Strain driven sequential magnetic transitions in strained GdTiO$_3$ on compressive substrates: a first-principles study

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Abstract

The compressive strain effect on the magnetic ground state and electronic structure of strained GdTiO$_3$ has been studied using the first-principles method. Unlike the cases of congeneric YTiO$_3$ and LaTiO$_3$, both of which become the A-type antiferromagnetism on the (0 0 1) LaAlO$_3$ substrate despite their contrastive magnetism, the ground state of strained GdTiO$_3$ on the LaAlO$_3$ substrate changes from the original ferromagnetism to a G-type antiferromagnetism, instead of the A-type one although Gd$^{3+}$ is between Y$^{3+}$ and La$^{3+}$. It is only when the in-plane compressive strain is large enough, e.g. on the (0 0 1) YAlO$_3$ substrate, that the ground state finally becomes the A-type. The band structure calculation shows that the compressive strained GdTiO$_3$ remains insulating, although the band gap changes a little in the strained GdTiO$_3$.

Keywords: titanate, strain, magnetic phase transition

(Some figures may appear in colour only in the online journal)

1. Introduction

Rare earth titanates (RTiO$_3$) are typical Mott insulators with emergent physical properties due to the delicate coupling of electrons, lattice, spin, and orbital degrees of freedom. With a single electron occupying Ti’s $t_{2g}$ orbitals, RTiO$_3$ shows magnetic orders, which change from the ferromagnetism (FM) to G-type antiferromagnetism (G-AFM) with increasing size of R$^{3+}$ [1–6]. The underlying physical mechanism is due to the orthorhombic GdFeO$_3$-type distortion, namely the magnetic ground state is closely coupled with the Ti–O bond angles and bond lengths [1,7–9]. As shown in figure 1, with small GdFeO$_3$-type distortions, RTiO$_3$ bulks exhibit the G-AFM order (R: from La to Sm), while with large distortions, RTiO$_3$ bulks show the FM order (R: from Gd to Y).

One should note that the lattice distortions of perovskite oxides can be tuned not only by the chemical pressure, but also the epitaxial strain/stress when grown as thin films [10–13]. In addition, thin films are always necessary to integrate devices. Therefore, controlling the magnetism of RTiO$_3$ in thin films is a physically interesting topic and may be technologically important. According to previous studies [14, 15], the A-type antiferromagnetism (A-AFM) was predicted to be the ground state for both LaTiO$_3$ and YTiO$_3$ on the compressive (0 0 1) LaAlO$_3$ substrate despite their different original magnetism. Since LaTiO$_3$ and YTiO$_3$ are two end materials of the RTiO$_3$ family, it is natural to ask whether every RTiO$_3$ becomes A-AFM when grown on the (0 0 1) LaAlO$_3$ substrate. Note when those materials are located close to the FM/G-AFM phase boundary, e.g. GdTiO$_3$, the ground states may be even more sensitive to external pressure compared with the end-cases, and thus significant strain effects may be expected.

In this work, the effects of compressive strain on the magnetic and electronic structures of strained GdTiO$_3$ have been studied based on the first-principles theory. Our density functional theory (DFT) calculation predicts that a FM to G-AFM (instead of the A-AFM) phase transition, can be realized by the in-plane compressive strain when using the...
close to the phase boundary of FM and G-AFM. Our previous DFT calculations predicted the strain induced A-AFM for both YTiO₃ and LaTiO₃ on the (001) LaAlO₃ substrate.

The forces are converged to be less than 10 meV Å⁻¹ for the unstrained case) are fully optimized as the Hellman–Feynman forces are converged to be less than 10 meV Å⁻¹. In the following, the in-plane compressive (001) Y AlO₃ substrates. In the strained case, the average in-plane lattice mismatch with the (001) LaAlO₃ substrate as stated before, the equilibrium lattice constant along the a-axis is searched from 7.0 to 9.0 Å.

Our DFT calculations are performed with the Hubbard U (GGA+U) method [18–20]. The 4f electrons of Gd are not included in the valence states since the f orbitals are not well treated in VASP. The physical consideration is that Gd’s magnetic order only occurs at low temperatures, much below Ti’s magnetic ordering temperature. Thus, here we only deal with the magnetism of Ti and leave the low-temperature Gd–Ti coupling to future works. All calculations, including the lattice relaxation and static computations, were performed with the Hubbard U eff = U − J = 3.2 eV by default on the d-orbitals of Ti ions using the Dudarev implementation [21]. The optimization and electronic self-consistent iterations are performed using the plane-wave cutoff of 550 eV and a 7 × 7 × 5 Monkhorst-Pack k-point mesh centered at Γ point in combination with the tetrahedron method. The inner atomic positions as well as the lattice constants (a-b-c for the unstrained bulk and c for the strained case) are fully optimized as the Hellman–Feynman forces are converged to be less than 10 meV Å⁻¹.

