligible due to clamping to the substrate. On the other hand, in vertically aligned nanostructures, the magnetoelectric effect may be significant, as was recently demonstrated for ferrimagnetic nanopillars embedded in a ferroelectric matrix [9,10].

The coupling between elastic components of the ferromagnetic and ferroelectric constituents through the strain is not, however, the only source of a magnetoelectric effect in composite multiferroics. There is another physical mechanism that may cause ferroelectricity to influence magnetism which may be sizable not only in vertical nanostructures but also in multilayers. It involves the coupling between ferroelectricity and magnetism through interface bonding. Displacements of atoms at the interface caused by ferroelectric instability alter the overlap between atomic orbitals at the interface which affects the interface magnetization. This produces a magnetoelectric effect caused by the sudden change in the interface magnetization induced by the polarization reversal in the ferroelectric under the influence of applied electric field.

In this Letter, we explore the significance of the magnetoelectric effect driven by interface bonding in ferromagnetic-ferroelectric multilayers. We consider a $\mathrm{Fe/BaTiO_3(100)}$ multilayer as a representative composite multiferroic to investigate this phenomenon. This choice is motivated by the fact that Fe and $\mathrm{BaTiO_3}$ are two ‘‘classical’’ ferroic materials which have well-known properties in the bulk. Also, bcc Fe and perovskite $\mathrm{BaTiO_3}$ have a very good match of the lattice constants (a mismatch is only about 1.4%) that allows layer-by-layer epitaxial growth of $\mathrm{Fe/BaTiO_3}$ multilayers with no misfit dislocations. We show a sizable difference in magnetic moments of Fe and Ti atoms at the two interfaces dissimilar by the orientation of the local electric dipole moments. The predicted magnetoelectric effect is comparable in magnitude with that observed in elastically coupled composites and opens a new direction to control magnetic properties of thin-film layered structures by electric fields.

We perform density-functional calculations of the electronic and atomic structure of $\mathrm{Fe/BaTiO_3(100)}$ multilayers using the Vienna *Ab Initio* Simulation Package (VASP) [11,12]. In the calculations, we build up supercells by aligning the body centered cubic iron [110] axis and the [100] axis of the $\mathrm{BaTiO_3}$. The in-plane lattice constant is fixed to be the experimental value of the bulk $\mathrm{BaTiO_3}$ (3.991 Å), which is smaller than the theoretical lattice constant we calculated for the cubic phase of $\mathrm{BaTiO_3}$ (4.033 Å). Hence, in our calculations $\mathrm{BaTiO_3}$ is assumed to have the tetragonal phase, which is known experimentally to be stable at room temperature, with the in-plane ferroelectric instability suppressed by the compressive strain [13]. This in-plane constraint is applied to relax the bulk structures of Fe and $\mathrm{BaTiO_3}$. Under this constraint, we find that the polarization of the bulk $\mathrm{BaTiO_3}$ is $0.32\ \mathrm{C/m^2}$, as calculated using Berry's phase method [14], and the magnetic moment of the bulk Fe is $2.20\mu_B$ per atom. The obtained tetragonal structures are then used as building blocks for the $Fe/BaTiO_3$ supercells.

We find that the most stable $Fe/BaTiO_3$ structure has a TiO_2 terminated interface with interfacial O atoms occupying atop sites on Fe which is similar to the result obtained previously for $Co/SrTiO_3$ [15]. Therefore, supercells are constructed as $(Fe_2)_9$-TiO_2-$(BaO$-$TiO_2)_m$, where $m = 2$, 4, 6, 8, 10, and 16. Figure 1 shows the atomic structure of the $m = 4$ multilayer. First, we analyze properties of $Fe/BaTiO_3$ multilayers assuming that $BaTiO_3$ is in a paraelectric state. For this purpose, we impose a mirror plane on the central TiO_2 layer and minimize the total energy of the whole system. We find that, although the net polarization of the $BaTiO_3$ film is zero, bonding at the interface induces interface dipole moments, which are oriented in the opposite directions at the two interfaces [16].

