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

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1. INTRODUCTION

Transition metal oxides in perovskite based structures exhibit a wide variety of phases with different electronic, magnetic, and structural properties, and show rich functionalities such as high-$T_C$ superconductivity, colossal magnetoresistance, and multiferroics. A recent advance in epitaxial growth techniques has made it possible to fabricate transition metal oxide heterostructures with sharp and smooth interfaces controlled at the atomic scale. 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 indicating the promising potential of oxide heterostructures for future technological applications.

The magnetic properties of similar superlattices (LaMnO$_3$)$_n$/(SrMnO$_3$)$_{2n}$ and SrMnO$_3$ would be observed. Several theoretical studies for (LaMnO$_3$)$_2n$/(SrMnO$_3$)$_n$ superlattices have been reported to understand their electronic and magnetic properties.

More recently, Bhattacharya et al. have experimentally studied the transport and the magnetic properties of similar superlattices (LaMnO$_3$)$_n$/(SrMnO$_3$)$_{2n}$ grown on SrTiO$_3$ (001) substrate. They have found that the ground state of these superlattices with $n = 1, 2$ are A-type antiferromagnetic insulators with $Néel$ temperature ($T_N$) which is higher than that observed in any alloy La$_{1-x}$Sr$_x$MnO$_3$ compound. Although the similar physical principles found in (LaMnO$_3$)$_2n$/(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 (LaMnO$_3$)$_n$/(SrMnO$_3$)$_{2n}$ superlattices.

Using first-principles calculations based on the density functional theory, we show a strong strain dependence of magnetic order in (LaMnO$_3$)$_n$/(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 magnetic 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$_3$ (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 [S. J. May et al., Nature Materials 8, 892 (2009)]. Instead, for the case of compressive strain induced by LaAlO$_3$ (001) substrate, we predict that the ground state is $C$-type antiferromagnetic and $d_{3z^2−r^2}$ orbital ordered.

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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\(_3\) substrate and LaAlO\(_3\) substrate are presented in Sec. III A and Sec. III B respectively, followed by discussion of the confinement potential in Sec. III C. Sec. IV summaries this paper.

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)\(^{15,16}\). 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\(^{17–19}\) with the effective \( U_{\text{eff}} \), i.e., \( U - J \), from 1 eV to 5 eV for \( d \) electron states. Compared to the GGA, the GGA+\( U \) approach gives an improved description of \( d \) electron localization.\(^{20}\) 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.\(^{21}\)

The supercells considered here consist of 6 MnO\(_2\) layers, 2 LaO layers, and 4 SrO layers for both \( n = 1 \) and 2, as shown in Fig. 1 (a) and Fig. 2 (a). We consider 12 and 10 different magnetic moment alignments to search for the ground state magnetic structures for LaMnO\(_3\)/(SrMnO\(_3\))\(_2\) and LaMnO\(_3\)/2/(SrMnO\(_3\))\(_4\) superlattices, as shown in Fig. 3 and Fig. 4 respectively. These magnetic structures include not only simple ferromagnetic, A-type, C-type, and G-type antiferromagnetic structures\(^{22}\) 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 the ones of substrates, i.e., \( a = 3.905 \) Å for SrTiO\(_3\) substrate\(^{23}\) and \( a = 3.81 \) Å for LaAlO\(_3\) substrate\(^{24}\) and the lattice constant \((c)\) perpendicular to MnO\(_2\) layers is fully relaxed. Atomic positions are also fully optimized.

