

# Strain-engineered magnetic order in $(\text{LaMnO}_3)_n/(\text{SrMnO}_3)_{2n}$ superlattices

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Using first-principles calculations based on the density functional theory, we show a strong strain dependence of magnetic order in  $(\text{LaMnO}_3)_n/(\text{SrMnO}_3)_{2n}$  (001) superlattices with  $n = 1, 2$ . The epitaxial strain lifts the degeneracy of Mn  $e_g$  orbitals, thus inducing an inherent orbital order, which in turn strongly affects the ferromagnetic double exchange of itinerant  $e_g$  electrons, competing with the antiferromagnetic superexchange of localized  $t_{2g}$  electrons. For the case of tensile strain induced by SrTiO<sub>3</sub> (001) substrate, we find that the ground state is A-type antiferromagnetic and  $d_{x^2-y^2}$  orbital ordered, which is in excellent agreement with recent experiments [May *et al.*, *Nat. Mater.* **8**, 892 (2009)]. Instead, for the case of compressive strain induced by LaAlO<sub>3</sub> (001) substrate, we predict that the ground state is C-type antiferromagnetic and  $d_{3z^2-r^2}$  orbital ordered.

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## I. INTRODUCTION

Transition-metal oxides in perovskite-based structures exhibit a wide variety of phases with different electronic, magnetic, and orbital structures, and show rich functionalities such as high- $T_C$  superconductivity, colossal magnetoresistance, and multiferroics.<sup>1</sup> A recent advance in epitaxial growth techniques has made it even possible to fabricate transition-metal oxide heterostructures with sharp and smooth interfaces controlled at the atomic scale.<sup>2</sup> In these heterostructures, many unique properties, not found in the corresponding alloy compounds made of the same composite elements, have been observed, which include, e.g., two-dimensional electron gas with high mobility at the heterostructure interfaces,<sup>3</sup> indicating the promising potential of oxide heterostructures for future technological applications.<sup>4</sup>

In the case of manganites,<sup>5</sup> LaMnO<sub>3</sub> is an A-type antiferromagnetic insulator and SrMnO<sub>3</sub> is a G-type antiferromagnetic insulator. On one hand, the randomly cation-doped alloy La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3</sub> exhibits a rich magnetic phase diagram, depending on the doping concentration  $x$ . On the other hand, La/Sr cation-ordered analogs forming superlattices behave quite differently from their alloy compounds.<sup>6-10</sup> For example, La<sub>2/3</sub>Sr<sub>1/3</sub>MnO<sub>3</sub> alloy has a mixed valence of Mn<sup>3+</sup>/Mn<sup>4+</sup>, and the ground state is ferromagnetic half metallic due to the double-exchange mechanism.<sup>5</sup> To the contrary, it is found experimentally that cation-ordered  $(\text{LaMnO}_3)_n/(\text{SrMnO}_3)_n$  (001) superlattices are insulating when  $n$  is larger than 3.<sup>6,8</sup> This change of behavior is easily understood because the number  $n$  of SrMnO<sub>3</sub> layers control the quantum confinement potential: when  $n$  is small, the confinement potential is small and the  $e_g$  electrons are distributed uniformly, thus expecting the phases similar to the alloy La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3</sub>. When  $n$  is large, the confinement potential becomes large enough to trap the  $e_g$  electrons in LaMnO<sub>3</sub> layers, and thus the bulk properties of LaMnO<sub>3</sub> and SrMnO<sub>3</sub> would be observed. Several theoretical studies for  $(\text{LaMnO}_3)_{2n}/(\text{SrMnO}_3)_n$  superlattices

have been reported to understand their electronic and magnetic properties.<sup>11,12</sup>

More recently, Bhattacharya *et al.*<sup>13,14</sup> have experimentally studied the transport and the magnetic properties of similar superlattices  $(\text{LaMnO}_3)_n/(\text{SrMnO}_3)_{2n}$  grown on SrTiO<sub>3</sub> (001) substrate. They have found that the ground state of these superlattices with  $n = 1, 2$  are A-type antiferromagnetic metals with Néel temperature ( $T_N$ ) which is higher than that observed in any alloy La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3</sub> compound.<sup>14</sup> Although the similar physical principles found in  $(\text{LaMnO}_3)_{2n}/(\text{SrMnO}_3)_n$  superlattices are certainly expected to apply here, the systematic theoretical investigations are required to understand the main ingredients which determine the electronic as well as the magnetic properties of  $(\text{LaMnO}_3)_n/(\text{SrMnO}_3)_{2n}$  superlattices.

Here, in this paper, performing first-principles calculations based on the density functional theory, we study the electronic and the magnetic structures of  $(\text{LaMnO}_3)_n/(\text{SrMnO}_3)_{2n}$  (001) superlattices with  $n = 1, 2$ . We show that the magnetic properties are governed not only by the quantum confinement potential caused by periodic alignment of cation ions La<sup>3+</sup>/Sr<sup>2+</sup>, but also by the strain induced by substrates on which the superlattices are grown. Namely, for the case of tensile strain induced by SrTiO<sub>3</sub> (STO) (001) substrate, our calculations show that the ground state of these superlattices are A-type antiferromagnetic and  $d_{x^2-y^2}$  orbital ordered with higher  $T_N$  for  $n = 1$  than for  $n = 2$ . This is indeed in excellent agreement with recent experimental observations.<sup>14</sup> Instead, for the case of compressive strain induced by LaAlO<sub>3</sub> (LAO) (001) substrate, we predict C-type antiferromagnetic and  $d_{3z^2-r^2}$  orbital orders with higher  $T_N$  for  $n = 1$  than for  $n = 2$ .

