Magnetoelectric Effects at the BiFeO$_3$/Fe Interface: A First Principles Study

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Abstract. We theoretically investigated the electronic structures and magnetoelectric properties of BiFeO$_3$/Fe heterostructure based on the first-principles calculations. We found that the magnetic coupling of the epitaxial Fe layer in the BiFeO$_3$/Fe heterostructure can be tuned by external electric field, which means the ferroelectronic state could control the magnetic ordering structure of the Fe layer. The corresponding magnetic-electric coupling coefficient was one order of magnitude higher than that for BaTiO$_3$/Fe.

1. Introduction

Epitaxial growth technology has facilitated the preparation of ferromagnetic/ferroelectric heterostructures at the nanoscale [1]. Duan et al. first proposed that ferroelectric polarization could influence magnetism at the interface between ferroelectric and ferromagnetic materials due to a chemical bond. They also studied the magnetoelectric coupling effect [2] using the first principle computation method by adopting typical ferroelectric and ferromagnetic interfaces using BaTiO$_3$/Fe as a prototype. The atomic displacement at the interface due to ferroelectric polarization led to changes in the magnetic moment. Sahoo et al. first performed epitaxial growth experiments using a 10 nm Fe layer on BaTiO$_3$ (100). They observed that the coercive field on the Fe surface could vary up to 20% upon application of an external electric field [3].

Although typical ferroelectric and ferromagnetic heterostructures like BaTiO$_3$/Fe can modulate the external electric field and magnetic moment distribution at the interface, only small changes in the magnetic moment amplitude can be achieved. Neither magnetization reversal in the external electric field, nor ferromagnetic-antiferromagnetic transitions driven by the magnetic interaction can occur. Thus, this approach cannot deliver multi-states in magnetoelectric storage devices. One alternative is to replace the ferroelectric and ferromagnetic heterostructures with multiferroic materials. Thus, the atomic displacement at the interface caused by ferroelectric polarization would affect the magnetism of the ferromagnetic material. It would also couple the different magnetic ordering structure across the two materials. This would affect the magnetism and thus modulate the effect on the ferromagnetic material.

This paper studied the heterostructure BiFeO$_3$/Fe containing the typical multiferroic materials BiFeO$_3$ and the typical magnetic material Fe. We investigated the electric structure and magnetic properties of the BiFeO$_3$/Fe heterostructure using first principle calculations. The results indicated that changing the polarization direction of the BiFeO$_3$ could change the magnetic interaction within the Fe
atomic layer. The ferromagnetic interaction in the Fe atom can be turned into an anti-ferromagnetic interaction.

2. Calculation details

All calculations were carried out using the projector augmented wave (PAW) formalism of density functional theory (DFT) [4], as implemented in the Vienna *ab initio* simulation package [5]. The valence charge configurations of Bi, Fe and O are $5d^{10}6s^26p^3$, $3d^64s^2$ and $2s^22p^4$, respectively. A plane-wave cutoff of 500 eV was used throughout and the convergence criterion for energy is $10^{-6}$ eV. Brillouin zone integrations were performed with a $\Gamma$-centered $6\times6\times1$ Monkhorst-Pack $\kappa$-points mesh [6]. All the calculations of TM doped configurations were performed optimizing all the atomic coordinates of the ions until the atomic forces were smaller than 0.01 eV /Å. Exchange-correlation functionals were treated both with Perdew, Burke and Ernzerhof (PBE) formulation of the generalized gradient approximation (GGA) method [7]. Non-DFT+$U$ methods do not correctly take into account the localization of the TM:3$d$ electrons. Thus the predicted band gap and magnetic ground state may be misleading [8]. In this work, the parameter $U_{\text{eff}}$ was set to 4 eV in the frame work of Dudarev’s effective-$U$ method on Fe ions, which has been proved to reproduce the electronic properties for Bi-based multiferroics very well [9].

3. Results and discussions

BiFeO$_3$ is the most widely studied single-phase multiferroic materials in recent years. It is the only material with both ferroelectric and magnetic properties at room temperature. Under normal pressure and temperature, its crystal structure exhibits a rhombohedral perovskite structure with a R3C space group [10]. However, experiments indicated that in the ultrathin films (2-35 nm), the crystal structure of BiFeO$_3$ could be a tetragonal phase with a space group of P2mm while retaining ferroelectricity [11]. Subsequent first principle calculations also indicated that the tetragonal phase of BiFeO$_3$ still had ferroelectric polarization along the (001) direction. The spin order of its Fe$^{3+}$ represented a G-type anti-ferromagnetic order [12]. The primitive cell of BiFeO$_3$ includes 5 atoms, which could be extended into a super cell to describe the various magnetic ordering structures of Fe$^{3+}$ in tetragonal phases of BiFeO$_3$ (Figure 1). The ground state energies calculated for ferromagnetic ordering and A-type, B-type, C-type and G-type anti-ferromagnetic ordering, respectively, were consistent with the literature [12]. These studies report that the ground state structure of magnetic ordering was G-type of anti-ferromagnetic ordering.

![Figure 1](image_url). Crystal structure of BiFeO$_3$ in tetragonal phase. (a) Side view. (b) Top view.

