Engineering charge ordering into multiferroicity

Xu He1 and Kui-juan Jin1,2,*

1Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China
2Collaborative Innovation Center of Quantum Matter, Beijing 100190, China

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Multiferroic materials have attracted great interest but are rare in nature. In many transition-metal oxides, charge ordering and magnetic ordering coexist, so that a method of engineering charge-ordered materials into ferroelectric materials would lead to a large class of multiferroic materials. We propose a strategy for designing new ferroelectric or even multiferroic materials by inserting a spacing layer into each two layers of charge-ordered materials and artificially making a superlattice. One example of the model demonstrated here is the perovskite (LaFeO3)2/LaTiO3 (111) superlattice, in which the LaTiO3 layer acts as the donor and the spacing layer, and the LaFeO3 layer is half doped and performs charge ordering. The collaboration of the charge ordering and the spacing layer breaks the space inversion symmetry, resulting in a large ferroelectric polarization. As the charge ordering also leads to a ferrimagnetic structure, (LaFeO3)2/LaTiO3 is multiferroic. It is expected that this work can encourage the designing and experimental implementation of a large class of multiferroic materials with novel properties.

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Multiferroic materials have attracted great interest, but there are few magnetic ferroelectric materials [1]. Recent technical advances in the atomic-scale synthesis of oxides make it possible to artificially design [2–4] composite structures, which paves the way for engineering materials to obtain novel properties. Thus, strategies of designing multiferroic structures can be developed. For instance, hybrid improper ferroelectrics [5–8] with ABO3/ABO3 ordered superlattice structures were designed by engineering the perovskite ABO3. In these materials, the antiferroelectric rotation mode of B-O octahedra and the A-site ordering are brought together to form cooperative polar distortion.

Though most of ferroelectrics are induced by geometric distortion, there is a group of materials in which ferroelectricity is induced by charge ordering, as observed in perovskite manganites (PrCa)MnO3 [9], magnetite Fe3O4 [10], quasi-one-dimensional organics [11], the frustrated charge-ordered LuFe2O4 [12], and complex manganites RMn2O5 [13]. Meanwhile, many materials with charge ordering are nonferroelectric. Here we propose a method to design ferroelectric structures (or multiferroic structures if ferromagnetism is already exhibited in them) by making use of the charge-ordering properties in these materials. The designing rule is to insert a spacing layer into each two layers of these charge-ordered materials and to make the structure as superlattice. Due to the multivalence nature of transition-metal elements, transition-metal oxides with charge ordering are abundant, and many of them are magnetic. Thus, by modifying them into ferroelectrics, a large class of multiferroics can be expected. Currently, there are only a few identified charge-ordering-induced multiferroic materials, in some of which the mechanisms of the multiferroicity are still controversial [14]. Although there are a lot of charge-ordered materials, no general rule for identifying which of them are multiferroic has been found yet. The artificial designing of charge-ordering-induced multiferroic materials would not only greatly increase the variety of these materials but also set up a platform for testing the microscopic mechanisms of charge-ordering-induced multiferroicity.

To demonstrate the mechanism of ferroelectricity induced by charge ordering, we start from a simple one-dimensional chain. There are two kinds of charge ordering, namely, the site-centered charge ordering and the bond-centered charge ordering as shown in Figs. 1(a) and 1(b), respectively. The former is that the electrons distribute alternately among sites so the charges on the neighboring sites are inequivalent; the latter is that the neighboring bonds become inequivalent. Neither of the two kinds alone leads to ferroelectricity as the space inversion symmetry is preserved, but the combination of both of them leads to a ferroelectric polarization, as shown in Fig. 1(c). The theories and experimental results on charge-ordering-induced ferroelectricity are reviewed in Refs. [14,15].

In the present work, the main point is to establish a method of designing superlattices by introducing the bond-centered charge ordering to the site-centered charge-ordered materials so that they become ferroelectric. The scheme of our design is shown in Fig. 1(d). The charge ordering due to the multivalence property of the transition-metal elements is mostly site centered. Layers of charge-ordered material A with two valence states denoted as A1 and A2 are aligned alternately, forming an A1A2A1A2 pattern. Our designing principle is simply using the analogy to the one-dimensional (1D) chain: the space inversion symmetry needs to be broken by two kinds of bonds between A1 and A2. By inserting a spacing layer of B into each two A layers, the pattern becomes A1A2B1A2A1A2B as shown in Fig. 1(d). If the A1–B–A1 is viewed as a kind of bond between A1 and A2, the two kinds of bonds of A1–A2 and A2–B–A1 are ordered. Thus, both site-centered charge ordering and bond-centered charge ordering exist in the (A1)2/B superlattice, leading to the ferroelectricity.

