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Magnetoelectric effect at the $SrRuO_3/BaTiO_3$ (001) interface: An *ab initio* study

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Ferromagnet/ferroelectric interface materials have emerged as structures with strong magnetoelectric coupling that may exist due to unconventional physical mechanisms. Here we present a first-principles study of the magnetoelectric effect at the ferromagnet/ferroelectric $SrRuO_3/BaTiO_3$ (001) interface. We find that the exchange splitting of the spin-polarized band structure, and therefore the magnetization, at the interface can be altered substantially by reversal of the ferroelectric polarization in the $BaTiO_3$. These magnetoelectric effects originate from the screening of polarization charges at the $SrRuO_3/BaTiO_3$ interface and are consistent with the Stoner model for itinerant magnetism. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3193679]

The interest in coupling between the electric and magnetic order parameters has increased in recent years due to the increasing demand for the high density magnetic recording and other spintronics-based devices as well as impressive development in the realization of single phase and composite multiferroic materials.[1,2] Both the magnetic control of ferroelectric polarization[3] and the electric control of magnetization[4,5] in such materials have been demonstrated. The search for alternative physical mechanisms of magnetoelectric (ME) coupling is encouraging as conventional ME coupling effects are often weak. In addition, alternative coupling mechanisms may offer the possibility of designing devices based on multiple logic states. In general, not only coupling between ferroelectricity and magnetism but also various related phenomena such as an electrically controlled exchange bias,[6,7] electrically controlled magnetocrystalline anisotropy,[8–11] and the effect of ferroelectricity on spin-dependent transport[12–15] are considered as ME effects.

An intrinsic ME coupling may be observed in single phase compounds if time reversal and space-inversion symmetries are absent in them. However, a stronger ME coupling may occur in composites of piezoelectric (ferroelectric) and magnetostrictive (ferromagnetic or ferrimagnetic) compounds, mediated by strain across interfaces.[16] Recently, two alternative mechanisms of ME coupling have been proposed based on theoretical studies,[17,18] where the ME coupling is confined mainly at the interface of the composite constituents. In the theoretical studies of heterostructures of $Fe/BaTiO_3$ (Refs. 17 and 19) and $Fe_3O_4/BaTiO_3$,[20] it was shown that bonding between the interface atoms and its dependence on the ferroelectric polarization results in interfacial ME coupling. A similar effect was recently found for $Co_2MnSi/BaTiO_3$ interface.[21] Another kind of the interface ME effect has been predicted, mediated by free carriers at the interface between $SrTiO_3$ (a nonmagnetic, nonpolar insulator) and $SrRuO_3$ (ferromagnetic metal).[18] In this case, an applied electric field results in the accumulation of spin-polarized carriers at the metal-insulator interface producing a change in the interface magnetization due to spin-dependent screening.[22] Recently, the linear surface ME effect was explored for ferromagnetic metal films.[23] It was found that spin-dependent screening leads to notable changes in the surface magnetization and the surface magnetocrystalline anisotropy.

In this article, we use first-principles (FP) methods to investigate an interfacial ME coupling in a $SrRuO_3/BaTiO_3$ (001) heterostructure. $BaTiO_3$ is a prototypical ferroelectric material and $SrRuO_3$ is a ferromagnetic oxide metal. Experimentally, $SrRuO_3$ has been used as a metal oxide electrode in combination with ferroelectric $BaTiO_3$ thin films.[24,25] We find a change in magnetization at the interface as the electric polarization in the ferroelectric film reverses. This ME effect originates from a change in the exchange splitting between majority-spin and minority-spin densities of states at the interface with the polarization reversal, which we will explain by using the Stoner model.[26]

Calculations are performed within the framework of density functional theory and the projected augmented wave method, as implemented within Vienna *ab initio* simulation package.[27] The Perdew–Burke–Ernzerhoff[28] form of the generalized gradient approximation for exchange and correlation is employed along with a plane wave basis set with a kinetic energy cutoff of 520 eV. We use a $10\times10\times1$ k-point mesh and the structures are relaxed until the largest force becomes less than 0.02 eV/Å.

The supercell is constructed of 6.5 unit cells of $BaTiO_3$ with 8.5 unit cells of $SrRuO_3$ on top along the [001] direction. The structure for a smaller supercell with the polarization (P) in $BaTiO_3$ pointing to the right is shown in Fig. 1.

