Magnetic orders of LaTiO₃ under epitaxial strain: A first-principles study

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Perovskite LaTiO₃ bulk is a typical Mott-insulator with G-type antiferromagnetic order. In this work, the biaxial strain effects on the ground magnetic order of LaTiO₃ films grown on various substrates have been studied. For the compressive strain, LaTiO₃ films grown on LaAlO₃, LaGaO₃, and SrTiO₃ substrates undergo a phase transition from the original G-type antiferromagnet to A-type antiferromagnet. The underlying physical mechanisms are the lattice distortions tunned by strain. While for the tensile strain, the BaTiO₃ and LaScO₃ substrates have been tested, which show a tendency to transit the LaTiO₃ to the C-type antiferromagnet. Furthermore, our calculations find that the magnetic transitions under epitaxial strain do not change the insulating fact of LaTiO₃.

Perovskite oxides ABO₃ have attracted continuing attention and been intensively investigated due to their novel physical properties and a broad range of technical applications. Among abundant perovskite compounds, the canonical Mott insulator RTiO₃ (R³⁺ denotes a rare-earth ions) are physically interesting due to the complex couplings between the orbital, spin, lattice degrees of freedom of Ti’s 3d electron which is localized by the strong Coulombic interaction. In RTiO₃ perovskites, the ligand crystal field from the oxygen octahedron splits the 5-fold 3d levels into two groups: the 3-fold t₂g orbitals and the 2-fold e_g orbitals. The Fermi level is located in the t₂g levels, and the t₂g orbitals are highly localized due to the p-d hybridization. Moreover, the GdFeO₃-type structure distortions, which combine the tilts and rotations of the oxygen octahedrons, are prominent in the orthorhombic RTiO₃. According to previous studies, the ground magnetic phase of RTiO₃ transits from the ferromagnetism to G-type antiferromagnetism, with increasing size of R or in other words with weak GdFeO₃-type distortions, as shown in Fig. 1(a).

In the RTiO₃ bulks, compounds with small GdFeO₃-type distortions exhibit the G-type antiferromagnetic (AFM) ordering, e.g., LaTiO₃, and the large ones tend to lead the ferromagnetic (FM) ordering, e.g., YTiO₃. In addition, it is well known that perovskite oxides may be sensitive to external factors. For example, recently the use of epitaxial strain has attracted great attentions due to many unexpected effects on thin films, which has been proved to be a useful route to design potential devices.

In this work, the effects of epitaxial strain on the ground magnetic order of LaTiO₃ films will be studied using the first-principles calculations, as illustrated in Fig. 1(b). Our calculations predict that a robust A-type AFM phase can be stabilized by the compressive strain. In contrast, LaTiO₃ films remain G-type AFM under moderate tensile strain, but have a tendency to become the C-type AFM with further increasing the tensile strain.

LaTiO₃ has the orthorhombic structure (space group Pbnm) with the experimental lattice constants of a = 5.636 Å, b = 5.618 Å, and c = 7.916 Å, containing 4 formula units. In the following, two different strains have been considered: in-plane compressive vs tensile. Five widely used substrates have been tested, including LaAlO₃ (2√2a = 2b = 5.366 Å), LaGaO₃ (a = 5.49 Å, b = 5.53 Å), SrTiO₃ (2√2a = 2b = 5.523 Å) for the compressive case and BaTiO₃ (2√2a = 2b = 5.65 Å), LaScO₃ (a = 5.678 Å, b = 5.787 Å) for the tensile case. Here, LaTiO₃ is assumed to be grown along the most studied (001) direction. Our first-principles density-functional theory (DFT) calculations are performed using the local density approximation (LDA) method with the Hubbard U and the projector-augmented wave (PAW) potentials, as implemented in the Vienna ab initio Simulation Package (VASP). The on-site Hubbard interaction is set as U – J = 2.3 eV using the Dudarev implementation for the localized 3d electrons of Ti. The lattice constants are fixed to match the particular substrate. Then the lattice constant along the crystallographic direction and inner atomic positions are fully optimized.

The cutoff energy of plane-wave is 500 eV and the Brillouin-zone integrations are performed with the tetrahedron method over a 7 × 7 × 5 Monkhorst-Pack k-point mesh centered at Γ.

LaTiO₃

(a) RTiO₃

(b) G-AFM

G-AFM

LaTiO₃ bulk

small Ionic radius

large

FIG. 1. (a) Sketch of experimental magnetic phase diagram of RTiO₃. (b) Sketch of our motivation: LaTiO₃ films grown on various substrates under compressive or tensile strain.

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TABLE I. The energy difference and corresponding magnetic moment per Ti in unit of $\mu_B$ of unstrained bulk LaTiO$_3$: $\Delta E$ (per Ti) $\sim$ $E$(magnetic)$-E$(FM).

| Magnetic order | NM  | FM  | A-AFM | C-AFM | G-AFM |
|---------------|-----|-----|-------|-------|-------|
| $\Delta E$    | 124 | 0   | -13   | 17    | -18   |
| Magnetic moment | 0.86 | 0.80 | 0.77  | 0.75  |

First, the ground state of bulk LaTiO$_3$ has been checked. The lattice is fully optimized, giving $a = 5.615$ Å, $b = 5.549$ Å, and $c = 7.828$ Å which are close to the experimental data. The non-magnetic (NM) state and four magnetic orders: FM, A-type AFM, C-type AFM, and G-type AFM are calculated and compared in energy. As shown in Table I, the G-type AFM is the most stable state, as found in experiments. The calculated magnetic moment is 0.75 $\mu_B$/per Ti, slightly larger than the experimental result 0.57 $\mu_B$. Our DFT calculations (Fig. 3(c)) find the insulating behavior with an energy gap of 0.45 eV, in agreement with previous DFT results and a little underestimated compared with experimental value 0.2 eV, implying a Mott-insulator.