For a proof of the concept, we use LaFeO3 and LaTiO3 as A and B, respectively, and stack them along the [111] direction. The structure is shown in Figs. 2(a) and 2(b). Based on density functional calculations, we show the multiferroicity

*Corresponding author: kjjin@iphy.ac.cn
induced by charge ordering in (LaFeO$_3$)$_2$/LaTiO$_3$ superlattice. Charge ordering is absent in LaFeO$_3$ by nature, therefore doping is needed. We used the LaTiO$_3$ layer not only as a spacing layer to break the space inversion symmetry, but also as an electron donor layer, which donates one electron to each two LaFeO$_3$ units. Thus half the Fe ions in LaFeO$_3$ become Fe$^{2+}$, while the other half or the ions remain Fe$^{3+}$. We found that charge ordering is formed in the LaFeO$_3$ layers along the [111] direction. So the (111) superlattice was designed so that the analogy to the 1D case is valid. With the charge ordering and the spacing layer, the structure is ferroelectric. The charge ordering in the present structure also introduces the ferrimagnetism. Thus, (LaFeO$_3$)$_2$/LaTiO$_3$ is multiferroic.

The first-principle calculations were performed with local spin density approximation (LSDA) [16] and projector augmented wave (PAW) [17] method as implemented in the Vienna *ab initio* simulation package [18] (VASP). We used a plane-wave basis set with the energy cutoff of 500 eV and a 5 × 5 × 5 $\Gamma$-centered $k$ points to integrate the Brillouin zone. The electron configurations of La 5s$^2$5p$^6$5d$^1$6s$^2$, Fe 2p$^6$3d$^6$4s$^2$, Ti 2s$^2$2p$^6$3d$^1$, and O 2s$^2$2p$^6$ were used. A Hubbard-like correction [19] with $U$(Fe) = 4.8 eV and $U$(Ti) = 3.0 eV is used to better describe the on-site electron-electron interaction in the transition-metal elements [20]. The structures are fully relaxed until the residual forces are below $10^{-3}$ eV/Å. The ferroelectric polarization was calculated using the maximally localized Wannier function [21] (MLWF) method, which is equivalent to the Berry phase approach [22,23]. The MLWFs were constructed using the WANNIER90 program and the VASP interface to it [24]. We also checked the value using the Berry phase method. Since the ferroelectricity in the structure is supposed to result from the transferring of the electrons, the MLWF method was used so that we could track the Wannier centers and gain some intuition on how the ferroelectric polarization is formed.

The scheme of the ferroelectricity induced by the charge ordering in the (LaFeO$_3$)$_2$/LaTiO$_3$ (111) structure is shown in Fig. 3. The following conditions need to be satisfied to ensure the structure being ferroelectric: (1) Electrons transfer from LaTiO$_3$ to LaFeO$_3$, otherwise all the Fe ions have the
formal valence +3 [as shown in Fig. 3(a)]. (2) The electron doped into LaFeO3 only localizes in every other Fe ion, so the Fe ions have mixed valences of +2 and −3 [as shown in Fig. 3(d) or 3(e)], otherwise no charge ordering in LaFeO3 can be developed [as in Fig. 3(b)]. (3) The alignment of the Fe2+−Fe3+ should be in-phase like that shown in Fig. 3(d) or 3(e), otherwise no long-range ferroelectric domain can be formed [as in Fig. 3(c)]. With all the above three conditions satisfied, the space inversion symmetry is broken and there is a macroscopic polarization in the structure as shown in Figs. 3(d) and 3(e).

In the following text, we will discuss the three conditions and the ferroelectric polarization in the (111) superlattice of (LaFeO3)2/LaTiO3 in more detail.

First, we discuss the electron transfer from the LaTiO3 layers into LaFeO3 layers. We used the LaTiO3 as the electron donor because the Ti3+ electrons of Ti3+ tend to transfer to Fe3+ [20,25]. We found that each LaTiO3 unit dopes about one electron into the LaFeO3 in the (LaFeO3)2/LaTiO3 (111) structure. The reconstruction of the Hubbard bands is the origin of the charge transfer, as Zhang et al. suggested [25]. The bulk LaTiO3 is a Mott-Hubbard insulator, in which each Ti ion has one electron on its t2g orbital. In bulk LaFeO3, the Fe has a d5 electronic configuration, and the conduction band minimum (CBM) is the unoccupied Fe 3d bands. The CBM of LaFeO3 is higher than the occupied t2g bands in LaTiO3. However, if a Ti t2g electron transfers to the Fe site, the Fe 3d bands would be reconstructed due to the on-site Coulomb interaction, so that the transferred electron to the Fe bands would have lower energy than the occupied Ti t2g bands. Therefore, the charge transfer is energetically favorable, resulting in the Ti 3d0 electronic configuration and half doping in Fe ions, as shown in Fig. 4.