### 2. Model and method

Bulk GdTiO₃ has an orthorhombic structure (space group Pbnm) with lattice constants of a = 5.403 Å, b = 5.7009 Å, and c = 7.6739 Å [8]. Such a primitive unit cell consists of four formula units. In the following, the in-plane compressive strain is imposed by fixing the lattice constants along both the a- and b-axis to match the substrates, e.g. 5.366 Å on the (001) LaAlO₃. Compared with the previously studied YTiO₃ and LaTiO₃ cases, the average in-plane lattice mismatch with the (001) LaAlO₃ substrate is modest (~3.4%), larger than YTiO₃ (~3%), but smaller than that of LaTiO₃ (~4.9%).

Our DFT calculations are performed using the Vienna ab initio Simulation Package (VASP) [16, 17] within the generalized gradient approximation plus the U (GGA+U) method [18–20]. The 4f electrons of Gd are not included in the valence states since the f orbitals are not well treated in VASP. The physical consideration is that Gd’s magnetic order only occurs at low temperatures, much below Ti’s magnetic ordering temperature. Thus, here we only deal with the magnetism of Ti and leave the low-temperature Gd–Ti coupling to future works. All calculations, including the lattice relaxation and static computations, were performed with the Hubbard U eff = U − J = 3.2 eV by default on the d-orbitals of Ti ions using the Dudarev implementation [21].

### 3. Results and discussion

First, the ground state of bulk GdTiO₃ is checked. Using the fully optimized crystal structure, four magnetic orders, FM, A-AFM, C-AFM, and G-AFM were calculated to compare the energies. As shown in table 1, the FM order has the lowest energy, implying the ground state, which is consistent with the experimental result [1, 8]. According to table 1, other magnetic order’s energies (per Ti) are higher than the FM one: 2.8 meV is higher for A-type AFM, 8.0 meV is higher for C-type AFM, and 9.9 meV is higher for G-type AFM. The fully relaxed lattice gives: a = 5.434 Å, b = 5.809 Å, c = 7.765 Å, very close to the experimental data. The FM ground state has also been confirmed within a wide range of U eff from 0 to 4 eV. When U eff = 3.2 eV, the calculated band gap is 1.68 eV from the band structure. The calculated magnetic moment is 0.88 μB/Ti. If the Hubbard U eff is not included, the pure GGA calculation will get a metallic DOS, implying the Coulomb repulsion between 3d electrons drives GdTiO₃ to be a Mott insulator.

Subsequently, our calculations are performed with the epitaxial strain. By fixing the in-plane lattice constants to fit the (001) LaAlO₃ substrate as stated before, the equilibrium lattice constant along the c-axis is searched from 7.0 to 9.0 Å. For each c-value, the internal atomic positions are relaxed with magnetism to obtain the optimal crystal structure with the lowest energies. According to figure 2(a), in the whole calculated region, the G-AFM state has the lowest energy of all the states. This result is quite different from the previously studied YTiO₃ and LaTiO₃ cases [14, 15], both of which show an A-AFM ground state despite their original magnetic orders. The C-AFM state is the first excited state, which is also nontrivially different from the strained YTiO₃ and LaTiO₃. The relaxed lattice constants along the c-axis are 8.28 Å for both the C-AFM and G-AFM. As summarized in table 2, the energy of the C-AFM state is 8.4 meV/Ti higher than the G-AFM state.

![Figure 1](image_url) A sketch of the compressive strain effect in RTiO₃. GdTiO₃ is located in the middle of two end materials, YTiO₃ and LaTiO₃, close to the phase boundary of FM and G-AFM. Our previous DFT calculations predicted the strain induced A-AFM for both YTiO₃ and LaTiO₃ on the (001) LaAlO₃ substrate.

