Structure, strain, and control of ground state property in LaTiO$_3$/LaAlO$_3$ superlattice

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Using first-principles density functional theory calculations, we examined the ground state property of LaTiO$_3$/LaAlO$_3$ superlattice. Total energy calculations, taking account of the structural distortions, $U$ dependence, and exchange correlation functional dependence, show that the spin and orbital ground state can be controlled systematically by the epitaxial strain. In the wide range of strains, ferromagnetic spin and antiferro orbital ordering are stabilized, which is notably different from the previously reported ground state in titanate systems. By applying large tensile strains, the system can be transformed into an antiferromagnetic spin and ferro-orbital-ordered phase.

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I. INTRODUCTION

Transition-metal oxide (TMO) heterostructures have attracted great attention in recent years due to their intriguing material characteristics and potential applications [1, 2]. Unexpected interface phenomena caused by the heterostructuring and the band structure change have been reported such as magnetism [3-5] and superconductivity [6, 7]. Importantly, the material property can be altered by the epitaxial strain through the strong couplings in TMO between the charge, spin, orbital, and lattice degrees of freedom [10, 11]. For example, previous studies have shown that the superconducting [12, 13], ferromagnetic (FM) [14], and metal-insulator transition temperature [15, 17] can be controlled by the strain.

LaTiO$_3$/LaAlO$_3$ (LTO/LAO) is an example that shows a significantly different electronic structure due to the quantum confinement [18]. A recent in-plane and out-of-plane optical conductivity measurement in combination with LDA+$U$ calculation demonstrated that the electronic structure of a classical Mott insulator, LTO, is significantly changed by making a heterostructure. In this study by Seo et al., antiferromagnetic (AFM) spin and ferro orbital order (OO) with one electron occupying Ti-$d_{xy}$ has been suggested as the ground state configuration [18]. The lifted degeneracy and the low-lying $d_{xy}$ band caused by the translational symmetry breaking along the c-axis also play an important role in SrTiO$_3$/LaAlO$_3$ (STO/LAO), which has been actively studied recently [4-8].

We note that the effect of strain and structural distortion have not been examined in detail in the previous studies of titanate superlattices. Most calculations, for example, do not consider the rotational degrees of freedom of the oxygen octahedra around the Ti ions in the superlattices [18, 21]. Importantly, however, the structure and strain can play crucial roles in determining the ground state spin and orbital configuration. Considering the structural property of bulk LTO, the possible rotation and distortion should be investigated carefully.

In this work, we examined LTO/LAO superlattice using first-principles density functional methods. Our calculations show that the spin and orbital ground state, which are qualitatively different from the previously reported $d_{xy}$-AFM phase, can be stabilized. Due to the interplay between spin, orbital, and lattice degrees of freedom, the FM spin and antiferro orbital order is stabilized in a wide range of strains while the AFM and ferro OO can be realized by applying ~2.8% of tensile strains. Our results suggest a possible way of controlling the ground state properties of TMO superlattices.

II. CALCULATION METHOD

The projector augmented wave (PAW) potentials [22] are adopted in our calculations. For the exchange-correlation functional, we used both the generalized gradient approximation (GGA) proposed by Perdew et al. (PBE) [23] and the revised PBE (PBEsol) [24] as implemented in the VASP code [25]. GGA+$U$ scheme was used to describe the effect of correlation with the functional form proposed by Liechtenstein et al. [26]; $U_{Ti}=3$ and 5 eV, and $J_{Ti}=0.5$ eV. Lattice parameters of the bulk orthorhombic LTO are shown in Table I. It is noted that the calculations with $U=5$ overestimate the experimental lattice parameters, while, with $U=3$, the differences are reduced. We examined our system with the four different sets: PBE or PBEsol and $U=3$ or 5 eV. The changes caused by these settings are found to be mostly quantitative. The only notable change was found in the rotation pattern of the (LTO)$_2$(LAO)$_2$ superlattice (see Sec.III.D). In this case, the relative stabilization

