Research articles

Strain-induced insulating ferromagnetism in LaMnO$_3$ thin films from first-principles investigations

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ABSTRACT

Previous experiments have found that LaMnO$_3$ thin films grown on SrTiO$_3$ substrate exhibit insulating ferromagnetism different from that of the bulk LaMnO$_3$. Utilizing first-principles calculations based on density functional theory, magnetic transitions, energy gaps and spin exchange interactions of LaMnO$_3$ thin films with different epitaxial strains are investigated, and the effect of the Jahn-Teller distortion, rotation and tilt of oxygen octahedrons on magnetic and electrical properties are analyzed in detail. A relative narrow insulating ferromagnetic area without structural phase transition is obtained during the transition from metallic ferromagnetic phase to insulating A-type antiferromagnetic phase. If the magnetic transition of LaMnO$_3$ film is attributed to Jahn-Teller distortion, then the metal-insulator transition should be ascribed to the tilt of the oxygen octahedron and large change of the O1-Mn-O2 angle in ab plane, which is helpful to understand the insulating ferromagnetic characters during the preparations of the LaMnO$_3$ superlattices or heterostructures, also indicates that the insulating ferromagnetic properties of LaMnO$_3$ films can be tuned by epitaxial strain-controlled oxygen octahedrons distortions.

1. Introduction

Perovskite manganite LaMnO$_3$ (LMO), a strongly correlated electron system, has attracted considerable attention recently not only because of their many interesting physical properties and applications, such as giant magnetoresistance effect, metal-insulator transition, electric dipole or spin order, but also due to their rich physical mechanisms and pictures including double exchange interaction, Jahn-Teller (JT) distortion, charge orbital ordering, phase separation and so on [1–3]. In LMO, the coexistences and competitions between all kinds of interactions make manganese oxides exhibit very sensitive properties to structural change, an important example is that there exists A-type antiferromagnetic (A-AFM) spin order due to the JT distortions-tuned-competitions between ferromagnetic (FM) double exchange and AFM superexchange interactions [4–6]. While for LMO thin films and thin film-related heterostructures or superlattices, the existed complex correlations among structure, orbit, magnetism, charge and electronic degrees of freedom are more important, because many related novel behaviors and properties different from those of bulk materials have been discovered in these structures [7–8].

Especially, it has been discovered that the surprising insulating ferromagnetism and film thickness-dependent magnetic transitions exist for these LMO thin films epitaxially grown on the square-lattice SrTiO$_3$ (STO) substrate [9–12]. Although a wide range of magnetic properties varying from metallic FM to insulating AFM state has been sufficiently researched [6,13–15], the origin of this confusing insulating FM is still not well explained, and given physical picture is also not very clear. The deficiency of La was thought to be answerable for ferromagnetism, but this is not consistent with the trend of cation deficiency to be metallic in LMO thin films [16,17]. Previous theoretical models and first-principles investigations on LMO thin films obtained the metallic FM phase rather than experimentally observed insulating FM phase [5,18,19]. Combining genetic algorithm optimizations and double-exchange model studies, this insulating FM phase was revealed to originate from the G-type $d_{x^2−y^2}/d_{z^2−r^2}$ orbital order, but this orbital order only exists in monoclinic P21/n structure [20,21]. Moreover, no experiments report the appearance of this monoclinic structure for LMO film by now. Consequently, it is significant to illuminate that how Mott AFM insulator transforms to FM insulator in strained LMO film without structural transition.
In order to clarify this exotic discovery and make its physical image clear, we resort to the first-principles calculations based on density functional theory (DFT) to analyze the electrical and magnetic properties of LMO films from four aspects, namely, JT distortions, rotations and tilts of MnO6 octahedrons, band structure, and magnetic exchange interactions. As we all know, the distortions of MnO6 octahedrons in microstructure almost play a conclusive role on macroscopic properties of materials, our first-principles analysis thus focus on the effect of MnO6 octahedral distortions on magnetic and metal-insulator transition. Our calculation verified insulating A-AFM phase of LMO bulk with orthorhombic Pnma structure, at the same time, we revealed that for tetragonal LMO thin films with biaxial plane strains derived from the mismatch of square lattice SrTiO3 substrate, a relative narrow insulating FM area exists during the transition from metallic FM phase to insulating A-AFM phase when the lattice constant increase due to strain relaxing.