The rest of this paper is organized as follows. After describing the computational details in Sec. II, the numerical results for the cases of SrTiO<sub>3</sub> substrate and LaAlO<sub>3</sub> substrate are presented in Secs. III A and III B, respectively, followed by discussion of the confinement potential in Sec. III C. Section IV summarizes this paper.

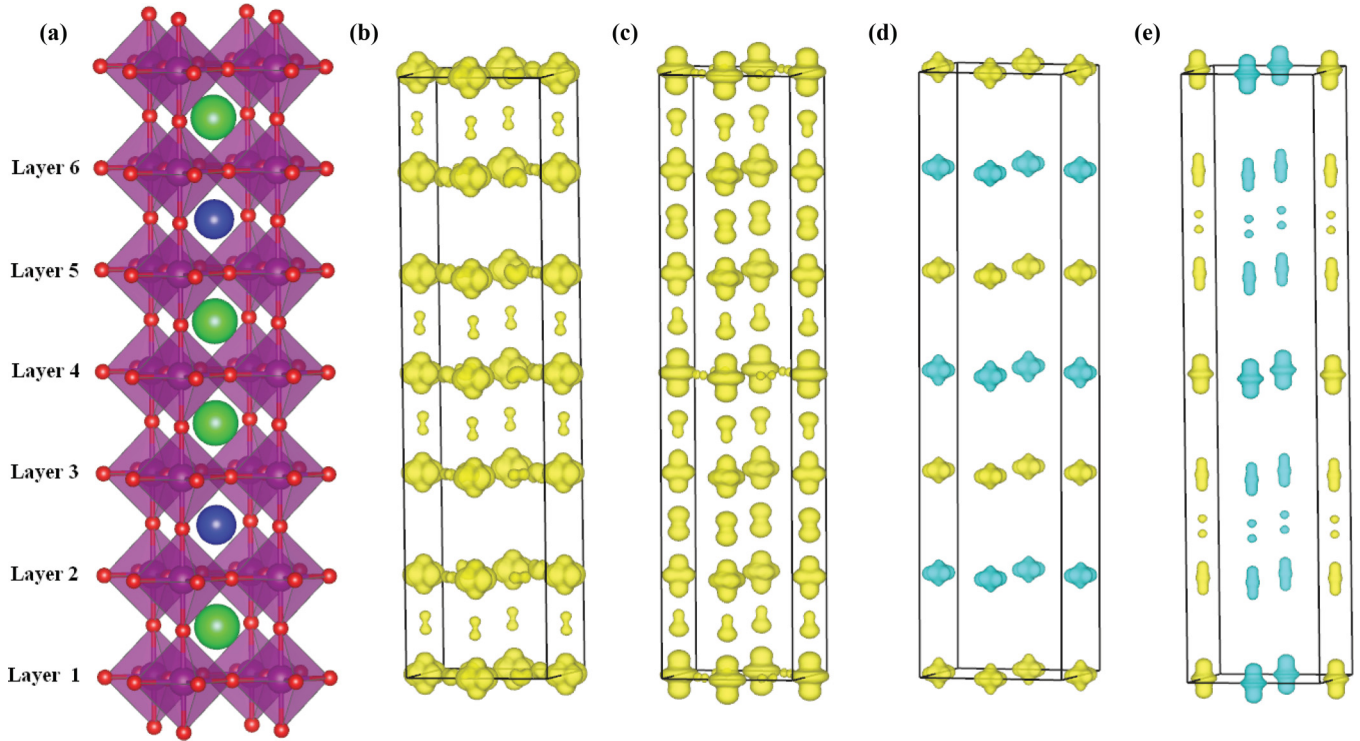


FIG. 1. (Color online) (a) A schematic figure of the supercell considered for  $\text{LaMnO}_3/(\text{SrMnO}_3)_2$  (001) superlattices, and the projected charge [(b) and (c)] and spin-density [(d) and (e)] distributions (integrated from Fermi level down to  $-0.5$  eV using GGA) for  $\text{LaMnO}_3/(\text{SrMnO}_3)_2$  superlattices grown on  $\text{SrTiO}_3$  [(b) and (d)] and  $\text{LaAlO}_3$  [(c) and (e)] (001) substrates. The loci of MnO layers are indicated in (a), where red, blue, green, and purple spheres indicate O, La, Sr, and Mn atoms, respectively. In (d) and (e), the up- and down-spin densities are denoted by yellow and light blue, respectively.