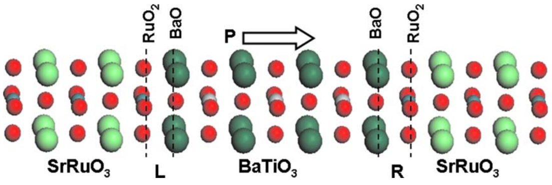

FIG. 1. (Color online) Atomic structure of the $SrRuO_3/BaTiO_3$ (001) interfaces.

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The state with the P pointing to the left is equivalent to our chosen state due to the symmetry of our structure. Since the second interface is equivalent to the first with polarization reversed, this geometry allows us to study the effect of polarization reversal at one interface by comparing properties of the two interfaces. We have chosen RuO_2/BaO interfaces for this study. Due to the chemical similarity of Ba and Sr, SrO/TiO_2 interface is expected to have similar properties.

The in-plane lattice constant of the superlattice is fixed to the experimental lattice constant of $SrTiO_3$ ($a=3.905$ Å) to simulate epitaxial growth on a $SrTiO_3$ substrate. The out-of-plane lattice constant of bulk $SrRuO_3$ and $BaTiO_3$ are obtained by minimizing the total energy giving the c/a ratios of 1.046 and 1.061, respectively. Subsequently, the interface separation distance is determined by minimizing the total energy of the superlattice keeping the in-plane lattice constant and out-of-plane separation in $BaTiO_3$ and $SrRuO_3$ subunits fixed. Under this constraint, the polarization of bulk $BaTiO_3$ in tetragonal phase was calculated to be 0.44 C/m^2 using the Berry phase method.[29] The magnetic moment of constrained bulk $SrRuO_3$ in the tetragonal phase was obtained to be $1.22\mu_B$/f.u. Next, we minimize the total energy of the $SrRuO_3/BaTiO_3$ (001) structure with respect to the cell size and atomic coordinates of all the atoms, resulting in a stable ferroelectric state in the $BaTiO_3$. Relative displacements of Ti atoms with respect to O atoms in the middle of $BaTiO_3$ film are found to be about 0.14 Å. These values are close to the bulk values of 0.16 Å, which correspond to a calculated polarization of 0.39 C/m^2 of the bulk $BaTiO_3$. These results are consistent with the previous calculations.[15,30]

As a result of the ferroelectricity in the $BaTiO_3$, the magnetizations of the $SrRuO_3$ at the left and right interfaces differ significantly. Integrating the spin density over the four unit cells of $SrRuO_3$ nearest the interfaces, we find a total magnetic moment of $3.20\mu_B$ and $3.51\mu_B$ for the left and right interfaces, respectively. Therefore the net change in interfacial magnetic moment per unit area caused by the polarization reversal is $\Delta M=0.31\mu_B/a^2$.

In a supercell where ferroelectric distortions in the $BaTiO_3$ are suppressed (i.e., $P=0$), we find a total magnetic moment of $3.55\mu_B$ for four interfacial $SrRuO_3$ unit cells. Comparing this with the ferroelectric state, we see that the change in magnetic moment induced by the polarization is $-0.35\mu_B$ for the left interface and $-0.04\mu_B$ for the right interface. This is quite different from what one expects from a linear effect where the changes in the moments at the two interfaces would be equal and opposite, as found in Refs. 18 and 23. Therefore our calculations clearly show that the ME coupling in our system displays a highly nonlinear dependence on the magnitude of the ferroelectric polarization.

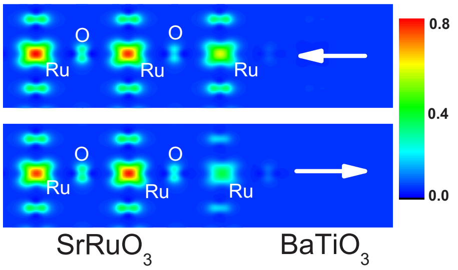

FIG. 2. (Color online) Spin density (in $Å^{-3}$) within the (100) plane cutting through the Ru atoms of the $SrRuO_3/BaTiO_3$ (001) heterostructure.

Figure 2 shows the change in spin density at the $SrRuO_3/BaTiO_3$ (001) interface with polarization reversal. It is apparent that the largest change occurs within the interfacial RuO_2 monolayer. Unlike the result of Refs. 17, 19, and 20, where the interface ME effect was largely determined by the interface bonding, there are no strong bonding effects dominating the ME coupling at the $SrRuO_3/BaTiO_3$ (001) interface. Due to the assumed RuO_2/BaO interface termination, there are no induced magnetic moments on the interfacial Ti ions, as was found for other interfaces.[17,31] As is evident from Fig. 2, a small magnetic moment (about $0.02\mu_B$) induced on the O atom within the interfacial BaO monolayer is only weakly influenced by polarization reversal.