Secondly, we discuss the charge ordering in the nearest LaFeO3 units. Each LaTiO3 unit dopes about one electron into two LaFeO3 units. The electron can either be shared by the two units equally (i.e., all Fe ions have the formal valence of +2.5) or be localized in one of them (i.e., Fe ions have mixed formal valences of +2 and +3). We compared the electronic structures without and with the charge ordering. The results of the density of states are shown in Fig. 5. Without mixed valence of the Fe ions developed in LaFeO3, the structure is metallic [Fig. 5(a)]. Otherwise, the structure becomes insulating [Fig. 5(b)]. We found that the structure with Fe site charge ordering is about 0.75 eV per formula unit (f.u.) lower in energy than that without charge ordering.

The localization of the doped electrons is because of the on-site Coulomb interaction of Fe electrons and the expansion of the Fe-O octahedra around the doped electrons staying on the Fe t2g orbitals. If the doped electron localizes on one Fe site, the on-site Coulomb interaction lowers the energy of the electron (more details are in Supplemental material Fig. S1 [26]). Also, the expansion of the octahedron decreases the Coulomb energy of the doped electron as the distances of the electron on the Fe site to the negatively charged O anions are reduced.

The charge-ordering modes in the LaFeO3 layers sandwiched in LaTiO3 layers were explored (more details are in Supplemental Material Fig. S2). The breathing mode charge ordering was found to be energetically favorable, in which the distribution of the doped electrons is shown in Fig. 2(c). Thus the LaFeO3 units in the same (111) plane are equivalent, and Fe2+ and Fe3+ align alternately along the [111] direction. All the neighboring Fe ions of the Fe2+ are Fe3+, and vice versa, as shown in Fig. 2(d). The breathing mode distortion of the Fe-O octahedra is the reason for the charge ordering in two LaFeO3 layers connected to each other due to the octahedron-vertex sharing structure in perovskites. The volumes of the Fe2+O octahedron and Fe3+O octahedron are 11.2 and 10.0 Å³, respectively (details of the Fe-O bond lengths are in Supplemental Material Fig. S3).

Thirdly, we discuss the alignment of electric dipoles along the [111] direction. In each unit of (LaFeO3)2/LaTiO3, there is an electric dipole of (LaTi4+O3)+ − (LaFe2+O3)−. The dipoles in the chain along the superlattice can align in-phase or out-of-phase, which correspond to two kinds of Fe valence alignments, namely, the Fe3+.Ti4+.Fe2+.Fe3+.Ti4+.Fe2+...
alignment [Fig. 3(d)] and the Fe$^{3+}$-Ti$^{4+}$-Fe$^{3+}$-Ti$^{4+}$-Fe$^{3+}$ alignment [Fig. 3(c)]. The in-phase alignment leads to a ferroelectric domain; the out-of-phase alignment can be the elasticity of the electronic structure cannot converge to the out-of-phase case, implying 180° electric domain; the out-of-phase alignment can be seen as the in-phase alignment [Fig. 3(c)]. The in-phase alignment leads to a ferroelectric polarization [Fig. 3(d)] and the Fe$^{3+}$ ions [28] (more details are in Supplemental Material Fig. S4). The antiferromagnetic interaction results in the spontaneous polarization about (214 + 30.9n) μC/cm$^2$, with n being an integer.

In the present work, we propose a method to engineer charge-ordered materials into ferroelectric materials or even multiferroic materials with magnetism being already presented. By inserting one spacing layer of B into each two layers of charge-ordered material A, an (A)$_2$/B superlattice is formed, in which the space inversion symmetry is broken, leading to the ferroelectricity. We designed a (LaFeO$_3$)$_2$/LaTiO$_3$ superlattice as a proof of the concept and investigate it by ab initio calculations. The antiparallel alignment of spins in Fe$^{3+}$...
and Fe$^{3+}$ leads to a total net magnetic moment, so the structure is also ferrimagnetic. Using the strategy proposed in this work, it can be ensured that the inversion symmetry is broken in the charge-ordered materials. Further designing and experimental implementing of a large class of new multiferroic materials stimulated by this work are highly expected.

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