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Magnetoelectric coupling at the epitaxial Ni/PbTiO$_3$ heterointerface from first principles

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ABSTRACT

The magnetoelectric coupling at the epitaxial ferromagnetic/ferroelectric heterointerface depends strongly on the detailed bonding mechanism and the type of magnetic interaction among the interfacial atoms. First-principles density-functional calculations of the electronic structure and magnetoelectric coupling at the epitaxial Ni/PbTiO$_3$ heterointerface are performed. Our results demonstrate that the interfacial magnetoelectric coupling in this system originates from the interface bonding and the peculiar *pdσ*-type magnetic interaction between interfacial Ni and O atoms, which results in a large change of magnetic moments on Ni atoms near the interface. Furthermore, it is this peculiar interfacial magnetic interaction that leads to an extraordinary oscillating behavior of magnetic moments across the entire Ni slab, which may have important practical implication in multiferroic devices.

1. Introduction

Multiferroics, with coexisting ferroelectric (FE) and magnetic orders that are mutually coupled, have attracted considerable interest due to their potential applications and fundamental science challenges [1–4]. The strong magnetoelectric (ME) coupling allows control of magnetism via an electric field or vice versa and could yield novel device concepts, such as multi-state data storage and electric-field controlled spintronics [5,6]. In the naturally existing single-phase multiferroics the ME coupling is often weak, and new class of artificially structured composite materials that combine dissimilar ferroelectric and magnetic systems are being developed to enhance the ME effect. More details about experimental and theoretical progress concerning the composite multiferroics have been presented in several recent reviews [3,7–9].

Current efforts focus on the so-called “interfacial magnetoelectricity” in which the ME coupling arises as an extrinsic effect at the interface of artificial composite multiferroics, [10–18] which can be fabricated in the form of multilayers of alternating FE and ferromagnetic (FM) layers [19,20] or vertically aligned columnar nanostructures [21,22]. There are several types of mechanisms giving rise to the interfacial ME coupling at the FM/FE heterointerface. The well established extrinsic ME coupling effect is mediated by strain across the interface in composites of piezoelectric (ferroelectric) and magnetostrictive (piezomagnetic) materials [23,24]. In such structures, an applied electric field induces strain in the piezoelectric component which is mechanically transferred to the magnetostrictive constitute, where it changes the magnetization. Besides the elastic interaction, the interfacial ME effects may originate from purely electronic mechanisms [11,12]. It was first predicted by Duan et al. [11] that the interface bonding can be the source of the interface ME coupling. Using Fe/BaTiO$_3$ (0 0 1) multilayer as a representative model, they demonstrated that displacements of atoms at the FM/FE interface caused by ferroelectric instability change the hybridization between atomic orbitals at the interface which affects the interface magnetization. This produces a sizeable ME effect which manifests itself in the interface magnetization when FE polarization reverses under the influence of applied electric field. This kind of ME effect is also expected to play a role for Co$_2$MnSi/BaTiO$_3$ [25] and Fe$_3$O$_4$/BaTiO$_3$ [16] interfaces. Just lately, the interface bonding ME effect is verified by the observation of room-temperature multiferroicity at the interfaces of BaTiO$_3$ ultrathin film with Fe or Co [26]. Another type of electronic mechanism for the interfacial ME coupling originates from spin-dependent screening [12]. In this case, an applied electric field induces accumulation of spin-polarized carriers at the FM/dielectric interface, resulting in a change in the interface magnetization. This mechanism is also relevant to the FM/FE heterointerface, such as the SrRuO$_3$/BaTiO$_3$ interface, [17] where the ME effect can be further enhanced and became nonlinear owing to field effect and nonlinear variation of the FE polarization with applied electric field. This type of carries-induced ME coupling is subsequently used to investigate the electric control of magnetization in ferromagnet/ferroelectric/normal metal (FM/FE/NM) tri-component superlattices [13,18].

