Strain-engineered A-type antiferromagnetic order in YTiO₃: a first-principles calculation

Xin Huang,¹ Yankun Tang,¹ and Shuai Dong¹,²

¹Department of Physics, Southeast University, Nanjing 211189, China
²Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, China

(Dated: 5 May 2014)

The epitaxial strain effects on the magnetic ground state of YTiO₃ films grown on LaAlO₃ substrates have been studied using the first-principles density-functional theory. With the in-plane compressive strain induced by LaAlO₃ (001) substrate, A-type antiferromagnetic order emerges against the original ferromagnetic order. This phase transition from ferromagnet to A-type antiferromagnet in YTiO₃ film is robust since the energy gain is about 7.64 meV per formula unit despite the Hubbard interaction and modest lattice changes, even though the A-type antiferromagnetic order does not exist in any RTiO₃ bulks.

PACS numbers: 75.25.Dk, 75.30.Kz

Transition metal oxides with the perovskite structure exhibit a wide variety of electronic phases with plenty charge-, magnetic-, and orbital-structures, and show many prominent functionalities including colossal magnetoresistance, high-T_C superconductivity, and metal-insulator transitions. Among these oxides, the RTiO₃ family (R is a rare earth cation), whose 3d t₂g bands lay near the Fermi level, have not been extensively studied. However, RTiO₃ is not a feature-less family, which also owns rich spin/orbital ordered phases. These phases also involve the couplings between charge, orbital, lattice, and spin degrees of freedom, which have the potential to be used in spintronic or correlated-electron devices.

RTiO₃’s with trivalent R cations are all prototype Mott-Hubbard insulators and their common crystal structure is a pseudocubic perovskite with an orthorhombic distortion (the GdFeO₃-type distortion). This distortion arises from the tilting TiO₆ octahedron around the [110] axis and a followed rotation around the [001] axis. The magnitude of this distortion depends on the ionic radius of R. Similar to the RMnO₃ case, the RSO₃ plane lattice constant of LaAlO₃ is more distorted with a small R and the Ti-O-Ti bond angle is decreased more significantly from 180°. The GdFeO₃-type distortion plays a crucial role in controlling the subtle competitive exchange interactions in these insulating titanates. The magnetic ground state of RTiO₃ exhibits a transition from ferromagnetic (FM) order to antiferromagnetic (AFM) order with increasing size of R cations.

It is very interesting to compare the phase diagrams of RTiO₃ and RMnO₃, both of which show magnetic transitions with increasing size of R cations. And the Curie (or Néel) temperatures show V-shape behaviors near the critical points in both families. However, there are also two key differences between RTiO₃ and RMnO₃. First, the FM-AFM tendency is opposite in these two families. With a smaller R, RMnO₃ is more AFM but RTiO₃ is more FM. Second, the phases revealed in RMnO₃ are more complex than those in RTiO₃. The AFM phase in RTiO₃ bulks is the simple G-type AFM one while the AFM phases (e.g. A-type AFM, spiral-spin order, E-type AFM) in RMnO₃ are more complex which can be more interesting than the simple G-type one. Thus it is non-trivial to ask whether is there any more (hidden) magnetic orders in RTiO₃? In a previous theoretical work Ref. 7, total energies of different magnetic structures including A-type AFM, FM and G-type AFM were calculated by using an effective spin-pseudospin Hamiltonian, which showed that the A-type AFM to FM phase transition occurs with increasing GdFeO₃-type distortion while the G-type AFM one has much higher energies. However, this result disagrees with the experimental phase diagram since the G-type AFM phase is very robust in RTiO₃ with large R while the A-type AFM phase has not been observed in any real RTiO₃ compounds so far.

In this paper, by using the first-principles calculations, we intend to investigate the effects of strain on magnetic structures of YTiO₃ film, focusing on the phase transition of the magnetic ground state. Our calculation predicts that a robust A-type AFM phase can be stabilized by an in-plane compressive strain by using small lattice substrates like LaAlO₃.