III. RESULTS

A. \((LaMnO_3)_n/(SrMnO_3)_{2n}\) on SrTiO\(_3\)

Let us first examine \((LaMnO_3)_n/(SrMnO_3)_{2n}\) (001) superlattices on 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 Fig. 3(g) and Fig. 2(a). Indeed, as shown in Fig. 1(d) and Fig. 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 to \( U_{\text{eff}} = 2 \) eV for \( n = 1 \) and \( U_{\text{eff}} = 1.3 \) eV for \( n = 2 \) (see Fig. 5).\(^{25}\)

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. Tab. 1 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 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 Tab. 1 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.\(^{26}\)

| \( n \) | SrTiO\(_3\) substrate | LaAlO\(_3\) substrate |
|---|---|---|
| \( n = 1 \) | FM | A-AMF | C-AFM | FM | A-AMF | C-AFM |
| | \(-466.262\) | \(-466.636\) | \(-465.854\) | \(-465.852\) | \(-465.459\) | \(-466.466\) |
| \( n = 2 \) | \(-465.637\) | \(-465.885\) | \(-465.151\) | \(-465.398\) | \(-465.015\) | \(-465.858\) |

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 Tab. 1 we find that the SrTiO\(_3\) substrate induces tensile strain with \( a > c \), in which \( d_{x^2-y^2} \) orbital is lower in energy than \( d_{3z^2-r^2} \) 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 Fig. 1(b) and Fig. 2(b), indicating that \( e_g \) electrons preferably occupy \( d_{x^2-y^2} \) 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 \( d_{x^2-y^2} \) orbital is occupied rather than \( d_{3z^2-r^2} \) orbital, the strong double exchange induces ferromagnetic order in the \( ab \) plane while the weak itineracy of \( d_{x^2-y^2} \) electrons along the c
FIG. 1. (Color online). (a) A schematic figure of the supercell considered for LaMnO$_3$/SrMnO$_3$$_2$ (001) superlattices, and the projected charge [(b) and (c)] and spin [(d) and (e)] density distributions (integrated from Fermi level down to $-0.5$ eV using GGA) for LaMnO$_3$/SrMnO$_3$$_2$ superlattices grown on SrTiO$_3$ [(b) and (d)] and 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 (LaMnO$_3$)$_2$/SrMnO$_3$$_4$ (001) superlattices, and the projected charge [(b) and (c)] and spin [(d) and (e)] density distributions (integrated from Fermi level down to $-0.5$ eV using GGA) for (LaMnO$_3$)$_2$/SrMnO$_3$$_4$ superlattices grown on SrTiO$_3$ [(b) and (d)] and 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.

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 Tab. III), which is also qualitatively in good agreement with experimental observations.
FIG. 3. (Color online). 12 different magnetic structures considered for LaMnO$_3$/(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.

TABLE II. The optimized lattice constant $c$ (averaged value within the supercell and in unit of Å) and $c/a$ of (LaMnO$_3$)$_n$/(SrMnO$_3$)$_{2n}$ superlattices ($n = 1, 2$) calculated using GGA. The magnetic structures are A-type and C-type antiferromagnetic for SrTiO$_3$ and LaAlO$_3$ substrates, respectively.

| $n$ | SrTiO$_3$ substrate | LaAlO$_3$ 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 |

B. (LaMnO$_3$)$_n$/(SrMnO$_3$)$_{2n}$ on LaAlO$_3$

Now, let us study the electronic and the magnetic properties of (LaMnO$_3$)$_n$/(SrMnO$_3$)$_{2n}$ superlattices ($n = 1, 2$) on (001) LaAlO$_3$ substrate. In the alloy manganites La$_{1-x}$Sr$_x$MnO$_3$, it is known that $c/a$ is a key parameter in determining the magnetic ground states. 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$_3$ is much smaller than that of LaMnO$_3$ (bulk lattice parameter is 3.935 Å), it is expected that the LaAlO$_3$ substrate induces compressive strain. In fact, we find in Tab. III 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 $d_{3z^2-r^2}$ orbital is lower in energy than $d_{x^2-y^2}$ 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 Fig. 1(c) and Fig. 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 [Fig. 3(b) and Fig. 4(b)]. This magnetic alignment can be indeed clearly seen in the projected spin density distribution as shown in Fig. 1(e) and Fig. 2(e). It is also interesting to note that the lattice distortion along the $c$ direction is less pronounced for the case of LaAlO$_3$ substrate as compared to the case of SrTiO$_3$ substrate. As shown in Fig. 6 Mn-O-Mn angles between the nearest layers along the $c$ direction for the superlattices on LaAlO$_3$ substrate is almost 180°, which certainly favors the ferromagnetic double exchange along this direction. We 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).