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The experimental indication of the ME effect driven by the spin-dependent screening mechanism was recently found for the $La_{0.8}Sr_{0.2}MnO_3/PbZr_{0.2}Ti_{0.8}O_3$ bilayers [27].

In addition, a novel type of interfacial ME effects due to the purely electronic mechanisms has been predicted for the Ni/$BaTiO_3$ heterointerface just recently [28]. This kind of ME coupling is determined by the change of magnetic moments on Ni atoms near the interface, instead of the induced moments on interfacial Ti atoms in the Fe/$BaTiO_3$ system, [11] which is also distinguished from the spin-polarized carriers screening mechanism [12]. The underlying physics is the strong interface bonding and the $pd\sigma$-type magnetic interactions between Ni $3d$ and O $2p$ spins. Furthermore, in the Fe/$PbTiO_3$ system, we have demonstrated that the interface ME effect is determined by the combination of different ME coupling mechanisms, [29] i.e., conjunction of the interface bonding and the spin-dependent screening. The combinations of different ME coupling mechanisms enhances the ME coefficient at the Fe/$PbTiO_3$ interface to be several times larger in magnitude than that of individual ME coupling mechanism.

Since the ME effect at the FM/FE interface is extrinsic, the magnitude and mechanism of the ME coupling depend on the properties of specific material system including the bulk properties of FM, FE, and the detailed interface interactions. It is necessary to explore the possible ME coupling mechanisms in order to design materials that exhibit strong coupling between magnetic and FE order parameters. In this manuscript, we choose the epitaxial Ni/$PbTiO_3$ heterostructure to investigate the interfacial electronic structure and the corresponding ME effect. We will demonstrate that, though the ME effect in this system is also determined by the $pd\sigma$-type magnetic interactions between Ni $3d$ and O $2p$ spins, magnitude of the ME coefficient is significantly larger than that of Ni/$BaTiO_3$ interface [28]. The improvement of the interfacial ME effect is attributed to the enhancement of the $pd\sigma$-type magnetic interactions between Ni $3d$ and O $2p$ moments, which is due to the remarkable change of distance between them during the reversion of the polarization in the $PbTiO_3$.

2. Structure and methods

We explore the ME effect at the Ni/$PbTiO_3$ interface using first-principles calculations based on density functional theory (DFT). In our calculations we use a supercell geometry in which the bcc Ni [1 1 0] axis is aligned with the [1 0 0] axis of tetragonal $PbTiO_3$. Periodic boundary conditions of the supercell geometry impose the short-circuit condition between the FM metals. We assume that the $PbTiO_3$ layers have TiO_2 terminations at both interfaces and the interfacial O atoms lie on top of Ni atoms, which is similar to that of Fe/$BaTiO_3$ [11] and Co/$SrTiO_3$ [30]. Thus the supercell we use is $(Ni_2)_9$-TiO_2-$(PbO\text{-}TiO_2)_6$ and the atomic structure is illustrated in Fig. 1(a). The in-plane lattice constant is fixed to the theoretical value we calculated for the $P4mm$ phase of bulk $PbTiO_3$ (3.890 Å), which is in good agreement with the experimental lattice constant (3.895 Å). Under this constraint, we find that the polarization of the bulk $PbTiO_3$ is 0.90 C/m^2 as calculated using the Berry's phase method [31] (Using Born effective charges and ionic displacements relative to the ideal positions in $P4/mmm$ structure, we estimate the polarizations is 0.85 C/m^2.), while the magnetic moments of the bulk Ni is 0.52 μ_B per atom.