Subsequently, the effects of strain will be studied. For the compressive strain, the small lattice SrTiO$_3$, LaGaO$_3$, and LaAlO$_3$ substrates are adopted as the weak, middle, and strong cases. The internal atomic positions are relaxed with various magnetic orders within a wide range from 7.6 Å to 8.6 Å for lattice constant along the $c$-axis to search the optimized structure and ground state. The obtained equilibrium values for the $c$-axis are around 7.93 Å, 7.94 Å, and 8.14 Å for SrTiO$_3$, LaGaO$_3$, and LaAlO$_3$, respectively. In all these cases, the total energies show that A-type AFM is the most stable state with the relaxed structure, instead of the G-type AFM in bulk. Moreover, the FM and C-type AFM are much higher in energy than the A- and G-type AFMs. Therefore, in the following, only the results of A- and G-type AFMs will be presented for the compressive substrates.

The energy differences between these two orders are shown in Fig. 2(a). The A-type AFM is most robust (17 meV/Ti lower in energy) when grown on the LaAlO$_3$ substrate with the smallest in-plane lattice, while it is very fragile (only 1 meV/Ti lower in energy) on SrTiO$_3$. As shown in Fig. 2(c), epitaxial LaTiO$_3$ films on these three substrates would have a biaxial compression of about ~3.8% for LaAlO$_3$, ~1.3% for LaGaO$_3$, and ~1.0% for SrTiO$_3$, suggesting the direct relation between the magnetism and strain. In fact, our previous calculation also predicted the A-type AFM state appeared in the YTiO$_3$ film on the (001) LaAlO$_3$ substrate which is FM in bulk. The A-type AFM state does not exist in any $RTiO_3$ bulk so far, but may be obtained in compressive films despite the original states (FM or G-type AFM).

Next, the tensile strain effects will be studied in the same way, using BaTiO$_3$ and LaScO$_3$ as the substrates. The relaxed lattice constant along the $c$-axis is about 7.65 Å for LaScO$_3$ substrate and 7.75 Å for BaTiO$_3$ substrate. Different from the strain-driven phase transition in compressive cases, LaTiO$_3$ films remain in the G-type AFM order as in the bulk. In the tensile case, the FM and A-type AFM states have relatively higher energies than the G- and C-type AFM ones which are very proximate in energy. As shown in Fig. 2(b), with decreasing length of $c$-axis, the energy differences between the G- and C-type AFMs decrease, e.g., 10 meV/Ti for equilibrium length on the BaTiO$_3$ substrate, and 3 meV/Ti for the LaScO$_3$ case. These results show that the tensile LaTiO$_3$ films have an obvious tendency to be C-type AFM if further large lattice substrates are used. These new phases (the A-type and possible C-type AFMs) are physical interesting, which enrich the magnetic phase diagram of the RTiO$_3$ family.

As stated before, the Ti-O-Ti bond angles can be used as a parameter to characterize the lattice distortions in RTiO$_3$. As shown in Fig. 2(d), with increasing biaxial compression, the bond angles decrease in the $ab$-plane but increase along the $c$-axis, while the tensile strain gives the opposite trend. According to RTiO$_3$ bulk’s phase diagram, the relation between lattice distortions and magnetic orders are well-established: FM order for strong distortions (small Ti-O-Ti bond angles), AFM order for weak distortions (large Ti-O-Ti bond angles). Thus, the compressive strain, which decreases the in-plane bond angles but increase the out-of-plane one, tends to make spins arrange parallel in-plane and anti-parallel along the $c$-axis, namely the A-type AFM order. In contrast, for the tensile cases, the opposite changes of bond angles favor the AFM coupling in-plane but FM coupling along the $c$-axis, namely the C-type AFM tendency although it has not be achieved on BaTiO$_3$ and LaScO$_3$ substrates.

Moreover, for all strained LaTiO$_3$, the insulating behavior has been preserved despite the magnetic phase transitions. For example, the DOSs of LaTiO$_3$ films grown on SrTiO$_3$ and BaTiO$_3$ substrates are shown in Figs. 3(a) and 3(b), respectively. In both cases, a gap exists at the Fermi level. The states near the Fermi level is dominated by Ti $t_{2g}$ levels. The tiny
difference of DOSs between the SrTiO$_3$ and BaTiO$_3$ can also reflect the strain effect on the electronic structure. As summarized in Fig. 3(c), the band gap increases slightly from the compressive strain to tensile strain.

In conclusion, the magnetic orders of LaTiO$_3$ films with the biaxial compressive and tensile strain have been studied using LDA + $U$ method. For the compressive strain, a phase transition from G-type AFM to A-type AFM has been found and this transition is much more robust when the strain increases. However, the G-type AFM still be the ground state for the tensile strain and the C-type AFM maybe appear if the strain is further increased. Furthermore, the LaTiO$_3$ films preserve the insulating behavior on all substrates studied here.

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