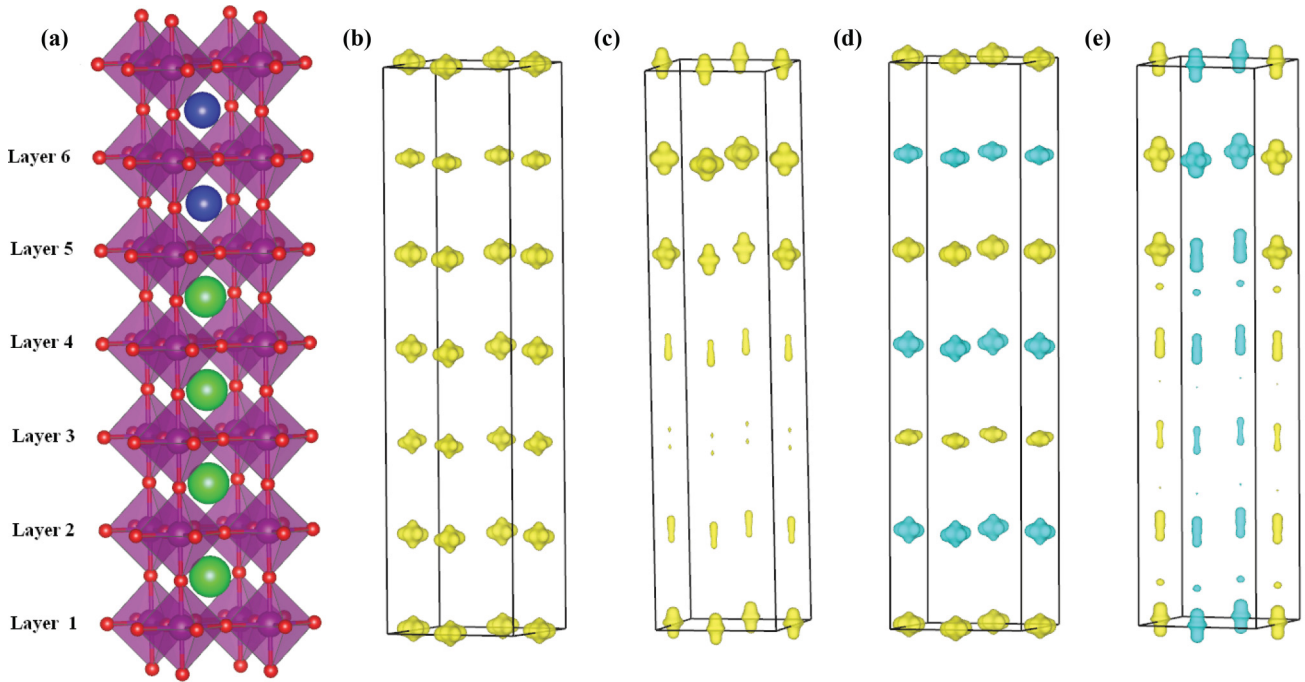


FIG. 2. (Color online) (a) A schematic figure of the supercell considered for  $(\text{LaMnO}_3)_2/(\text{SrMnO}_3)_4$  (001) superlattices, and the projected charge [(b) and (c)] and spin-density [(d) and (e)] distributions (integrated from Fermi level down to  $-0.5$  eV using GGA) for  $(\text{LaMnO}_3)_2/(\text{SrMnO}_3)_4$  superlattices grown on  $\text{SrTiO}_3$  [(b) and (d)] and  $\text{LaAlO}_3$  [(c) and (e)] (001) substrates. The loci of MnO layers are indicated in (a), where red, blue, green, and purple spheres indicate O, La, Sr, and Mn atoms, respectively. In (d) and (e), the up- and down-spin densities are denoted by yellow and light blue, respectively.