The magnetic properties of the multilayer are due to ferromagnetism of Fe. In the paraelectric state, by symmetry, the magnetic moments of the interfacial atoms are exactly the same at the bottom and top interfaces. The calculated magnetic moment of the interface Fe atoms is notably enhanced up to about $2.64\mu_B$ compared to the bulk moment of $2.20\mu_B$. This enhancement is, however, not as significant as that for the Fe(100) surface ($2.98\mu_B$), indicating the involvement of bonding and charge transfer effects at the $Fe/BaTiO_3$ interface. The latter fact is reflected in the presence of induced magnetic moments on O and Ti atoms. We find that the magnetic moment of the interface O atom is about $0.05\mu_B$ and is parallel to the magnetic moment of Fe. On the other hand, the magnetic moment of Ti atom is about $0.30\mu_B$ and is antiparallel to the magnetic moment of Fe.

Next, we relax the constraint of reflection symmetry and minimize the total energy with respect to atomic coordinates of all atoms in the multilayer. For a $m = 2$ supercell, we obtain no ferroelectric instability, making all the results essentially the same as those in the presence of the symmetry constraint. The thickness $t \approx 1$ nm of the $BaTiO_3$ film corresponding to $m = 2$ appears to be the critical value for ferroelectricity. Increasing the thickness up to $t \approx 1.8$ nm ($m = 4$) is sufficient for ferroelectric instability to develop (Fig. 1). This is consistent with the previous calculations of the critical thickness in $BaTiO_3$ [17,18].

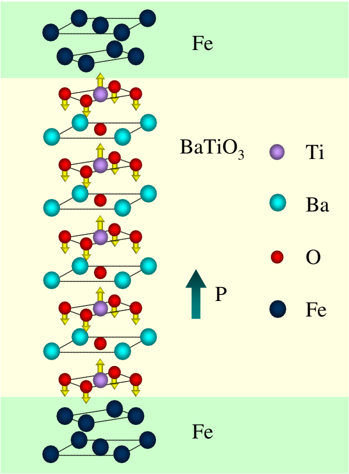

FIG. 1 (color online). Atomic structure of $Fe/BaTiO_3$ multilayer for $m = 4$. Arrows indicate schematically displacements of Ti and O atoms in $BaTiO_3$ with the net polarization pointing up.

Ferroelectric displacements break the symmetry between the top and bottom interfaces, causing magnetic moments of Fe and Ti atoms at the two interfaces to deviate from their values in the paraelectric state. For the $m = 4$ multilayer, the magnetic moment of Fe atoms at the bottom interface (the one at which the ferroelectric polarization is pointing away from the Fe layer as in Fig. 1) is enhanced up to $\mu = 2.67\mu_B$, while the magnetic moment of Fe atoms at the top interface (the one at which the ferroelectric polarization is pointing toward the Fe layer as in Fig. 1) is reduced down to $\mu = 2.61\mu_B$, which makes a difference in the Fe magnetic moments at the two interfaces $\Delta\mu_{Fe} = 0.06\mu_B$. A more sizable asymmetry is produced by ferroelectric displacements between the Ti magnetic moments at the two interfaces: $\mu = -0.40\mu_B$ and $\mu = -0.18\mu_B$ for the top and bottom interfaces, respectively, so that the magnetic moment difference is $\Delta\mu_{Ti} = 0.22\mu_B$. We note here that, since we do not take into account the spin-orbit interaction, the magnetic moments do not depend on the magnetization orientation. This effect is expected to be very small for $3d$ elements.