Under G-type anti-ferromagnetic ordering, the optimized lattice constants and atom coordinates were $a = 3.905$ Å, $c = 4.00$ Å, Bi (0, 0, 0), Fe (0, 0, 0.594), O$_\perp$ (0, 0, 0.126), and O$_\parallel$ (0, 0.5, 0.673), respectively. The density of electronic states for BiFeO$_3$ with a P4mm structure is shown in Figure 2. Its energy gap is approximately 2 eV. The Fe$^{3+}$ ion presented a significant spin splitting. The spin state is approximately
7 eV below the Fermi energy level and overlapped with a O:2p orbital. Therefore it can form very stable anti-ferromagnetic ordering.

Figure 2. Density of electronic states of BiFeO$_3$ in tetragonal phase. (dashed line denotes the Fermi energy)

The thin film structure (slab method) of tetragonal phase BiFeO$_3$ in the (001) direction can be built by increasing the vacuum layer in the (001) direction (the vacuum layer calculation in this paper is 25Å). This approach uses the crystal lattice parameters for bulk, tetragonal phase BiFeO$_3$. The film on the BiO termination surface included six BiO layers and five FeO$_2$ layers. The film on the FeO$_2$ termination surface included five BiO layers and six FeO$_2$ layers. Considering the volatility of the Bi element, the film of the FeO$_2$ termination surface was adopted for this study. It was comprised of six FeO$_2$ layers and five BiO layers with a total thickness of 2.04 nm. To simulate the epitaxial growth of the Fe film on the surface of tetragonal phase BiFeO$_3$, one body-centred cubic ferrous metal film was added to one surface of tetragonal phase BiFeO$_3$. The Fe lattice constant of the body centered cubic is 2.87 Å. Therefore, Fe body centered cubic 2 x 2 super cells matched well with the film surface—the lattice mismatch was only 3.9%. The original location of one epitaxial layer of Fe atoms is just above the O atom of BiFeO$_3$ film surface. Thus, the BiFeO$_3$/Fe heterostructure was obtained (Figure 3).
There are four Fe atoms on the epitaxial layer. They consist of three magnetic ordering structures including ferromagnetic coupling C1 and anti-ferromagnetic structures C2 and C3 (Figure 4). Using the ferroelectric polarization state (Figure 3), three BiO and four FeO$_2$ layers were fixed on the bottom surface of the BiFeO$_3$/Fe heterostructure. The atomic coordinates of the epitaxial Fe layer and the nearest two BiFeO$_3$ layers were optimized to compute the total energy of the system. Table 1 shows the total energy results under various ferroelectric polarization states and magnetic ordering structures. For convenience of comparison, Table 1 also provides the energies for three magnetic ordering structures that correspond to isolated single layers of Fe atoms. That is, the Fe atom is not on the epitaxial BiFeO$_3$ surface with two surfaces contacting the vacuum. Rather, we used an epitaxial, single layer of Fe atoms to determine the lattice constant. We noted that when the ferroelectric polarization direction of BiFeO$_3$ was upward, the epitaxial single Fe atom had anti-ferromagnetic coupling (C2). When the ferroelectric polarization was downward, the Fe atomic layer had ferromagnetic coupling. A Fe atom with an isolated single Fe atomic layer also had ferroelectric coupling.

Table 1. Energy difference under various ferroelectric polarization states.

| Magnetic order | $P_{↑}$ | $P_{↓}$ | isolated |
|---------------|--------|--------|----------|
| C1            | 336    | 0      | 123      |
| C2            | 0      | 948    | 644      |
| C3            | 129    | 46     | 649      |

When the ferroelectric polarization direction was upward, the Fe atom of the FeO$_2$ at the interface was above the O atom. The Fe/Fe/O layered structure was formed at the interface—this also formed
anti-ferromagnetic coupling between Fe atoms. This observation is very similar to that of Fechner et al. [14,15]. Their study indicated that when the epitaxial Fe atom in BaTiO$_3$/Fe structure had two layers, the epitaxial Fe layer turned into an anti-ferroelectric structure. When the ferroelectric polarization direction was downward, a Fe/O/Fe structure was formed at the interface, and the epitaxial Fe layer was closer to the Fe metal. Therefore, it leadsto ferromagnetic coupling. The change in ferroelectric polarization state resulted in a change of atomic structure at the interface. This altered the magnetic coupling state of the epitaxial Fe layer.

Therefore, for ferroelectric polarization states in two directions, the magnetic moment variation of the BiFeO$_3$/Fe heterostructure was 3.5 μB/Fe and exhibited a significant change versus the magnetic moment variation of 0.03 μB/Fe for BaTiO$_3$/Fe heterostructures [16]. More importantly, under two ferroelectric polarization states, the magnetic exchange between Fe atoms turned from ferromagnetic to anti-ferromagnetic. This observation has not yet been reported for ferroelectric/ferromagnetic interface heterostructures. In our BiFeO$_3$/Fe heterostructure, the magnetic state of surface Fe electronic layer could be changed between ferromagnetic/anti-ferromagnetic by controlling the external electric field, i.e. the self-spinning state is controlled through an external electric field.

4. Conclusion
In conclusion, we have performed first-principles calculations to study the electronic structures and magnetic properties of BiFeO$_3$/Fe heterostructure consisting of tetragonal phase BiFeO$_3$ and Fe film. Our results reveal intriguing magnetoelectric coupling at the interface. This magnetoelectric coupling can be attributed to the electronic distribution of Fe ions caused by electric field. This means that the ferroelectronic state could control the magnetic ordering structure of the Fe layer.

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