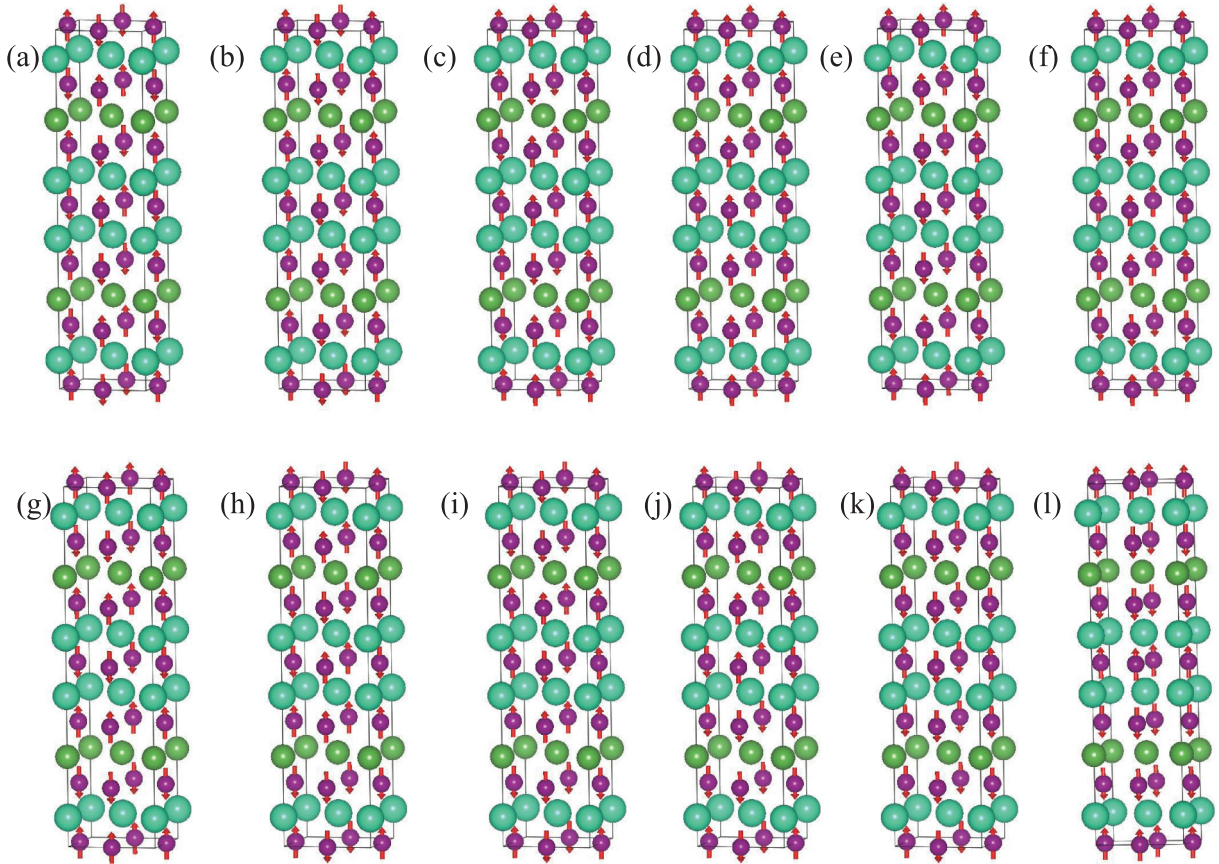


FIG. 3. (Color online) 12 different magnetic structures considered for  $\text{LaMnO}_3/(\text{SrMnO}_3)_2$  superlattices: G-AFM (a), C-AFM (b), M1-AFM (c), FM (d), M2-AFM (e), D-AFM (f), A-AFM (g), M3-AFM (h), M4-AFM (i), M5-AFM (j), M6-AFM (k), and D1-AFM (l). Mn spins are indicated by arrows. Aqua, lime, and violet spheres stand for Sr, La, and Mn atoms, respectively. O atoms are omitted for clarity.

## II. COMPUTATIONAL METHODS

We perform the first-principles electronic-structure calculations based on the projected augmented wave pseudopotentials using the Vienna *ab initio* simulation package (VASP).<sup>15,16</sup> The valence states include  $3p4s3d$  and  $2s2p$  for Mn and O, respectively. The electron interactions are described using the generalized gradient approximation (GGA) and the rotationally invariant GGA +  $U$  method<sup>17-19</sup> with the effective  $U_{\text{eff}}$ , i.e.,  $U - J$ , from 1 to 5 eV for  $d$  electron states. Compared to the GGA, the GGA +  $U$  approach gives an improved description of  $d$  electron localization.<sup>20</sup> The atomic positions of superlattices are fully optimized iteratively until the Hellman-Feynman forces are 0.01 eV/Å or less. The plane-wave cutoff is set to be 500 eV and a  $12 \times 12 \times 12$  Monkhorst-Pack  $k$ -point grid is used in combination with the tetrahedron method.<sup>21</sup>

The supercells considered here consist of six  $\text{MnO}_2$  layers, two LaO layers, and four SrO layers for both  $n = 1$  and 2, as shown in Figs. 1(a) and 2(a). We consider 12 and 10 different magnetic moment alignments to search for the ground-state magnetic structures for  $\text{LaMnO}_3/(\text{SrMnO}_3)_2$  and  $(\text{LaMnO}_3)_2/(\text{SrMnO}_3)_4$  superlattices, as shown in Figs. 3 and 4, respectively. These magnetic structures include not only simple ferromagnetic, A-type, C-type, and G-type antiferromagnetic structures,<sup>22</sup> but also magnetic structures with

mixed combinations of these simple magnetic structures. The epitaxial constraint on these superlattices, which is grown on substrates, is to fix the in-plane lattice constants. Thus, to simulate the strain effect, we fix the in-plane lattice constants ( $a$ ) of the superlattices to those of substrates, i.e.,  $a = 3.905$  Å for  $\text{SrTiO}_3$  substrate<sup>23</sup> and  $a = 3.81$  Å for  $\text{LaAlO}_3$  substrate,<sup>24</sup> and the lattice constant ( $c$ ) perpendicular to  $\text{MnO}_2$  layers is fully relaxed. Atomic positions are also fully optimized.

## III. RESULTS

### A. $(\text{LaMnO}_3)_n/(\text{SrMnO}_3)_{2n}$ on $\text{SrTiO}_3$

Let us first examine  $(\text{LaMnO}_3)_n/(\text{SrMnO}_3)_{2n}$  (001) superlattices on  $\text{SrTiO}_3$  (001) substrate. Our systematic GGA calculations reveal that the ground states of these superlattices with  $n = 1$  and 2 are both A-type antiferromagnetic metals. A schematic spin alignment of A-type antiferromagnetic order is shown in Figs. 3(g) and 4(a). Indeed, as shown in Figs. 1(d) and 2(d), the projected spin-density distribution, calculated by integrating spin density of occupied states from Fermi level down to  $-0.5$  eV, clearly indicates the A-type antiferromagnetic spin order. Our GGA +  $U$  calculations also find that these A-type antiferromagnetic states are robust against electron correlations, and they are indeed stable up