YTiO₃ bulk has an orthorhombic structure (space group Pbnm) with lattice constants of a=5.358 Å, b=5.696 Å, and c=7.637 Å. Such a minimum unit cell consists of 4 formula units. To simulate the effect of in-plane compressive strain induced by the substrate, the lattice constants along the a-axis and b-axis are fixed to a=b=5.366 (3.794 × √2) Å to match the (001) LaAlO₃ substrate. Here LaAlO₃ is adopted as the substrate to give a weak in-plane compressive strain to YTiO₃ film since the in-plane lattice constant of LaAlO₃ is a little smaller (∼ 3%) than that of YTiO₃ itself. Such a small difference between lattice constants also promises probable epitaxial growth of YTiO₃ thin films on LaAlO₃ substrate.

Our first-principles calculations were performed using density-functional theory (DFT) within the generalized gradient approximation GGA+U method with the Perdew-Burke-Ernzerhof parametrization as implemented in the Vienna ab initio simulation package (VASP). The valence states include 4d¹5s², 3d²4p²
and $2s^22p^4$ for Y, Ti and O, respectively. The lattice optimization and all other static computations have been done with the Hubbard $U$ on the $d$-electrons of Ti$^{3+}$ ion, and the Dudarev$^{13}$ implementation with $U_{\text{eff}} = 3.2$ eV has been used if not noted explicitly$^{14}$. The atomic positions are fully optimized as the Hellman-Feynman forces are converged to less than 1.0 meV/Å. This optimization and the electronic self-consist iterations are performed using the plane-wave cutoff of 500 eV and a $9 \times 9 \times 6$ Monkhorst-Pack $k$-point mesh$^{15}$ centered at $\Gamma$ grid in combination with the tetrahedron method$^{16}$.

First, the ground state of YTiO$_3$ bulk is checked. Using the experimental crystal structure, non-magnetic (NM) state and four magnetic orders: FM, A-type AFM, C-type AFM and G-type AFM, have been calculated to compare the energies. Within GGA+$U$, our calculations confirm that the FM order has the lowest energy and the calculated local magnetic moment is $0.88 \mu_B$/per Ti in agreement with the experimental magnetic moment ($0.84 \mu_B$)$^{17}$. The detail results of calculated total energy are summarized in Table I. According to Table I, other magnetic orders’ energies (per Ti) are higher than the FM one: 3 meV higher for A-type AFM, 6 meV higher for C-type AFM and 7 meV higher for G-type AFM. It should be noted that the FM ground state is robust within a large region of $U_{\text{eff}}$ from 0 eV to 5 eV (not shown here). Thus, our calculations agree quite well with the experimental results and previous DFT studies$^{14,18}$.

Subsequently, DFT calculations with the epitaxial strain are performed. Epitaxial strain is here realized by fixing the in-plane lattice constants to fit the LaAlO$_3$ substrate as stated before, while the lattice constant along c-axis is varied from 7.0 Å to 9.0 Å to search the equilibrium one under the strain, as shown in Fig. (a). In our calculations, the internal atomic positions are relaxed with magnetism under each fixed lattice framework to obtain optimal crystal structures for calculating accurate energies. According to Fig. (a), it is obvious that the C-type AFM and G-type AFM states are much higher in energy than the FM and A-type AFM states. Thus, in the following, we will mainly focus on the FM and A-type AFM states. The relaxed lattice constant along c-axis is 8.25 Å for the A-type AFM state and 8.26 Å for the FM state. These two values are very close, implying that the magnetostriction is weak in YTiO$_3$, at least along the c-axis. And with the optimized c-axis lattice constant, the A-type AFM state has a lower energy than FM one, e.g. the energy difference between FM and A-type AFM reaches 7.64 meV per Ti. The A-type AFM state appeared in strained YTiO$_3$ films is quite nontrivial since it does not exist in any RTiO$_3$ bulk, namely it is a new phase for RTiO$_3$ family. More importantly, this strain-induced phase transition from FM to A-type AFM is quite promising according to our calculation. As shown in Fig. (b), the energy difference between these two orders does not change sign for a large range of c-axis lattice constant around the optimized one, which means this transition is not sensitive to the optimized c-axis lattice constant. Noted that the energy difference is relatively significant since the energy difference in bulk YTiO$_3$ is only 3 meV per Ti. To confirm that this phase transition is robust against the change of Hubbard parameter, the energy difference between FM and A-type AFM states is calculated with different $U_{\text{eff}}$ from 0 eV to 5 eV stepped by 1 eV, which changes from 16 meV to 2 meV (always positive). In other words, this FM to A-type AFM transition will not change by varying the Hubbard interaction $U_{\text{eff}}$ in a large value (from 0 eV to 5 eV) In short, this strain-induced A-type AFM phase will be very promising to be found in real thin films even if the experimental lattice constant along c-axis and its Hubbard interaction are not exactly the same with those in our calculations.