2. Computational details

We used a periodic $\sqrt{2} \times \sqrt{2} \times 2$ perovskite super-cell containing 4 formula units (20 atoms) for DFT simulations. Allowing for the LMO epitaxial thin films grown in a rigid substrate, the two in-plane lattice vectors are fixed at $a_{\text{LMO}} = b_{\text{LMO}}$ to match the experimentally epitaxial strain induced by the square lattice substrate SrTiO3. Furthermore, because the lattice mismatch between the film and substrate relaxes in magnitude with increasing thin films thickness, lattice constant is varied for these thin LMO films with different thickness. Here, because of the lattice constant of LMO being larger than that of STO substrate, the lattice constant of tetragonal LMO film increases during compressive strain relaxing with film growing. For each different lattice constant $a_{\text{LMO}}$ and $b_{\text{LMO}}$, the length of the out-of-plane lattice vector $c_{\text{LMO}}$ and internal atomic coordinates are fully optimized within Pbnm symmetry in our DFT calculations.

Our first-principles calculations are performed using the generalized gradient approximation (GGA) plus Hubbard U method with the Perdew-Burke-Ernzerhof (PBE) type exchange correlation potential as implemented in the Vienna ab Initio Simulation Package (VASP) [22–24]. The convergence criteria of the Hellmann-Feynman force in every atom for the structure optimization is $< 0.01$ eV/Å. Considering that the Coulomb interaction exists in orbital electrons of transitional element Mn and theoretical proof, we apply the on-site coulomb energy $U = 3.5$ eV, $J = 0.9$ eV for the Mn d electrons [20,25,26]. The projector augmented wave potentials including 11 valence electrons for La ($5s^25p^66s^26p^2$), 13 for Mn ($3p^63d^{10}$), and 6 for O ($2s^22p^4$) are considered. A plane wave cutoff energy of 500 eV is used for total energy calculations. The Brillouin zone is sampled with a $7 \times 7 \times 5$ k-point mesh centered at the Γ point, and integrations are performed with Blöch modified tetrahedron method.

3. Results and discussions

First, in order to insure the correctness of our calculation method and $U$, $J$ parameters, we reproduced the ground state and band gap, and JT distortion magnitude $Q$ for bulk LMO at $U_{\text{eff}} = U - J = 2.4, 2.6, 2.8$ and 3.0 eV, and verified the effect of JT distortion on magnetic order in orthorhombic bulk LMO. Using the fully optimized crystal structure and constrained high symmetric structure, four magnetic orders including FM, A-AFM, G-AFM and C-AFM were considered at different $U$, respectively, to obtain the ground state and band gaps. It was then found that the application of $U = 3.5$ eV and $J = 0.9$ eV for the Mn 3d electrons can yield these results in most consistent with the experiments. The detailed results are summarized in Table 1. It indicated that for fully optimized crystal structure of bulk LMO, the A-AFM magnetic state has the lowest total energy in all magnetic phases, and obtained direct energy gap $E_g$ and JT distortion magnitude $Q$ of bulk LMO in the A-AFM magnetic phase is 1.157 eV and 0.65 a.u., respectively, in good agreement with the optical measurements [27,28], DFT calculations [5,29], and previous neutron powder diffraction experiment [30].