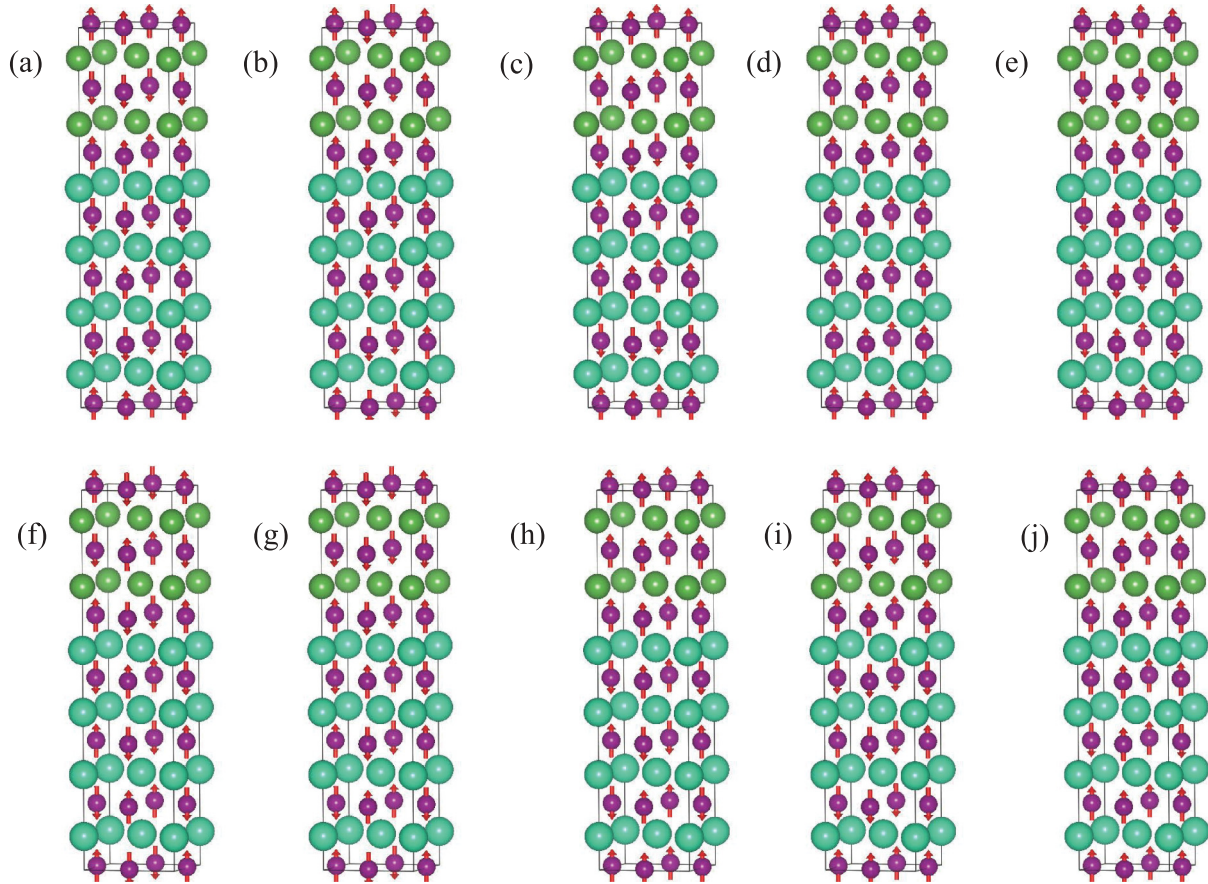


FIG. 4. (Color online) 10 different magnetic structures considered for  $(\text{LaMnO}_3)_2/(\text{SrMnO}_3)_4$  superlattices: A-AFM (a), C-AFM (b), D-AFM (c), FM (d), M2-AFM (e), G-AFM (f), M1-AFM (g), M3-AFM (h), M4-AFM (i), and M5-AFM (j). Mn spins are indicated by arrows. Aqua, lime, and violet spheres stand for Sr, La, and Mn atoms, respectively. O atoms are omitted for clarity.

to  $U_{\text{eff}} = 2$  eV for  $n = 1$  and  $U_{\text{eff}} = 1.3$  eV for  $n = 2$  (see Fig. 5).<sup>25</sup>

Since the supercell sizes and the numbers of each type of atoms are the same, we can simply compare the total energy of these two different superlattices. Table I summarizes

the total energies for the A-type antiferromagnetic states and other magnetic states. Since the A-type (C-type) magnetic structure is ferromagnetic (antiferromagnetic) within the  $ab$  plane and antiferromagnetic (ferromagnetic) along the  $c$  direction, we can approximately estimate an effective magnetic

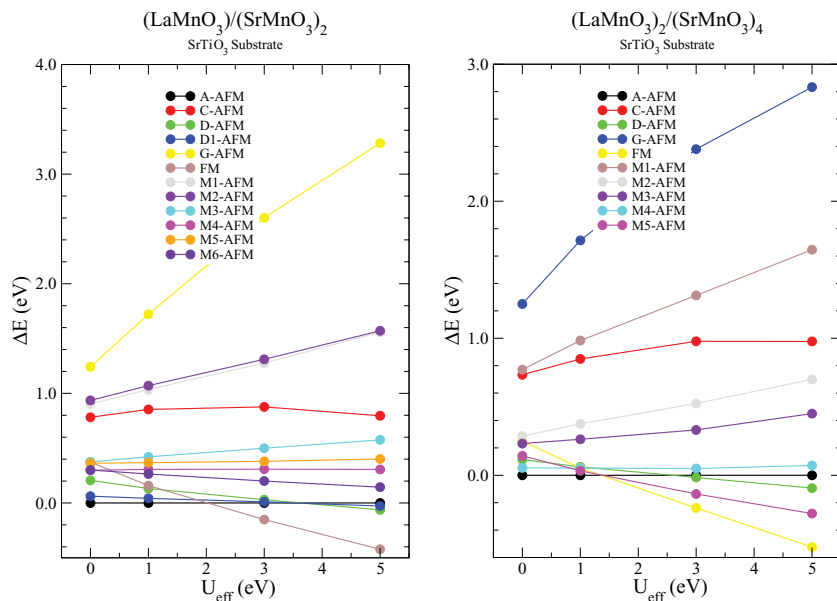


FIG. 5. (Color online)  $U_{\text{eff}}$  dependence of the relative energies (calculated using GGA +  $U$ ) for various magnetic structures (see Figs. 3 and 4) compared to A-type antiferromagnetic state for  $(\text{LaMnO}_3)_n/(\text{SrMnO}_3)_{2n}$  with  $n = 1$  (left) and  $n = 2$  (right) on  $\text{SrTiO}_3$  substrate.

TABLE I. Total energies (in units of eV) of (LaMnO<sub>3</sub>)<sub>n</sub>/(SrMnO<sub>3</sub>)<sub>2n</sub> superlattices ( $n = 1, 2$ ) calculated using GGA. FM, A-AFM, and C-AFM stand for ferromagnetic, A-type antiferromagnetic, and C-type antiferromagnetic states, respectively.