To understand the underlying physical mechanism, it is meaningful to compare the Ti-O-Ti bond angle in YTiO$_3$ with and without the strain, as shown in Table I. According to Fig. (c), the bond angle in the ab-plane decreases but the one along c-axis increases with the increasing c-axis. These results imply that YTiO$_3$ is compressed and thus more distorted in the ab-plane but elongates and thus is less distorted along the c-axis.

As stated before, it is well known that in RTiO$_3$ compounds, small Ti-O-Ti bond angles with more dis-
In summary, we have studied the effects of epitaxial strain on the magnetic ground states in YTiO$_3$ films. Our results predicted a new magnetic ground phase A-type antiferromagnet which had not been realized in any RTiO$_3$ bulk compounds. This robust A-type AFM phase is stabilized by an in-plane compressive stress induced by LaAlO$_3$ substrate. Its origin is understood as the ferromagnetism with decreasing bond angle in the $ab$-plane and antiferromagnetism with increasing bond angle along the $c$-axis. Furthermore, the density of states calculation confirmed that the insulating behavior and the energy gap would not be significantly affected by this strain driven magnetic transition.

We thank X. Z. Lu, H. J. Xiang, Q. F. Zhang, H. M. Liu for helpful discussion. Work was supported by the 973 Projects of China (Grant No. 2011CB922101) and NSFC (Grant Nos. 11004027 and 11274060).

1. E. Dagotto, Science 309, 257 (2005).
2. Y. Tokura, Rep. Prog. Phys. 69, 797 (2006).
3. M. Mochizuki and M. Imada, New J. Phys. 6, 154 (2004).
4. T. Katsufuji, Y. Taguchi, and Y. Tokura, Phys. Rev. B 56, 101454 (1997).
5. J. E. Greedan, J. Less Common Met. 111, 335 (1985).
6. S. Dong, R. Yu, S. Yunoki, J.-M. Liu, and E. Dagotto, Phys. Rev. B 78, 064414 (2008).
7. M. Mochizuki and M. Imada, J. Phys. Soc. Jpn. 70, 1777 (2001).
8. P. E. Blöchl, Phys. Rev. B 50, 17953 (1994).
9. G. Kresse and D. Joubert, Phys. Rev. B 59, 1758 (1999).
10. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
11. G. Kresse and J. Hafner, Phys. Rev. B 47, 558 (1993).
12. G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996).
13. S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, and A. P. Sutton, Phys. Rev. B 57, 1505 (1998).
14. H. Sawada, Y. Morikawa, K. Terakura, and N. Hamada, Phys. Rev. B 56, 12154 (1997).
15. H. Monkhorst and J. D. Pack, Phys. Rev. B 13, 5188 (1976).
16. P. E. Blöchl, O. Jepsen, and O. K. Andersen, Phys. Rev. B 49, 16223 (1994).
17. J. D. Garrett, J. E. Greedan, and D. A. MacLean, Mater. Res. Bull. 16, 145 (1981).
18. H. Sawada, N. Hamada, and K. Terakura, Physica B 237, 46 (1997).
19. H. Lee and K. M. Rabe, Phys. Rev. Lett. 104, 207204 (2010).
20. S. Picozzi, K. Yamauchi, B. Sanvaj, I. A. Sergienko, and E. Dagotto, Phys. Rev. Lett. 99, 227201 (2007).
21. W. Li, S. Dong, C. Fang, and J. P. Hu, Phys. Rev. B 85, 100407 (2012).

TABLE II. Bond angles in the ab-plane and along c-axis of YTiO$_3$ film on LaAlO$_3$ substrate and bulk YTiO$_3$.

| Bond angle | YTiO$_3$ film (A-AFM) | YTiO$_3$ film (FM) | bulk YTiO$_3$ |
|------------|----------------------|------------------|--------------|
| $ab$-plane | 139.6° | 139.5° | 144.3° |
| $c$-axis  | 143.7° | 143.5° | 141.9° |
22 Y. Okimoto, T. Katsufuji, T. Arima, and Y. Tokura, Phys. Rev. B 51, 9581 (1995).