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energy among the various possible rotation patterns (i.e., the relative rotation angles of oxygen octahedral cages) is sometimes changed by $U$ value and the energy difference is typically an order of a few meV per LTO/LAO. Importantly, for a given structure, the ground state spin and orbital ordering patterns are found to be always the same. In this manuscript, we mainly present the result of PBE and $U=3$ for the distorted structure, as the Mott gap of LTO by optical spectra [27], $\Delta \sim 0.2$ eV, is in better agreement with the result of $U=3$ ($\Delta \sim 0.56$ eV) than that of $U=5$ result ($\Delta \sim 1.88$ eV). Since the gap is not opened with $U=3$ eV for the case of tetragonal structure (with no distortion), we present $U=5$ result in Sec.III.A.

We used the $2a \times 2b$ supercell, where the in-plane lattice parameter is fixed to the STO value ($2a_0=2a=2b=7.81$ Å). It should be noted that the most stable distorted structure we found in this study cannot be obtained with the $\sqrt{2} \times \sqrt{2}$ supercell. To check the magnetic stability, we considered all possible magnetic configurations and compared their total energies.

III. RESULTS AND DISCUSSION

A. Tetragonal structure

The bulk LTO has the lattice parameter of $a=3.972$ and the GdFeO$_3$-type distortion ($Pbnm$), while LAO has $a=3.778$ [24] and $Imma$ under the tensile strain [30]. Therefore, our system LTO/LAO can also have the structural distortion. In this subsection, we first focus on the tetragonal structure without such distortions to clarify their effects (see Fig.1(a)-(b)). In bulk LTO, the lowest-$t_{2g}$ band is formed by the mixture of $d_{xy}$, $d_{yz}$, and $d_{xz}$ orbitals, while the amount of their mixture depends on the position of Ti atoms [31, 33]. On the other hand, in many Ti-based superlattices, it is believed that the $d_{xy}$ band is in the lowest energy due to the quantum confinement caused by heterostructuring. A recent X-ray absorption linear dichroism measurement for STO/LAO [8] reported that the position of $d_{xy}$ band is lowered and the $d_{yz}/d_{zx}$ degenerate in higher energy. Previous calculations (without considering GdFeO$_3$-like distortion) for STO/LAO [30] and LTO/LAO [18] also concluded that the lowering of the $d_{xy}$ band occurred due to the confinement.

However, as the spin, orbital, and structural degrees of freedom are strongly coupled in these systems, the $t_{2g}$-band split in LTO/LAO superlattice may not be as simple as previously reported. Even in the tetragonal phase, we found that the $t_{2g}$ band split is sensitive to the in-plane and out-of-plane lattice parameters and the lowest-lying $t_{2g}$ band can be reversed by strain. In Fig. 2(a), we present the calculated total energies as a function of $c/(2a_0)$ and of the orbital configuration with $U=5$. As the $c/(2a_0)$ ratio varies, there are two minima in the total energy curve. At around the first minimum of $c/(2a_0)=0.995$ ($c_{LTO}=4.06$ Å and $c_{LAO}=3.72$ Å), the $d_{xy}$ orbital occupation is stabilized. This is the state obtained by the previous LDA+U calculation [18], where the lattice parameters have been obtained by the extrapolation from the experimentally determined values of the unit-

| System | Type | $a$ | $b$ | $c$ |
|--------|------|-----|-----|-----|
| Bulk LTO | PBE ($U=3$) | 3.987 | 3.987 | 7.982 |
| | PBE ($U=5$) | 4.082 | 4.082 | 8.051 |
| | PBEsol ($U=3$) | 3.944 | 3.944 | 7.875 |
| | PBEsol ($U=5$) | 4.082 | 4.082 | 7.983 |
| | PBE ($U=3$) | 3.905 | 3.905 | 7.998 |
| | PBE ($U=5$) | 3.905 | 3.905 | 8.025 |
| | PBEsol ($U=3$) | 3.905 | 3.905 | 7.828 |
| | PBEsol ($U=5$) | 3.905 | 3.905 | 7.862 |

TABLE I: The optimized lattice parameters with the different $U$ values and the exchange correlation functionals.
cell and the geometrical relaxation was performed within the cell. Fig. 2(b) shows the ground state spin density of this \( d_{xy} \)-ordered phase. AFM spin order is stabilized over FM by 55 meV per LTO/ LAO, which is consistent with the conclusion of Ref. 18.