However, for the constrained higher symmetric bulk LMO with $Q$ approximating to 0, the FM ground phase can be obtained, indicating the JT distortion of oxygen octahedron has significant influence on the magnetic ground state. As has been shown by Solovyev et al. that exchange coupling between Mn atoms in the $ab$ plane is FM irrespective of the magnitude of the JT distortion, while the interlayer exchange coupling is also FM for weak JT distortion and can be AFM only with significant magnitude of the JT distortion [31]. Here, JT distortion magnitude $Q$ is described by normal mode $Q_2$ and $Q_3$, that is $Q = \sqrt{Q_2^2 + Q_3^2}$, while the mode $Q_2$ and $Q_3$ represent the distortion in the $ab$ plane and along the principle axis [5,29,30], respectively. These results also indicate that the selected $U$ and $J$ are most suitable for further discussions on the JT distortions, magnetic orders and band gaps of LMO thin films with different strains.

For the sake of exploring the intriguing insulating FM property in LMO thin films strained on STO substrate, DFT calculations for the LMO thin films with different epitaxial strains are then performed. Epitaxial strain is here achieved by fixing the in-plane lattice constants at given values, while equilibrium lattice constant $c_{\text{LMO}}$ internal atom positions are relaxed fully within above four magnetic configurations. The corresponding relative total energy at different lattice constants are obtained, as be shown in Fig. 1. It is obvious that the C-AFM and G-AFM phase are much higher in energy than the A-AFM and FM phase, and the competition between A-AFM and FM order is in dominant position, thus, we will focus on these two phases and their band gaps. With the optimized structure for every fixed lattice constant $a_{\text{LMO}}$ ranging from 3.78 Å to 4.18 Å, the FM and A-AFM phases have a obvious dividing point at $a_{\text{LMO}} = 3.98$ Å. The FM phase has lower energy than the A-AFM phase at $a_{\text{LMO}} < 3.98$ Å, indicating the FM phase appears in the relative greater strained LMO thin films [5–7,11]. While the $a_{\text{LMO}}$ is $> 3.98$ Å, that is, LMO thin film has relative smaller strain, and the A-AFM phase appears, indicating the film approaches to the bulk property.

To check this magnetic transition of LMO thin film at different compression strains, the changes of magnetic exchange constants of different nearest neighbors were evaluated by considering an Ising model for different magnetic structures. The intraplane and interplane spin exchange coupling $I_{ab}$ and $I_{c}$ can be obtained by the energy difference of different magnetic phases [29,31,32], in which the $S = 2$ spin moment of Mn ion is considered:

$$I_{ab} = \frac{1}{64} [E^{G-AFM} - E^{A-AFM} - E^{C-AFM}]$$ (1)

$$I_{c} = \frac{1}{32} [E^{A-AFM} - E^{FM}]$$ (2)

The changes of $I_{ab}$ and $I_{c}$ with lattice constant $a_{\text{LMO}}$ is given in Fig. 2. We find that the value of $I_{ab}$ is always positive throughout the range of considered lattice constants, indicating that the intraplane FM exchange coupling remain invariable. However, the symbol of the $I_{c}$ changes with lattice constants, and when the $a_{\text{LMO}}$ is relatively smaller, $I_{c} > 0$ indicates an interplane FM coupling along c direction. For the lattice of $a_{\text{LMO}} > 3.98$ Å, $I_{c} < 0$ manifest the interplane spin exchange interactions from FM coupling to AFM coupling, which is also consistent with the previous analysis on magnetic transition.

Indeed, the biaxial strain-induced magnetic transition in LMO thin films is uncontroversial and has been verified by many experimental and theoretical investigations [5,9–12,33]. Importantly, how do the conductivity of LMO films relate to the magnetic states? Whether the insualtion of thin films is only linked to the single A-AFM phase while the metal state is only connected to FM phase? From Fig. 3, in which the changes of the band gaps, and the magnitude of JT distortion $Q$ for FM and A-AFM phases as functions of lattice constant are plotted, it is easy find that although the A-AFM phase is linked really to the insualtion,
the band gap will still appear in FM phase with decreasing lattice constant \( a_{\text{LMO}} \) to 3.98 Å, and vanishes until \( a_{\text{LMO}} = 3.92 \) Å, the system then enters into the metallic phase, showing a very obvious insulating FM property existed at 3.92 Å < \( a_{\text{LMO}} \) < 3.98 Å. Note that these band gaps are indirect ones for LMO films. Although the lattice range of corresponding to insulating FM phase is relatively narrow, this phase does exist in orthorhombic \( Pbnm \) structure and there is no necessary structural phase transition.

