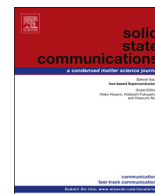




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Fast-track Communication

## Ferroelectric control of metal–insulator transition

Xu He<sup>a</sup>, Kui-juan Jin<sup>a,b,\*</sup>, Chen Ge<sup>a</sup>, Zhong-shui Ma<sup>b,c</sup>, Guo-zhen Yang<sup>a,b</sup><sup>a</sup> Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China<sup>b</sup> Collaborative Innovation Center of Quantum Matter, Beijing 100190, China<sup>c</sup> School of Physics, Peking University, Beijing 100871, China

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## ABSTRACT

We propose a method of controlling the metal–insulator transition of one perovskite material at its interface with another ferroelectric material based on first principle calculations. The operating principle is that the rotation of oxygen octahedra tuned by the ferroelectric polarization can modulate the superexchange interaction in this perovskite. We designed a tri-color superlattice of  $(\text{BiFeO}_3)_N/\text{LaNiO}_3/\text{LaTiO}_3$ , in which the  $\text{BiFeO}_3$  layers are ferroelectric, the  $\text{LaNiO}_3$  layer is the layer of which the electronic structure is to be tuned, and  $\text{LaTiO}_3$  layer is inserted to enhance the inversion asymmetry. By reversing the ferroelectric polarization in this structure, there is a metal–insulator transition of the  $\text{LaNiO}_3$  layer because of the changes of crystal field splitting of the Ni  $e_g$  orbitals and the bandwidth of the Ni in-plane  $e_g$  orbital. It is highly expected that a metal–transition can be realized by designing the structures at the interfaces for more materials.

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## 1. Introduction

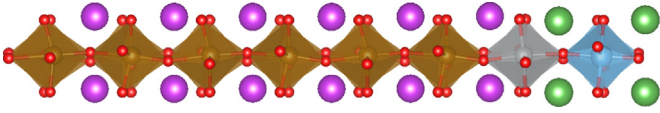
In transitional metal oxides, the strong correlation between lattice, charge, orbital, and spin leads to many novel properties. At their interfaces, even richer physics bring about emerging properties. Technical advances in the atomic-scale synthesis of oxide heterostructures make it possible for these interfaces to be artificially designed [1–3]. In perovskite oxide heterostructures where the oxygen octahedra share their vertices, the interplay among different distortion of octahedral units can dictate many novel functional properties [4]. One kind of interfaces between ferroelectric and other materials, of which the electronic properties are to be controlled, is very interesting because of the bi-stable property, with which two states can be reached by reversing the ferroelectric polarization with an electric field, with both changes from structure and from electric polarization involved. The controlling of the electronic structure can be through either the change of electric boundary condition [5], or structural distortion [6]. In this paper, we propose a strategy to control the electronic bandwidths and to achieve a metal–insulator transition in a material by stacking it onto a ferroelectric layer resulting in a modulation of structural distortion.

In this work, we use  $\text{LaNiO}_3$  as the electronic active material, of which the band gap is to be controlled. Nickelates, with the chemical formula  $\text{RNiO}_3$ , have a prominent feature that there is a metal–insulator transition connected to the sizes of the R site ions by the rotation angles of octahedra [7]. The rotation of the octahedra can also be controlled by a strain, causing many works on the straining control of the electronic structure of nickelates such as in Refs. [8–10]. In addition, nickelate heterostructures have drawn great attentions since Chaloupka and Khaliullin proposed the possible superconductivity by modulating the orbitals [11]. With the proposed structure, the orbital occupations can also be tuned. We chose  $\text{BiFeO}_3$  as the ferroelectric material because of its large polarization. It has a relative small band gap, which enables it to be used as semiconductor materials such as in switchable diodes [12–15], therefore it is easier for charges to transfer from or to  $\text{BiFeO}_3$ . One can make use of this effect to manipulate the charge transfer.

By stacking a ferroelectric and non-ferroelectric layers together, it is natural to think that the electronic properties can be tuned by reversing the ferroelectric polarization. While it is true for the asymmetric thin films, in a periodic superlattice, the structures of the two polarization states are the same (or very similar) by a  $180^\circ$  rotation if the two interfaces of a non-ferroelectric to the ferroelectric are the same (or very similar). For example, in a  $(\text{BiFeO}_3)_N/\text{LaNiO}_3$  superlattice, the two sides of  $\text{LaNiO}_3$  are the  $\text{LaO}$  and  $\text{BiO}$  planes. Since the La and Bi ions are close in radius and the same in

\* Corresponding author at: Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China.

E-mail address: [kjjin@iphy.ac.cn](mailto:kjjin@iphy.ac.cn) (K.-j. Jin).