$n$	SrTiO <sub>3</sub> substrate			LaAlO <sub>3</sub> substrate		
	FM	A-AFM	C-AFM	FM	A-AFM	C-AFM
$n = 1$	-466.262	-466.636	-465.854	-465.852	-465.459	-466.466
$n = 2$	-465.637	-465.885	-465.151	-465.398	-465.015	-465.858

exchange ( $J_{\text{eff}}$ ) simply by comparing the total energy of the A-type and the C-type antiferromagnetic states. It is clearly observed in Table I that the stabilization energy of the A-type antiferromagnetic state, i.e.,  $J_{\text{eff}}$ , is larger for  $n = 1$  than for  $n = 2$ . This implies that  $T_N$  for  $n = 1$  is higher than that for  $n = 2$ . These results are in excellent agreement with experimental observations by May *et al.*<sup>14</sup>

Since the epitaxial constraint of substrates is to fix the in-plane lattice constant  $a$  of the superlattices, the tetragonal distortion should inevitably occur, which in turn affects the relative occupation of Mn  $e_g$  electrons. Indeed, as shown in Table II, we find that the SrTiO<sub>3</sub> substrate induces tensile strain with  $a > c$ , in which the  $d_{x^2-y^2}$  orbital is lower in energy than the  $d_{3z^2-r^2}$  orbital. This can be seen in the projected charge-density distribution, the integrated charge density from Fermi level down to  $-0.5$  eV, shown in Figs. 1(b) and 2(b), indicating that  $e_g$  electrons preferably occupy the  $d_{x^2-y^2}$  orbital. Because of this orbital order induced inherently by the substrate strain, the A-type antiferromagnetic order is stabilized. Remember that the magnetic interaction between Mn ions is determined by competition between the ferromagnetic double exchange via itinerant Mn  $e_g$  electrons and the antiferromagnetic superexchange between localized Mn  $t_{2g}$  electrons. When the  $d_{x^2-y^2}$  orbital is occupied rather than the  $d_{3z^2-r^2}$  orbital, the strong double exchange induces ferromagnetic order in the  $ab$  plane, while the weak itinerancy of the  $d_{x^2-y^2}$  electrons along the  $c$  direction reduces substantially the double exchange and as a result, the superexchange between  $t_{2g}$  electrons stabilizes antiferromagnetic order along this direction. Finally, it is also interesting to note that the optimized lattice constant  $c$  for  $n = 1$  is shorter than that for  $n = 2$  (see Table II), which is also qualitatively in good agreement with experimental observations.<sup>14</sup>

### B. (LaMnO<sub>3</sub>)<sub>n</sub>/(SrMnO<sub>3</sub>)<sub>2n</sub> on LaAlO<sub>3</sub>

Now, let us study the electronic and the magnetic properties of (LaMnO<sub>3</sub>)<sub>n</sub>/(SrMnO<sub>3</sub>)<sub>2n</sub> superlattices ( $n = 1, 2$ ) on (001) LaAlO<sub>3</sub> substrate. In the alloy manganites La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3</sub>,

TABLE II. The optimized lattice constant  $c$  (averaged value within the supercell and in units of Å) and  $c/a$  of (LaMnO<sub>3</sub>)<sub>n</sub>/(SrMnO<sub>3</sub>)<sub>2n</sub> superlattices ( $n = 1, 2$ ) calculated using GGA. The magnetic structures are A-type and C-type antiferromagnetic for SrTiO<sub>3</sub> and LaAlO<sub>3</sub> substrates, respectively.

$n$	SrTiO <sub>3</sub> substrate		LaAlO <sub>3</sub> substrate	
	$c$	$c/a$	$c$	$c/a$
$n = 1$	3.806	0.9746	4.006	1.0115
$n = 2$	3.825	0.9795	4.010	1.0525

it is known that  $c/a$  is a key parameter in determining the magnetic ground states.<sup>26</sup> Here, we demonstrate that even in these superlattices, the magnetic structure can be controlled by the substrate strain which varies  $c/a$ .

Because the in-plane lattice constant of LaAlO<sub>3</sub> is much smaller than that of LaMnO<sub>3</sub> (bulk lattice parameter is 3.935 Å), it is expected that the LaAlO<sub>3</sub> substrate induces compressive strain. In fact, we find in Table II that the lattice constant  $c$  in the superlattices is larger than the in-plane lattice constant  $a$ . As a result of this tetragonal distortion, Mn  $e_g$  orbitals are split and the  $d_{3z^2-r^2}$  orbital is lower in energy than the  $d_{x^2-y^2}$  orbital, which thus induces  $d_{3z^2-r^2}$  orbital order. A signature of this orbital order can be seen in the projected charge-density distributions shown in Figs. 1(c) and 2(c). Because of this orbital order, the magnetic ground state is expected to be C-type antiferromagnetic. Considering 10–12 different candidates for possible magnetic structures as shown in Figs. 3 and 4, our GGA calculations find that the ground states for  $n = 1$  and 2 are both C-type antiferromagnetic metals [Figs. 3(b) and 4(b)]. This magnetic alignment can be indeed clearly seen in the projected spin-density distribution as shown in Figs. 1(e) and 2(e). It is also interesting to note that the lattice distortion along the  $c$  direction is less pronounced for the case of LaAlO<sub>3</sub> substrate as compared to the case of SrTiO<sub>3</sub> substrate. As shown in Fig. 6, Mn-O-Mn angles between the nearest layers along the  $c$  direction for the superlattices on LaAlO<sub>3</sub> substrate are almost 180°, which certainly favors the ferromagnetic double exchange along this direction. We