For the thin film epitaxially grown in the square-lattice substrate, whose lattice constant can be not only experimentally tuned by selecting different substrates, but also controlled with different thin film thickness. When the STO serve as the substrate of growing LMO films, the lattice constant \( a_{\text{LMO}} \) of films ranges from the completely confined \( a_{\text{STO}} = 3.905 \) Å of the STO substrate to the completely relaxed \( a_{\text{LMO}} = 3.992 \) Å of the pseudocubic LMO [28]. Therefore, it is absolutely reasonable and possible for LMO thin film strained on STO substrate that the insulating FM phase accompanies these films with lattice constant \( a_{\text{LMO}} \) falling in between 3.92 Å and 3.98 Å. This is also obviously different from the previous calculated results, in which insulating FM phase appears just in monoclinic \( P21/n \) structure [20]. Experiments obtained that most of LMO thin films or superlattices with the compressive strains, regardless of the growth methods, exhibit insulating FM behaviors. For example, the as-grown LMO films fabricated on STO substrate by using pulsed laser deposition show FM insulating properties with a small band gap [34,35]. The occurrence of the insulating FM phase without structural transition in our DFT calculations is also very consistent with experimental results [9,10,12,17].

### Table 1

<table>
<thead>
<tr>
<th>Magnetic order</th>
<th>A-AFM</th>
<th>FM</th>
<th>G-AFM</th>
<th>C-AFM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetic configure</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( Q = 0.65 ) a.u.</td>
<td>TE (eV/f.u.)</td>
<td>-40.801</td>
<td>-40.758</td>
<td>-40.116</td>
</tr>
<tr>
<td></td>
<td>( E_g ) (eV)</td>
<td>1.16</td>
<td>0.99</td>
<td>1.26</td>
</tr>
<tr>
<td></td>
<td>( E_g ) (eV)</td>
<td>0.65</td>
<td>0.00</td>
<td>0.76</td>
</tr>
</tbody>
</table>

**Fig. 1.** The changes of relative energy for four magnetic structures with lattice constant in tetragonal LMO films. The inset is the relative energy for FM and A-AFM phases near \( a_{\text{LMO}} = 3.98 \) Å.

**Fig. 2.** The changes of magnetic exchange constants with lattice constant. Square dots (Blue line) represent the intraplane magnetic coupling \( J_{ab} \) and circle dots (red line) represent interplane magnetic coupling \( J_c \). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**Fig. 3.** (a) Band gaps for the FM and A-AFM magnetic structures, (b) The magnitudes of the JT distortion \( Q \), as the functions of lattice constant \( a_{\text{LMO}} \) in LMO films.
because no experiment shows that the insulating FM phase in LMO thin film has to be linked to structural transition.

On the other hand, we found from the Fig. 3(b) that when the JT distortion $Q$ is smaller than the critical 0.873 a.u, the system is FM, while the $Q$ is larger than this critical value, the system appears AFM phase, again indicating that the magnetic transition is closely associated to the larger JT distortion [5,29,31,32]. In addition, we also found that the JT distortion of $Q = 0.635$ a.u. is the critical point of the metal-insulator transition of LMO thin films, which is a little smaller than critical value of magnetic transitions. Only when the $Q$ falls in between 0.635 a.u. and 0.873 a.u., the system displays the insulating FM property. This is thus an intriguing issue whether the metal-insulator transition is only controlled by the JT distortions or not?