**Fig. 1.** (Color online) The structure of the  $\text{BiFeO}_3/\text{LaNiO}_3/\text{LaTiO}_3$  superlattice in the  $ac$  plane view. The purple, brown, red, green, gray, and blue balls represent the Bi, Fe, O, La, Ni, and Ti atoms, respectively.

valence states, large difference in electronic properties caused by reversing the polarization is not expected.

A method to enlarge the difference is to make the structure more asymmetric by inserting another layer. By inserting a  $\text{LaTiO}_3$  layer, tri-color superlattices of  $(\text{BiFeO}_3)_N/\text{LaNiO}_3/\text{LaTiO}_3$  are formed as shown in Fig. 1. According to Chen et al. [16], in  $\text{LaTiO}_3$ , the  $\text{Ti}^{3+}$  ion has a  $3d$  electron with energy higher than that of the unoccupied  $\text{Ni } e_g$  band in  $\text{LaNiO}_3$ . Therefore electrons can transfer from Ti to Ni, forming a  $\text{Ti } d^0$  and a  $\text{Ni } d^8$  configuration [17], so there is an electric polarization pointing from  $\text{LaNiO}_3$  to  $\text{LaTiO}_3$  at their interface. Thus the structures with opposite ferroelectric polarizations also differ in polarization continuity, which offers another way of controlling the electronic property by reversing the ferroelectric polarization. In the  $\text{LaNiO}_3/\text{LaTiO}_3$  heterostructures, the crystal field splitting of the  $\text{Ni } e_g$  orbitals is largely affected by the distortion of the oxygen octahedra caused by the polarity of the structure [16]. Thus the control of the ferroelectric polarization in the tri-color superlattice can also tune the electronic structure by influencing the octahedra distortion.

## 2. Methods

We carried out first principle calculations to investigate the ferroelectric controlled metal-insulator transition in the superlattices. We set 6 layers of  $\text{BiFeO}_3$  in one supercell of  $(\text{BiFeO}_3)_N/\text{LaNiO}_3/\text{LaTiO}_3$  ( $N=6$ ) in our models as shown in Fig. 1. The spontaneous polarization of the bulk  $\text{BiFeO}_3$  is along the [111] direction of the pseudo-cubic unit. With the compressive strain, the in-plane polarization tends to be suppressed so that the total polarization rotates towards [001]. When the in-plane lattice constant is about  $3.71 \text{ \AA}$ , the  $\text{BiFeO}_3$  only films tend to transform to a “ $T$ -like” phase with a large  $c/a$  ratio about 1.2 to 1.3 and a large polarization approximately along [001] [18,19]. However, in the  $(\text{BiFeO}_3)_6/\text{LaNiO}_3/\text{LaTiO}_3$  structure, the cooperative shift of the Bi ions along the out-of-plane direction is impeded by the  $\text{LaNiO}_3$  and  $\text{LaTiO}_3$  layers. Thus, the  $\text{BiFeO}_3$  layers are in the “ $R$ -like” phase with the  $c/a$  ratio of about 1.1 and the out-of-plane polarization of about  $60 \mu\text{C}/\text{cm}^2$ , which is alike to the  $\text{BiFeO}_3$  films with in-plane lattice constants larger than  $3.71 \text{ \AA}$ . Here we only make use of the out-of-plane component of the polarization, because the only change of the structure by reversing of the in-plane component is a rotation around the out-of-plane axis and there is no difference in the electronic structure. Therefore we refer the polarization to the out-of-plane component of it in this paper. We define the state which the ferroelectric polarization orientation pointing from  $\text{LaNiO}_3$  to  $\text{LaTiO}_3$  as  $+P$ , while the state with opposite polarization as  $-P$ . A  $\sqrt{2} \times \sqrt{2}$  pseudo-cubic in-plane lattice was used so that the oxygen octahedra can rotate freely. We kept the  $ab$  in-plane lattice parameters fixed as  $3.71 \text{ \AA}$ , which is the LDA value of the substrate of  $\text{LaAlO}_3$ , and relax all the other degrees of freedom of the structure. The  $G$ -type antiferromagnetic structure was found to be stable in the  $(\text{BiFeO}_3)_6/\text{LaNiO}_3/\text{LaTiO}_3$  structure.