Following the previous work,[20] we can estimate the magnitude of the surface magnetoelectric coefficient α_s, which is defined as[23]

$$\mu_0 \Delta M = \alpha_s E, \tag{1}$$

where E is the strength of the applied electric field. The relationship between ΔM and E in our case is nonlinear since the ferroelectric polarization is a nonlinear function of applied electric field. Nevertheless, one can get an order-of-magnitude estimate of α_s from Eq. (1) by assuming that the polarization of $BaTiO_3$ can be switched at the coercive field $E_c=100$ kV/cm. Taking into account that $\Delta M=0.31\mu_B/a^2$, we find the surface ME coefficient $\alpha_s \approx 2.3 \times 10^{-10}$ G cm^2/V. This value is close to the value of $\alpha_s \approx 2.1\times 10^{-10}$ G cm^2/V found for $Fe/BaTiO_3$ interface[17] (and $Fe_3O_4/BaTiO_3$ interfaces[20]) where the atomic bonding at the interface is the dominant mechanism of ME coupling.

Figure 3(a) shows the spin-polarized density of states projected onto the Ru $3d$ orbitals at the right and left interfaces. It is seen that there is a clear change in the exchange splitting between the two interfaces giving rise to a change in the relative population of the two spin channels and therefore to the change in magnetic moment. The origin of the change in exchange splitting is the screening of the bound polarization charges of the ferroelectric at the interface, which we

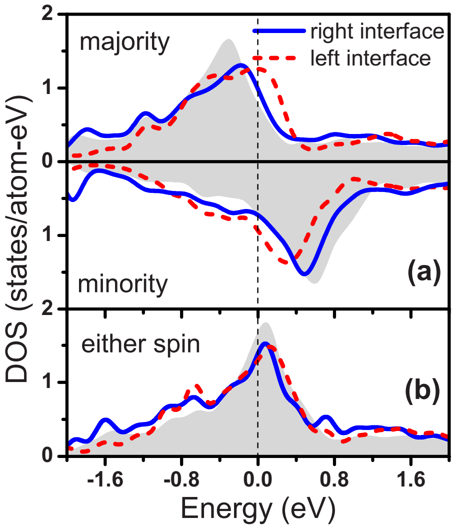

FIG. 3. (Color online) Spin-polarized (a) and nonspin-polarized (b) local density of states projected onto the Ru $3d$ orbitals at the right (solid lines) and left (dashed lines) interfaces in the $SrRuO_3/BaTiO_3$ (001) heterostructure. The shaded plots are the Ru $3d$ density of states in the bulk. The zero along the horizontal axis refers to the Fermi energy.

TABLE I. Parameters extracted from the nonspin-polarized calculation used in Eq. (3) to estimate the exchange splitting Δ. The estimated and FP values of Δ are also compared.

	ρ_F (eV^{-1})	b (eV^{-2})	Δ (eV) Equation (3)	Δ (eV) FP
Left	1.35	1.2	0.35	0.32
Right	1.4	1.2	0.71	0.66

demonstrate below using the Stoner model of ferromagnetism. We can estimate the magnitude of the splitting at the right and the left interfaces using parameters obtained from the results of a nonspin-polarized calculation. It is known that the ferromagnetic state is stabilized by the condition

$$\Delta = Im, \tag{2}$$

where m is the magnetic moment, Δ is the exchange splitting, and I is the Stoner exchange parameter.[32] Figure 3(b) shows the nonspin-polarized Ru 3d density of states at the left and right interfaces. In a simple approximation, we assume that the nonspin-polarized density of states (per spin) is a linear function of energy (ε) near the Fermi level $(\varepsilon_F): \rho(\varepsilon) = b(\varepsilon - \varepsilon_F) + \rho_F$. Here ρ_F is the density of states at the Fermi energy in the nonspin-polarized calculation which, as can be seen in Fig. 3(b), depends on the sign of the bound polarization charge at the interface. Using Eq. (2) we find that the equilibrium exchange splitting is

$$\Delta = \frac{2\sqrt{\rho_F^2 I^2 - 1}}{Ib}. \tag{3}$$

The Stoner parameter I is obtained using Eq. (2) and the exchange splitting and magnetic moment of a bulk Ru atom as $I = 0.75$ eV. From Fig. 3(b) we find ρ_F and b for both the left and right interfaces and estimate the exchange splitting using Eq. (3). The parameters and results are presented in Table I. We see that the exchange splittings from the Stoner model are in reasonable agreement with those from FP calculations.

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