<table>
<thead>
<tr>
<th>Magnetic order</th>
<th>FM</th>
<th>A-AFM</th>
<th>C-AFM</th>
<th>G-AFM</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔE (meV/Ti)</td>
<td>0</td>
<td>+2.8</td>
<td>+8.0</td>
<td>+9.9</td>
</tr>
<tr>
<td>M (μB/Ti)</td>
<td>0.878</td>
<td>0.869</td>
<td>0.848</td>
<td>0.842</td>
</tr>
</tbody>
</table>

Figure 1. A sketch of the compressive strain effect in RTiO₃. GdTiO₃ is located in the middle of two end materials, YTiO₃ and LaTiO₃, close to the phase boundary of FM and G-AFM. Our previous DFT calculations predicted the strain induced A-AFM for both YTiO₃ and LaTiO₃ on the (001) LaAlO₃ substrate.
G-AFM at \( c = 8.28 \ \text{Å} \), while others are even higher. As shown in figure 2(b), the energy difference between the G-AFM and C-AFM states does not change very much by varying the \( c \)-axis lattice constant from 8.2 to 8.3 Å, suggesting the result is not sensitive to the \( c \)-axis lattice constant near the optimal value. Note that the energy difference between the ground state and the first excited state is only 1.9 meV/Ti in bulk GdTiO\(_3\). Thus, the G-AFM state should be very robust under such a compressive strain. To further check the reliability, the energy difference between the G-AFM and C-AFM states is calculated with different \( U_{\text{eff}} \) from 0 to 5 eV stepped by 1 eV, which varies from \(-17.1\) to \(-4.8\) meV, as shown in figure 2(c). All these data illustrate that the G-AFM state is very promising for strained GdTiO\(_3\) on the (001) LaAlO\(_3\) substrate.

As mentioned before, the magnetic ground state of \( \text{RTiO}_3 \) depends on the GdFeO\(_3\)-type distortion. Thus, the Ti–O–Ti bond angles and bond length in strained GdTiO\(_3\) on the LaAlO\(_3\) substrate (G-AFM) are compared in table 3, together with the bulk’s values (FM), which may help us to understand the underlying physical mechanism. The bond angle along the \( c \)-axis increases by 6.2° but the one in the \( ab \)-plane decreases by 2.8°. The increased bond angle and bond length along the \( c \)-axis certainly prefer the antiferromagnetic coupling, according to the bulk phase diagram and previous experience of YTIO\(_3\) and LaTiO\(_3\). However, the antiferromagnetic coupling, accompanied by the decrease in plane bond angle and bond length, is exotic, and cannot be simply understood from the bond angle/length effect, suggesting a more complex physical mechanism is involved.

It is important to check the density of states (DOS) of GdTiO\(_3\) under strain to study the conductance accompanying the magnetic transition, as shown in figure 3(a). The GGA+\( U \) calculation found the gap to be 1.76 eV for strained GdTiO\(_3\) on a (001) LaAlO\(_3\) substrate, which is a little larger than the bulk value 1.68 eV. In figure 3(b), this band gap is plotted as a function of \( U_{\text{eff}} \) from 0 eV (pure GGA) to 5 eV. As in the bulk case, the pure GGA calculation gives a metallic behaviour, while the band gap increases almost linearly with \( U_{\text{eff}} \), suggesting a Mott insulator fact for strained GdTiO\(_3\) on the LaAlO\(_3\) substrate.

The physical reason for such a strain-driven G-AFM can be understood as following. According to the bulk phase diagram, GdTiO\(_3\) locates very close to the FM/G-AFM phase boundary, implying proximate energy between these contrastive phases and strong quantum fluctuation. According to the bulk’s phase diagram and previous studies, the compressive strain suppresses the FM order and favours...
Figure 3. (a) Total DOS of strained GdTiO$_3$ on the LaAlO$_3$ substrate. The Fermi energy is positioned at zero. (b) The band gap as a function of $U_{\text{eff}}$. The critical $U_{\text{eff}}$ value to induce a gap is estimated to be 0.4 eV by extrapolation.

Table 4. The energy difference $\Delta E$/meV (per Ti) between various magnetic states for strained GdTiO$_3$ on the YAlO$_3$ substrate: $E(X) - E(\text{A-AFM})$, the corresponding value of $c$ per Å and local magnetic moments $M/\mu_B$ (per Ti) are also shown.

<table>
<thead>
<tr>
<th>Magnetic order</th>
<th>FM</th>
<th>A-AFM</th>
<th>C-AFM</th>
<th>G-AFM</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E$</td>
<td>+4.6</td>
<td>0</td>
<td>+9.5</td>
<td>+5.2</td>
</tr>
<tr>
<td>$c$</td>
<td>8.64</td>
<td>8.63</td>
<td>8.64</td>
<td>8.63</td>
</tr>
<tr>
<td>$M$</td>
<td>0.880</td>
<td>0.874</td>
<td>0.856</td>
<td>0.854</td>
</tr>
</tbody>
</table>