It is known that the JT distortion is defined only by the Mn-O bond distances [5,19,29], so it do not directly reflect the cases of rotation, tilt and angle distortion of oxygen octahedrons in LMO films. To understand the underlying physical mechanism of metal-insulator transition process and explore the effect of the rotation, tilt and angle distortion of oxygen octahedrons on this transition of LMO films, we investigated the changes of not only Mn-O bond lengths but also bond angles of MnO6 octahedrons of LMO films with different lattice constants in detail, as are shown in Fig. 4, in which the changes of the Mn-O1-Mn and Mn-O3-Mn bond angle reflect the rotation of oxygen octahedrons around the c axis and the tilt relative to c axis, respectively, while the change of O1-Mn-O2 denotes the angle distortion of oxygen octahedrons.

According to Fig. 4(c), it can be deduced that the changes of the Mn-O1 and Mn-O3 bond length are very obvious throughout lattice relaxation process, which is an important cause of the JT distortion, while the Mn-O2 bond makes little change. When the lattice constant $a_{LMO}$ is close to 3.82 Å, the lengths of three Mn-O bonds tend to equalize, and JT distortion attains to the minimum, and the Q approach to zero. This is also consistent with the previous discussions. For the rotation and tilt of oxygen octahedrons, it is not difficult to see from Fig. 3(d) that with increasing the lattice constant from 3.75 Å to 4.05 Å, the Mn-O1-Mn bond angle almost keeps constant, and only increases from 154° to 155°, while the Mn-O3-Mn angle quickly decreases from 156° to 142°, indicating that lattice relaxations from compression strain can drive the great tilts and little rotations of oxygen octahedrons.

Maybe all of these changes still cannot provide obvious indications for explaining the metal-insulator transition, however, from the change of the O1-Mn-O2 bond angle in ab plane (see Fig. 4(d)), we find that the metal-insulator transition can be significantly linked to the mutation of O1-Mn-O2 bond angle. When lattice constant attains to 3.92 Å, the bond angle of the O1-Mn-O2 increases to an inflection point, the system enters into the insulating phase. That is, the larger band gaps of LMO thin films should be attributed to the enough larger O1-Mn-O2 bond angles in the FM phase. So, aside from the distortions of bond lengths included in the JT distortion, the distortions of the bond angles are responsible for the insulating of the LMO films. Moreover, according to the changes of energy gap $E_g$ and the O1-Mn-O2 bond angles at different lattice constants, it is not difficult to find that the insulating of LMO films in the FM phase can be dramatically enhanced by properly increasing the O1-Mn-O2 bond angle and tilt of the oxygen octahedron.

4. Conclusions

Using first-principles calculations based on DFT, the physical origin of puzzling insulating ferromagnetism experimentally observed in the LMO thin films has been investigated. By analyzing the effect of lattice mismatch on crystal structure, magnetic properties, and energy band of LMO thin films, we find that the intrinsic properties of the LMO thin film can be tuned by strain-controlled JT distortion, oxygen octahedron tilts and distortion of O1-Mn-O2 bond angle. On the one hand, the magnitude of JT distortion $Q$ has a significant influence on the magnetic transitions from A-AFM phase to FM phase in LMO thin films. On the other hand, the metal-insulator transition of LMO thin film is intrinsically from the tilt of the oxygen octahedron and large distortion of the O1-Mn-O2 bond angle in ab plane, instead of extrinsic reasons such as defects. However, we also find that the rotation of the oxygen octahedrons has a negligible effect on magnetic transition and metal-insulator transition. Thus, the observed insulating FM property in the LMO thin films should be attributed to the effect of JT distortion in combination with oxygen octahedron tilts and distortion of O1-Mn-O2 bond angle. We expect that this mechanism for the insulating FM property can be confirmed by experimental explorations of LMO thin films.

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Fig. 4. The Mn-O1-Mn, O1-Mn-O2 and Mn-O3-Mn bond angle in LMO film are shown in (a) and (b), respectively. The changes of Mn-O bond lengths and Mn-O-Mn and O1-Mn-O2 bond angle with the lattice constant are given in (c) and (d). The orange shadows in (c) and (d) represent the area of FM insulating phase. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
References