DFT calculations are performed using the projector augmented wave (PAW) method as implemented in the Vienna *ab initio* simulation package (VASP) [32–34]. The exchange correlation potential is treated in the generalized gradient approximation (GGA), using the Perdew–Burke–Ernzerhof functional revised recently for solids (PBEsol) [35], which is known to be very accurate in predicting the volume of solids [36]. The PAW potentials [37] were used with the following valence-electron configurations: $3p^6 3d^8 4s^2$ for Ni, $5d^{10} 6s^2 6p^2$ for Pb, $3s^2 3p^6 3d^2 4s^2$ for Ti, and $2s^2 2p^4$ for O atom. For structural relaxations, Gaussian broadening technique [38] of 0.1 eV is used and the ions were relaxed until the Hellmann–Feynman forces are less than 20 meV/Å. We use the energy cutoff of 500 eV for the plane wave expansion of the PAWs and a 6 × 6 × 1 Monkhorst–Pack grid [39] centered at Γ for k-point sampling. For density of states calculations, the grid was increased to 12 × 12 × 2. The spin-orbit interaction is not included in our calculation since this effect is expected to be very small for $3d$ elements.

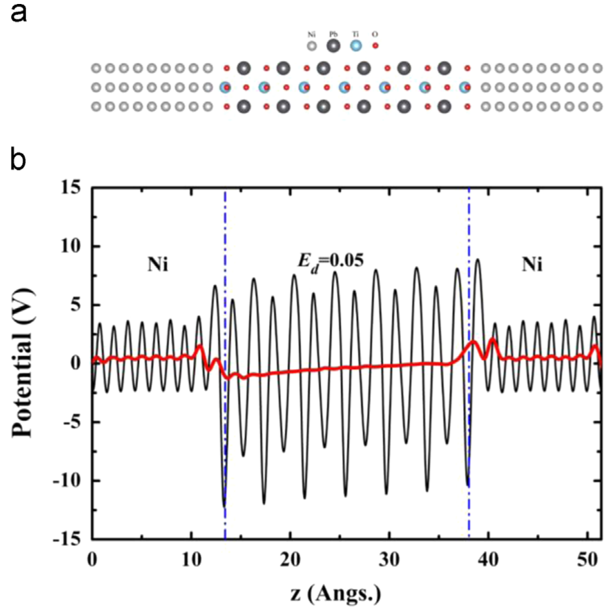

Fig. 1. (a) Atomic structure of the Ni/$PbTiO_3$ superlattice. The planar (thin black curve) and macroscopic averaged electrostatic potential (thick red curve) along the [0 0 1] direction of (b) the Ni/$PbTiO_3$ superlattice. The polarization direction of $PbTiO_3$ film is pointing leftward. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3. Results

3.1. Cohesive energy and ferroelectricity

To simulate the paraelectric (PE) state of the Ni/$PbTiO_3$ supercell, we impose a mirror plane on the central TiO_2 layer and minimize the total energy by relaxing all the atomic positions of the system. Although the net polarization of the $PbTiO_3$ film is zero, bonding at the interface induces interface dipole moments with opposite directions at the two interfaces [11,40]. Relative displacement of the interfacial Ti–O and Pb–O atoms is 0.140 and 0.106 Å, respectively. We estimated the magnitude of the interface polarization P_i=0.22 C/m^2 pointing toward the $PbTiO_3$ layer using the bulk Born effective charges averaged over the $PbTiO_3$ unit cell.

We start with determining the separation work[1] that quantifies the cohesive energies between Ni and $PbTiO_3$. Table 1 reports the calculated values of the separation work together with the bond lengths at the interface. First, though the separation work (2.10 J/m^2) for PE state of the Ni/$PbTiO_3$ system is less than that of the PE Ni/$BaTiO_3$ superlattice (2.18 J/m^2), [28] the larger cohesive energy

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[1] The interfacial separation work is defined as $W_{sep}=(E_{Ni}+E_{PbTiO3}-E_{Ni/PbTiO3/Ni})/2A$, where $E_{Ni/PbTiO3/Ni}$ is the total energy of the supercell, E_{Ni} and E_{PbTiO3} are the energies of the same supercell containing relaxed single slab of either Ni or $PbTiO_3$, A is the surface area of the interface, and the factor 2 accounts for the two interfaces present in the supercell. For the ferroelectric state of the Ni/$PbTiO_3$ supercell, the work of separation is the average of the two nonequivalent interfaces.