the A-AFM. However, when the strain is modest, the energy of A-AFM does not remain low enough. Alternatively, the G-AFM beats the FM due to its antiferromagnetic correlation. In other words, the intrinsic quantum competition in GdTiO$_3$ is the dominant driven force, while the compressive strain plays an assistant’s role. In contrast, for the previously studied LaTiO$_3$ and YTiO$_3$ cases, both of them locate far from the FM/G-AFM boundary, implying a weak quantum fluctuation. Therefore, the strain effect is almost the pure driven force for phase transition, giving rise to the expected A-AFM phase under compressive strain. Of course, the ‘unexpected’ G-AFM in strained GdTiO$_3$ predicted in the present calculation requires further experiments to verify it and further theoretical studies to understand the underlying mechanism.

In this sense, it is interesting to expect that a stronger compressive strain may overcome the intrinsic competition and act as the main role. To confirm this speculation, we fix the in-plane lattice constants of GdTiO$_3$ to 5.1377 and 5.2736 Å, fitting an even smaller (0 0 1) YAlO$_3$ substrate. For this substrate, the biaxial strain is 6.2% for the YAlO$_3$ substrate, larger than the LaAlO$_3$ one ($\sim$ 3.4%). In addition the internal atomic positions and the lattice constant along the $c$-axis are relaxed with various magnetic orders to search the optimized structure and the ground state. As shown in table 4, the A-AFM state is now the ground state with the lowest energy, and the FM state is the first excited state, consistent with the previously studied compressive YTiO$_3$ and LaTiO$_3$. The relaxed lattice constant along the $c$-axis is 8.63 Å for the A-AFM state, longer than the above case on the LaAlO$_3$ substrate. The energy difference between the A-AFM state and FM state is also calculated by varying $U_{\text{eff}}$ to further check the reliability. As shown in figure 4(b), the energy difference between them is always negative. All these results suggest that the A-AFM state is a robust state for the strained GdTiO$_3$ on an extremely compressive YTiO$_3$ substrate. The DOS is also checked, as shown in figure 4(a). The gap is 1.64 eV, remaining as a Mott insulator.

At last, the band structures for bulk GdTiO$_3$ and strained GdTiO$_3$ (G-AFM and A-AFM) are also calculated, as shown in figure 5. First, these band structures again prove that the ground states for bulk GdTiO$_3$ and strained GdTiO$_3$ are all Mott insulators. Secondly, the topmost valence bands close to the Fermi level are from the $t_{2g}$ orbitals of Ti, which are nearly degenerated. Thirdly, the lowest conducting bands are also from the $t_{2g}$ orbitals of Ti, which are more than 1 eV higher than the occupied bands. Such a large splitting of $t_{2g}$ levels is due to the orbital ordering associated with the Jahn-Teller distortion, as well as the inter-orbital Hubbard repulsion. Fourthly, the bandwidth of these occupied $t_{2g}$ levels is very narrow, or nearly flat, implying that these occupied states are almost isolated, with weak kinetic energy. However, the bandwidth changes when GdTiO$_3$ is strained: shrinking from 0.445 eV (FM, bulk) to 0.248 eV (G-AFM, on a LaAlO$_3$ substrate), then to 0.412 eV (A-AFM, on a YAlO$_3$ substrate). This change, together with the change of bands above the Fermi level, is the driving force for phase competition in such a multi-orbital correlated system.

In summary, the magnetic orders of strained GdTiO$_3$ on two compressive substrates have been studied based on density functional theory calculations. A phase transition from the original FM in bulk to G-AFM has been found on the (0 0 1) LaAlO$_3$ substrate, which is different from the previously studied LaTiO$_3$ and YTiO$_3$. The underlying physics for such
Figure 4. (a) Total DOS of strained GdTiO$_3$ on the YAlO$_3$ substrate. The Fermi energy is positioned at zero. (b) The energy difference (per Ti) between the A-AFM and FM as a function of the Hubbard $U_{eff}$.

Figure 5. The band structure of GdTiO$_3$. (a, b) FM bulk. (a) Spin up. (b) Spin down. (c) G-AFM state on the LaAlO$_3$ substrate. (d) A-AFM state on the YAlO$_3$ substrate.

A unique transition is the intrinsic phase competition which dominates the modest strain. Only when the compressive strain is very large, e.g. using the (001) YAlO$_3$ substrate, does the ground state change to A-AFM as the compressive strain on LaTiO$_3$ and YTiO$_3$. Furthermore, these strain-induced magnetic transitions will not change the insulating behavior of GdTiO$_3$ but will only tune the band gap a little.

Acknowledgments

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References