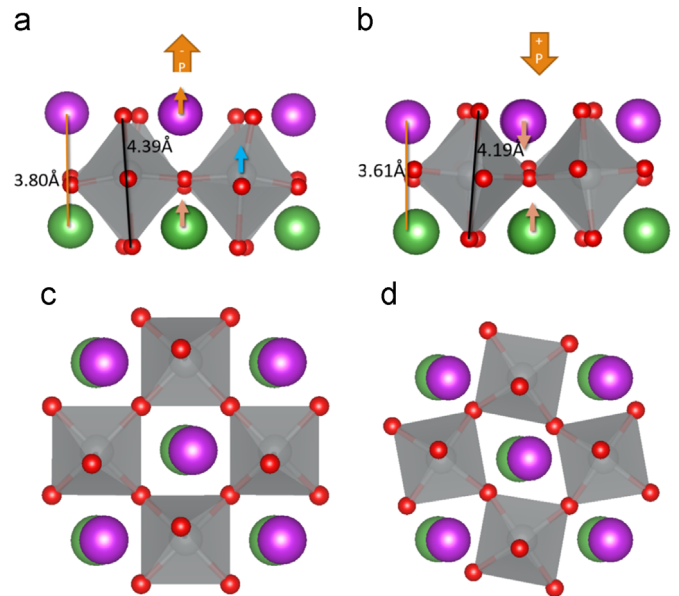
We performed the density functional theory (DFT) calculation based on the projected augmented wave [20] (PAW) and local spin density approximation (LSDA) [21] +Hubbard  $U$  method [22] as implemented in the Vienna  $ab initio$  simulation package (VASP) [23]. The filled valence states include the orbitals  $5d6s6p$ ,  $3d4s$ ,

$5p5d6s$ ,  $3s3p3d4s$ ,  $3s3p3d4s$ , and  $2s2p$  for Bi, Fe, La, Ni, Ti, and O, respectively. A plane-wave basis set with energy cutoff of  $500 \text{ eV}$  and a  $5 \times 5 \times 2 \Gamma$ -centered  $k$ -point grid were used. The structures were relaxed until the forces are less than  $0.03 \text{ eV/\AA}$ . Though the LSDA + $U$  method cannot well describe the paramagnetic and insulating ground state in bulk  $\text{LaTiO}_3$  simultaneously, it can describe the  $\text{LaNiO}_3/\text{LaTiO}_3$  structure [16]. Effective  $U(\text{Ni})=0 \text{ eV}$ ,  $U(\text{Ti})=4 \text{ eV}$ , and  $U(\text{Fe})=6 \text{ eV}$  are used throughout the work we presented here unless otherwise stated. The  $U(\text{Fe})$  is used only to make the band gap of  $\text{BiFeO}_3$  close to the experiment value. By following Ref. [16],  $U(\text{Ti})=4 \text{ eV}$  was used to better align the Ti and Ni bands. We also found that  $U(\text{Ti})$  has no significant effect on the overall results, because the Ti  $3d$  bands are higher than the Ni  $3d$  bands and are thus almost empty no matter how large the  $U(\text{Ti})$  is. Disa et al. [24] used the  $U(\text{Ni})$  of 0 in a similar structure of  $\text{LaAlO}_3/\text{LaNiO}_3/\text{LaTiO}_3$  and they found good agreement with the experimental results. We also compared the results with a series of  $U(\text{Ni})$  ranging from 0 to  $6 \text{ eV}$  to see the effect of the Coulomb repulsion.

Two sets of maximally localized Wannier functions (MLWFs) [25] were constructed to investigate the mechanism of the metal-insulator transition using the Wannier90 package and its interface to VASP [26]. The first set of MLWFs is  $d$  band only, each function is of hybridized transitional metal  $3d$  orbital and the neighboring O  $2p$  feature. The other set of WLWFs, which is constructed to calculate the layer resolved polarization, consists of all the occupied-orbital-like wave functions.

## 3. Results and discussion

In the  $(\text{BiFeO}_3)_N/\text{LaNiO}_3/\text{LaTiO}_3$  structure, the bands near the Fermi energy are  $e_g$  bands of Ni. We first look into the local structural distortions near the  $\text{LaNiO}_3$  layer as shown in Fig. 2. The charge transfer between the  $\text{LaTiO}_3$  and  $\text{LaNiO}_3$  stays the same as in  $\text{LaNiO}_3/\text{LaTiO}_3$  superlattices. La ions between  $\text{NiO}$  and  $\text{TiO}$  planes move towards the  $\text{NiO}$  plane to compensate the dipoles caused by the charge transfer. Bi ions at the  $\text{BiFeO}_3/\text{LaNiO}_3$  interface shift away from the  $\text{NiO}$  plane in the  $-P$  state because of the ferroelectric polarization, while they shift towards the  $\text{Ni-O}$  plane



**Fig. 2.** (Color online) The structure near the  $\text{LaNiO}_3$  layer. (a) The  $-P$  state, the  $ac$  plane view. The brown arrows on the Bi and La atoms show the shifts of them. The blue arrow shows the shift of the Ni atom. (b) The  $+P$  state, the  $ac$  plane view. (c) The  $-P$  state, the  $ab$  plane view. (d) The  $+P$  state, the  $ab$  plane view. The red arrows show the rotation of the oxygen octahedron.

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