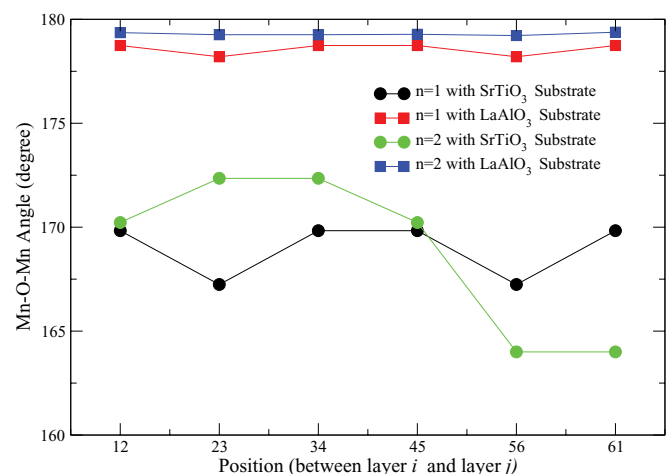


FIG. 6. (Color online) Mn-O-Mn angles between the nearest layers along the  $c$  direction for the relaxed crystal structures (calculated using GGA) for (LaMnO<sub>3</sub>)<sub>n</sub>/(SrMnO<sub>3</sub>)<sub>2n</sub> (001) superlattices grown on different substrates indicated in the figure. The layer positions in the horizontal axis are indicated in Figs. 1(a) and 2(a).

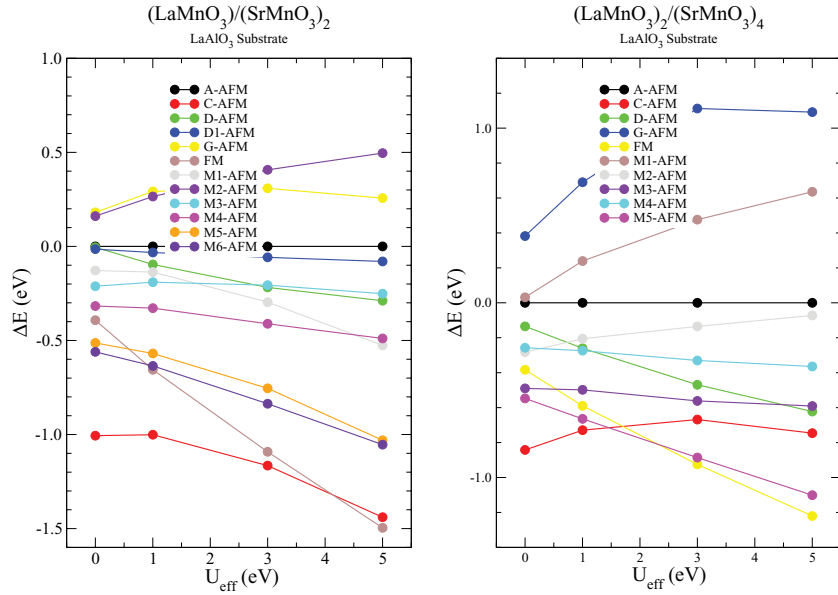


FIG. 7. (Color online)  $U_{\text{eff}}$  dependence of the relative energies (calculated using GGA +  $U$ ) for various magnetic structures (see Figs. 3 and 4) compared to A-type antiferromagnetic state for  $(\text{LaMnO}_3)_n/(\text{SrMnO}_3)_{2n}$  with  $n = 1$  (left) and  $n = 2$  (right) on  $\text{LaAlO}_3$  substrate.

also find that the C-type magnetic structure is robust against electron correlations in Mn  $d$  orbitals up to  $U_{\text{eff}} = 4$  eV for  $n = 1$  and  $U_{\text{eff}} = 1.5$  eV for  $n = 2$  (see Fig. 7).<sup>25</sup>

As in the case of  $\text{SrTiO}_3$  substrate, we can discuss the Néel temperature  $T_N$  for the C-type antiferromagnetic order by calculating the total energy, and the results are summarized in Table I. Simply by comparing the total energies of the C-type and the A-type antiferromagnetic states, the difference of which gives a rough estimate of an effective magnetic exchange  $J_{\text{eff}}$ , we find that the stabilization energy of the C-type antiferromagnetic state, i.e.,  $J_{\text{eff}}$ , is larger for  $n = 1$  than for  $n = 2$ . This implies that  $T_N$  for  $n = 1$  is higher than that for  $n = 2$ . Since  $(\text{LaMnO}_3)_n/(\text{SrMnO}_3)_{2n}$  superlattices ( $n = 1, 2$ ) on (001)  $\text{LaAlO}_3$  substrate have not been studied experimentally, these results provide the theoretical prediction which should be tested experimentally in the future.