As the \( c \) lattice parameter increases (within the tetragonal symmetry; with no distortion), a new orbital ordered phase stabilizes at \( c/(2a_0)=1.015 \) (\( c_{\text{LTO}}=4.22 \) Å and \( c_{\text{LAO}}=3.73 \) Å) in which the electron occupies \( (d_{yz} \pm d_{zx})/\sqrt{2} \) orbitals for Ti(1) and Ti(2), respectively (see Fig. 2(c)). This antiferro OO is more stable than the previously discussed ferro OO \( (d_{xy}) \) by 0.29 eV per LTO/LAO. The spin order is a checkerboard AFM, as shown in Fig. 2(c), which is more stable than FM by 6.8 meV per LTO/LAO.

The change of the orbital occupation as a function of \( c/(2a_0) \) can be understood by examining the Ti–O bond lengths. Since the STO substrate imposes the in-plane compressive strain onto the LTO layer, the out-of-plane Ti–O bond is elongated. As a result, the out-of-plane bond length of the \( (d_{xz} \pm d_{zx})/\sqrt{2} \)-phase is longer than that of the \( d_{xy} \)-phase by 0.08 Å, while the in-plane bond lengths remain the same. The reduced Coulomb repulsion is, therefore, responsible for the \( d_{y,z,x} \) configuration becoming stabilized.

B. Distorted structure

As mentioned, considering the structural distortions in the bulk LTO and the strained LAO, it is important to study the possible distortions such as the oxygen octahedra rotations and their impact on the electronic structure and magnetic property. From our total energy calculations, the most stable structure of \( \text{(LTO)}_{1}/(\text{LAO})_{1} \) is presented in Figs. 1(c)-(d) and Fig. 3(a)-(b), which is similar to the \( P2_1/m \) structure (\( a^+b^-c^- \) in Glazer notation). This structure is more stable than the tetragonal phase (with no rotation) by 0.93 eV per LTO/ LAO with \( U=5 \). The calculated band gap by \( U=3 \) is 0.74 (Figs. 3(c)-(d)) while that of \( U=5 \) is 2.06 eV. The \( c/(2a_0) \) of this phase is 1.023, which is longer than that of the tetragonal \( d_{xy} \)-phase (see Fig. 2(a)).

Interestingly a different type of OO is found to be stabilized in the distorted structure. As presented in Figs. 3(a)-(b), \( d_{yz} \) and \( d_{zx} \) orbitals are singly occupied at Ti(1) and Ti(2) site, respectively. Again, the ground state OO can be understood by considering the bond length and the electrostatic energy: two in-plane bond lengths, Ti(1)–O(1) and Ti(1)–O(2), are 2.063 and 1.970 Å, respectively, while the out-of-plane Ti–O is 2.135 Å (see Fig. 3(b)). Therefore, the \( d_{yz} \) configuration at Ti(1) minimizes the Coulomb repulsion between the electrons. The same argument holds for \( d_{zx} \) at Ti(2) since the distances of Ti(2)–O(2) and Ti(2)–O(3) are 2.073 and 1.964 Å, respectively.

The ground state spin structure is also changed accordingly. Different from the checkerboard AFM in the tetragonal phase, the FM spin order is favored in this \( P2_1/m \) structure having the less total energy than AFM by 11.3 meV per LTO/ LAO. The stabilization of FM spin order is again well understood by the superexchange mechanism, which is consistent with the Ti(1)–O(1)/Ti(1)–O(2) OO. It is important to note that, by making heterostructure, FM ground state has been realized out of the AFM material, LTO. Our results demonstrate a possible control of the ground state property. Figs. 3(c) and (d) show the projected density of states (DOS) of Ti-\( t_{2g} \) orbitals. One can clearly see the bandwidths of \( d_{yz} \) and \( d_{zx} \) below Fermi level are quite small \( \sim 0.52 \) eV due to the two dimensional confinement.