The nature of the induced interface magnetic moments can be understood from orbital-resolved local densities of states (DOS). Figures 2(a)–2(c) show the DOS for Ti $3d$, Fe $3d$, and O $2p$ orbitals, indicating the presence of hybridizations between these states. Because of exchange splitting of the $3d$ bands in Fe, these hybridizations produce exchange-split bonding and antibonding states which are the origin of the induced magnetic moments on the interface Ti and O atoms. The induced magnetic moment on the O atom is relatively small ($0.05\mu_B$) because, as is seen from Fig. 2(c), the O $2p$ orbitals lie well below the Fermi energy (E_F) and, hence, have a small overlap with the Fe $3d$ states. However, the Ti $3d$ band is centered at about 2 eV above the Fermi energy [the shaded plot in Fig. 2(a)] and overlaps strongly with the minority-spin Fe $3d$ band which has a significant weight at these energies [the shaded plot in the lower panel in Fig. 2(b)]. The hybridization between the Fe and Ti $3d$ orbitals produces bonding states which are pushed down in energy and peaked just below E_F [the peaks indicated by arrows in Figs. 2(a) and 2(b)]. Thus, the minority-spin Fe-Ti $3d$ bonding states cause charge redistribution between majority and minority spins, resulting in a larger occupation of the minority-spin states of Ti. This implies an induced magnetic moment on Ti aligned *antiparallel* to the magnetic moment of Fe where majority-spin states have (by definition) greater occupation than minority-spin states.

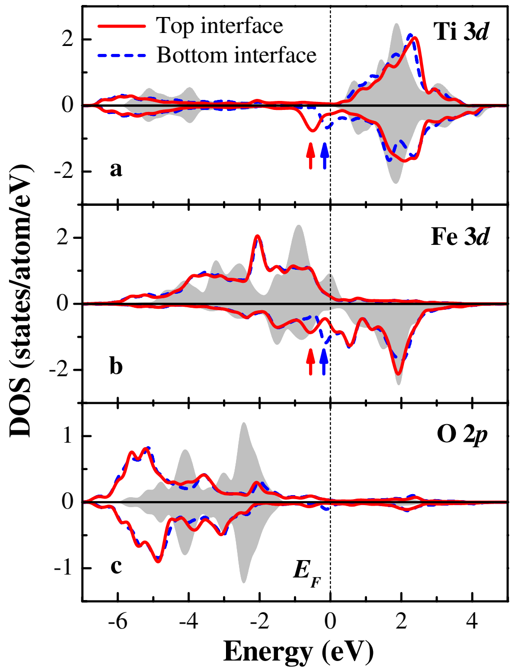

FIG. 2 (color online). Orbital-resolved DOS for interfacial atoms in a Fe/$BaTiO_3$ multilayer for $m = 4$: (a) Ti 3*d*, (b) Fe 3*d*, and (c) O 2*p*. Majority- and minority-spin DOS are shown in the upper and lower panels, respectively. The solid and dashed curves correspond to the DOS of atoms at the top and bottom interfaces, respectively. The shaded plots are the DOS of atoms in the central monolayer of (b) Fe or (a),(c) TiO_2 which can be regarded as bulk. The vertical line indicates the Fermi energy (E_F).

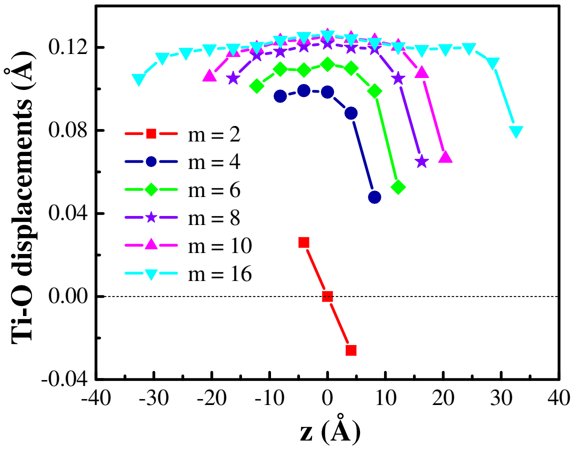

FIG. 3 (color online). Relative Ti-O displacements in a ferroelectric $BaTiO_3$ film for different *m*. Positive values correspond to the local electric dipole moment pointing up as in Fig. 1. The midpoint of the ferroelectric film lies at $z = 0$.