### C. Confinement potential

Finally, let us briefly discuss why the magnetic and orbital ground states found here are spatially uniform, in spite of apparent periodic potential modulation caused by different ionic charges, i.e.,  $\text{La}^{3+}$  in  $\text{LaMnO}_3$  layers, and  $\text{Sr}^{2+}$  in  $\text{SrMnO}_3$ . As reported in Ref. 12, one way to estimate the effective potential modulation is to evaluate the oxygen  $1s$  core energy level. The results for  $(\text{LaMnO}_3)_n/(\text{SrMnO}_3)_{2n}$  superlattices with  $n = 1$  and 2 are shown in Fig. 8. From these figures, we see that (i) the potentials are almost the same for both substrates, and (ii) as is expected, the confinement potential becomes larger with  $n$ . The calculated charge density

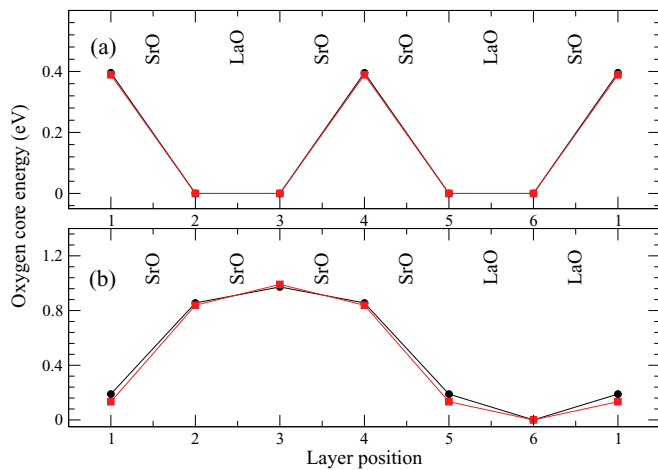


FIG. 8. (Color online) The variations of the relative oxygen  $1s$  core energy (calculated using GGA) in each  $\text{MnO}_2$  layer of (a)  $(\text{LaMnO}_3)_n/(\text{SrMnO}_3)_2$  and (b)  $(\text{LaMnO}_3)_2/(\text{SrMnO}_3)_4$  superlattices. Results for  $\text{SrTiO}_3$  and  $\text{LaAlO}_3$  substrates are indicated by black circles and red squares, respectively. The layer positions are indicated in Figs. 1(a) and 2(a).

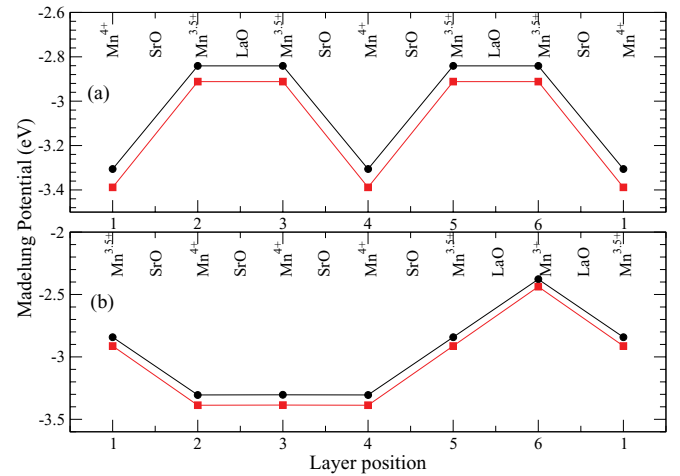


FIG. 9. (Color online) The variation of the Madelung potential for Mn ions in each  $\text{MnO}_2$  layer of (a)  $(\text{LaMnO}_3)_n/(\text{SrMnO}_3)_2$  and (b)  $(\text{LaMnO}_3)_2/(\text{SrMnO}_3)_4$  superlattices. Results for  $\text{SrTiO}_3$  and  $\text{LaAlO}_3$  substrates are indicated by black circles and red squares, respectively. Here, the ideal crystal structures with no distortion, and the ideal Mn valency (indicated in the figures) with  $\text{O}^{2-}$ ,  $\text{La}^{3+}$ , and  $\text{Sr}^{2+}$  are assumed. The layer positions are indicated in Figs. 1(a) and 2(a). Note that the sign convention of the Madelung potential used here is that electrons prefer to locate in  $\text{LaMnO}_3$  layers.

shows that  $e_g$  electrons in LaMnO<sub>3</sub> layers are  $\sim 0.2$  (0.1) more than that in SrMnO<sub>3</sub> layers for  $n = 2$  ( $n = 1$ ). This suggests that the thickness is still thin enough not to confine  $e_g$  electrons in LaMnO<sub>3</sub> layers. However, we naturally expect that the bulk properties may recover far away from interface when  $n$  is increased further and a metal-insulator transition should eventually occur.

It is also found that the confinement potential can be more easily estimated simply by calculating the Madelung potential. As shown in Fig. 9, the Madelung potential can indeed semiquantitatively reproduce the values estimated from oxygen  $1s$  core energy level. This finding should be very useful in estimating the confinement potential for more complex superlattices in which first-principles electronic-structure calculations are computationally expensive.

#### IV. SUMMARY

Using first-principles calculations based on the density functional theory, we have studied the effects of epitaxial strain on the magnetic ground states in (LaMnO<sub>3</sub>) <sub>$n$</sub> /(SrMnO<sub>3</sub>) <sub>$2n$</sub>  (001) superlattices with  $n = 1, 2$ . Our results clearly demonstrate that as in alloy manganites, even in superlattices, the epitaxial strain induced by substrates enforces tetragonal distortion, which in turn governs the ground-state magnetic

structure via the inherent orbital ordering. We have found that for the tensile strain induced by SrTiO<sub>3</sub> (001) substrate, the ground state is A-type antiferromagnetic metal with  $d_{x^2-y^2}$  orbital order. The approximate estimation of an effective magnetic exchange suggests that the Néel temperature  $T_N$  of the A-type antiferromagnetic order is higher for  $n = 1$  than that for  $n = 2$ . These results are in excellent agreement with experimental observations.<sup>14</sup> Furthermore, we have predicted that for the compressive strain induced by LaAlO<sub>3</sub> (001) substrate, the ground state is C-type antiferromagnetic metal with  $d_{3z^2-r^2}$  orbital order with higher Néel temperature  $T_N$  for  $n = 1$  than that for  $n = 2$ . These predictions should be confirmed experimentally in the future.

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