C. The effect of strain

Considering the strong interplay between spin, orbital, and lattice degrees of freedom, one may expect the possible control of the ground state properties of this superlattice by epitaxial strain. In order to address this point, we performed the calculations with the three different in-plane lattice parameters: i) \( a = b = 3.905 \) Å (corresponding to STO substrate as discussed so far; \(-2.1\% \) of compressive strain to LTO layer), ii) \( a = b = 4.022 \) Å (PrScO\(_3\) (PSO) substrate; \(+0.9\% \) tensile strain), and iii) \( a = b = 4.100 \) Å (\(+2.8\% \) tensile strain).

As schematically summarized in Fig. 4, the ground state spin and orbital configuration is changed as a function of strain. While the FM spin and antiferro OO is stabilized under the compressive and moderate tensile strain, the AFM spin and ferro OO is stabilized under...
D. The case of (LTO)$_2$/LAO$_2$

In order to understand the thickness dependence we performed the calculations for (LTO)$_2$/LAO$_2$. As the layer thickness increases, more structural distortions can be stabilized. At $a = 3.905$, the most stable structure is the one in which two in-plane rotation angles of TiO$_6$ octahedra are the same in their signs. The ground state configuration of the spin, orbital, and lattice is shown in Figs. 5(a)-(b). The spins are ferromagnetically aligned within the $ab$-plane and antiferromagnetically along the out-of-plane direction. As in the case of (LTO)$_1$/LAO$_1$, the $d_{yz}/d_{zx}$ in-plane OO is accompanied with the structural distortion and the spin order. Along the out-of-plane direction, the $d_{yz}/d_{zx}$ occupation is alternating in such a way that the occupied orbitals make some tilting angles between the layers, as clearly seen in Fig. 5(b). This OO is found to be more stable energetically than other types (with the same spin order) by 1.1–2.6 meV per LTO/LAO.

Under the tensile strain, the ground state configuration can be changed. As in the case of (LTO)$_1$/LAO$_1$, at $a = 4.100$ (the tensile strain of +2.8%), the $d_{xy}$ orbital is singly occupied and the checkerboard AFM is stabilized within the $ab$-plane. Along the out-of-plane direction, the spin order is AFM, and therefore G-type spin order, is stabilized as shown in Fig. 5(c). The in-plane rotation angles are also same in their signs, as shown in Fig. 5(d).

IV. SUMMARY

The structural distortion and strain significantly change the ground state spin and orbital configurations in LTO/LAO superlattice. In (LTO)$_1$/LAO$_1$, the FM and antiferro OO ($d_{yz}$ and $d_{zx}$) phase is stabilized in a wide range of strain while the AFM and ferro OO ($d_{xy}$) can be realized by applying a large tensile strain of ~2.8%. Similar patterns of spin, orbital, and structural ground state are also found in (LTO)$_2$/LAO$_2$. Our result not only demonstrates the distinctive nature of the electronic and magnetic properties in the TMO heterostructures but also shows a possible way of controlling them by strain.
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[37] We note that this antiferro OO cannot be described with the 1×1 unitcell, which is the part of the reason why previous studies found the d_{xy} configuration as the ground state (Ref. [13,21]). With the same setting, we could also get this ferro OO.
[38] As mentioned in Sec.II, we mainly present U=3 eV result in this sub-section in order to present more realistic electronic structures to be compared with experiments.
[39] The strain values are estimated with respect to the optimized lattice parameter of LTO (with PBE and U=3). These values are slightly changed if the experimental lattice parameters are used as the reference: −1.7%, +1.3% and +3.2% for a = 3.905, 4.022 and 4.100, respectively.