As shown before, the presence of ferroelectricity in $BaTiO_3$ causes the magnetic moments of interface Fe and Ti atoms to deviate from their values in the paraelectric state. This is due to the change in the strength of bonding between the Fe and Ti atoms induced by ferroelectric displacements. For the electrically polarized multilayer ($m \geq 4$), the upward polarization makes Ti atoms move away from the bottom interface and towards the top interface (Fig. 1). This causes the Fe-Ti bond length to be shorter and, hence, the overlap between the Fe 3*d* and Ti 3*d* orbitals to be stronger at the top interface compared to the bottom interface. As a result, the minority-spin bonding state lies deeper in energy and, hence, is more populated for Fe and Ti atoms at the top interface than at the bottom interface, as indicated by the arrows in Figs. 2(a) and 2(b). Thus, ferroelectric instability enhances the induced magnetic moment on top Ti atoms but reduces the magnetic moment of bottom Ti atoms. The change is opposite for Fe atoms: Their magnetic moments are enhanced at the bottom interface but reduced at the top interface.

With increasing $BaTiO_3$ thickness, the net polarization of the ferroelectric film grows and gradually approaches its bulk value. This is evident from Fig. 3, revealing the increasing relative displacements between Ti and O atoms which saturate at the bulk value of 0.125 Å. (These displacements are inhomogeneous across the ferroelectric film, reflecting an inhomogeneous polarization similar to that found for Pt/$KNbO_3$ [16] and $SrRuO_3$/$BaTiO_3$ [18] multilayers.) This enhances the asymmetry in the strength of the bonding and, consequently, in the magnetic moments at the top and bottom interfaces. As is seen from Table I, with increasing thickness of the $BaTiO_3$ layer from $m = 4$ to $m = 16$, the difference in the Fe magnetic moments increases from $\Delta\mu_{\mathrm{Fe}} = 0.06\mu_B$ to $\Delta\mu_{\mathrm{Fe}} = 0.12\mu_B$, and the difference in the Ti magnetic moments increases from $\Delta\mu_{\mathrm{Ti}} = 0.22\mu_B$ to $\Delta\mu_{\mathrm{Ti}} = 0.25\mu_B$.

Dissimilar magnetic moments at the two interfaces reflect the change which occurs at *one* interface if the polarization in $BaTiO_3$ reverses. To illustrate this change, we calculated the interface electronic charge density for two opposite polarization orientations in $BaTiO_3$. Figure 4 shows the minority-spin charge density calculated in the energy window from $E_F - 1$ eV to E_F covering the region where the Fe-Ti minority-spin bonding states are located [see Figs. 2(a) and 2(b)]. As is seen from Figs. 4(a) and 4(b), the charge distribution at the interface Ti atom has a shape of the $d_{xy}(d_{yz})$ orbital which is hybridized with the respective *d* orbitals on the nearest Fe atoms. It is evident

TABLE I. Magnetic moments (in units of μ_B) of Fe and Ti atoms at the top and bottom interfaces of Fe/$BaTiO_3$ multilayers. $\Delta\mu = \mu_{\mathrm{bot}} - \mu_{\mathrm{top}}$ is the difference between the magnetic moments at the top and bottom interfaces. The polarization of the $BaTiO_3$ film is pointing upward.

	$m = 2$	$m = 4$	$m = 6$	$m = 8$	$m = 10$	$m = 16$
$\mathrm{Fe}_{\mathrm{top}}$	2.59	2.61	2.60	2.59	2.58	2.56
$\mathrm{Fe}_{\mathrm{bot}}$	2.59	2.67	2.67	2.67	2.67	2.68
$\Delta\mu_{\mathrm{Fe}}$	0.0	0.06	0.07	0.08	0.09	0.12
$\mathrm{Ti}_{\mathrm{top}}$	−0.30	−0.40	−0.40	−0.40	−0.40	−0.40
$\mathrm{Ti}_{\mathrm{bot}}$	−0.30	−0.18	−0.17	−0.16	−0.16	−0.15
$\Delta\mu_{\mathrm{Ti}}$	0.0	0.22	0.23	0.24	0.24	0.25

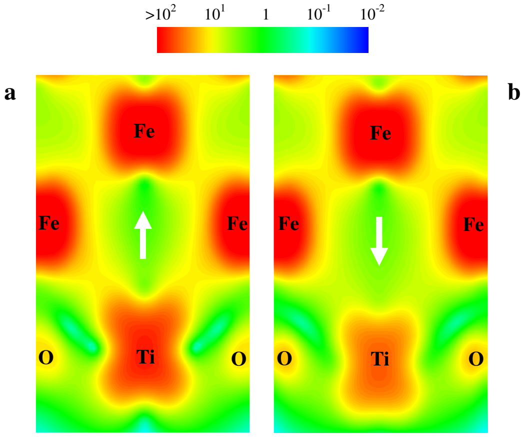

FIG. 4 (color online). Minority-spin charge density (in arbitrary units) at the Fe/BaTiO$_3$ interface for two opposite polarizations in BaTiO$_3$. The charge density is calculated in the energy window from $E_F - 1$ eV to E_F in the (010) plane for the $m = 4$ multilayer. (a) Net polarization pointing up; (b) net polarization pointing down.

from the comparison of the charge density shown in Figs. 4(a) and 4(b) that the overlap between the Ti and Fe electronic clouds is much stronger for the polarization pointing into the Fe film than for the polarization pointing away from the Fe film, which reflects a stronger hybridization for the former. Since the majority-spin density on the interface Ti atoms is small for the energies from $E_F -$ 1 eV to E_F [see Fig. 2(a)], the minority-spin density shown in Figs. 4(a) and 4(b) on the Ti atoms reveals the difference in the spin density on these atoms which is the source of the magnetic moment change for opposite polarizations in BaTiO$_3$.

The predicted results suggest a possibility to observe a *net* magnetization change in a Fe/BaTiO$_3$ *bilayer* deposited on a proper substrate. In this case, there is only *one* Fe/BaTiO$_3$ interface which has magnetic properties dependent on the orientation of the ferroelectric polarization, and hence the polarization reversal will inevitably change the magnetic moment of the entire system. We estimate the magnetoelectric coefficient α of this multiferroic bilayer by taking the ratio of the magnetization change ΔM to the coercive electric field E_c of the BaTiO$_3$ film. Assuming that the Fe and BaTiO$_3$ layers have thicknesses of 1 and 2.5 nm ($m = 6$), respectively, and taking the change in the interface magnetic moment per unit cell of $0.3\mu_B$ (as follows from our calculations for $m = 6$), we find that the average magnetization change in the Fe/BaTiO$_3$ bilayer is about $\mu_0 \Delta M \approx 120$ G. Since coercive fields of BaTiO$_3$ films are in the range of $E_c \approx 10$ kV/cm, we obtain $\alpha \simeq \mu_0 \Delta M / E_c \approx 0.01$ G cm/V, which is of the same order in magnitude as the magnetoelectric coefficient measured in epitaxial BiFeO$_3$/CoFe$_2$O$_4$ columnar nanostructures [10]. Thus, the magnetoelectric effect induced by interface bonding can be as large as that induced by strain.

The predicted phenomenon is qualitatively different from the "standard" magnetoelectric effect which is the volume effect and for which the magnetization is a linear function of the applied electric field. In our case, the magnetoelectric effect is confined to the interface and represents a change of the interface magnetic moment at the coercive field of the ferroelectric. Since this phenomenon is primarily due to the electronic hybridization between the transition metal elements with less than half occupied *d* bands (Ti) and more than half occupied *d* bands (Fe), any ferromagnetic-ferroelectric multilayer with such a combination of elements is predicted to have the magnetoelectric coefficient similar to that found for Fe/BaTiO$_3$. We therefore hope that our theoretical predictions will stimulate experimental studies of such multilayers to search for the magnetoelectric effect driven by interface bonding.

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