As in the case of SrTiO$_3$ substrate, we can discuss the Néel temperature $T_N$ for the C-type antiferromagnetic...
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.

FIG. 5. (Color online). \( U_{\text{eff}} \) dependence of the relative energies (calculated using GGA+\( U \)) for various magnetic structures (see Fig. 3 and Fig. 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 SrTiO\(_3\) substrate.

order by calculating the total energy, and the results are summarized in Tab. 1. 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., $J_{eff}$ 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) 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., La$^{3+}$ in LaMnO$_3$ layers, and Sr$^{2+}$ in SrMnO$_3$. As reported in Ref. 12, one way to estimate the effective potential modulation is to evaluate the oxygen 1$s$ 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 shows that $e_g$ electrons in LaMnO$_3$ layers is $\sim$0.2 (0.1) more than that in SrMnO$_3$ layers for $n = 2$ ($n = 1$). This suggests that the thickness is still thin enough not to confine $e_g$ electrons in LaMnO$_3$ 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 Madelung potential. As shown in Fig. 9 Madelung potential can indeed semi-qualitatively reproduce the values estimated from oxygen 1$s$ 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.

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**FIG. 7.** (Color online). $U_{eff}$ dependence of the relative energies (calculated using GGA+$U$) for various magnetic structures (see Fig. 3 and Fig. 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 LaAlO$_3$ substrate.

**FIG. 8.** (Color online). The variations of the relative oxygen 1$s$ core energy (calculated using GGA) in each MnO$_2$ layer of (a) LaMnO$_3$/SrMnO$_3$ and (b) LaTiO$_3$/SrMnO$_3$ superlattices. Results for SrTiO$_3$ and LaAlO$_3$ substrates are indicated by black circles and red squares, respectively. The layer positions are indicated in Fig. 4 (a) and Fig. 5 (a).

**FIG. 9.** (Color online). The variation of Madelung potential for Mn ions in each MnO$_2$ layer of (a) LaMnO$_3$/SrMnO$_3$ and (b) LaTiO$_3$/SrMnO$_3$ superlattices. Results for SrTiO$_3$ and 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 O$^{2-}$, La$^{3+}$, and Sr$^{2+}$ are assumed. The layer positions are indicated in Fig. 4 (a) and Fig. 5 (a). Note that the sign convention of Madelung potential used here is that electrons prefer to locate in LaMnO$_3$ layers.
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$_3$)$_n$/(SrMnO$_3$)$_{2n}$ (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$_3$ (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. Furthermore, we have predicted that for the compressive strain induced by LaAlO$_3$ (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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1 M. Imada, A. Fujimori, and Y. Tokura, Rev. Mod. Phys. 70, 1039 (1998).
2 C. H. Ahn, A. Bhattacharya, M. Di Ventra, J. N. Eckstein, C. D. Frisbie, M. E. Gershenson, A. M. Goldman, I. H. Inoue, J. Mannhart, A. J. Millis, A. F. Morpurgo, D. Natelson, and J. M. Triscone, Rev. Mod. Phys. 78, 1185 (2006).
3 A. Ohtomo and H. Y. Hwang, Nature 427, 423 (2006).
4 H. Y. Hwang, Y. Iwasa, M. Kawasaki, B. Keimer, N. Nagaosa, and Y. Tokura, Nature Mater. 11, 103 (2012).
5 E. Dagotto, T. Hotta, and A. Moreo, Phys. Rep. 344, 1 (2001).
6 C. Adamo, X. Ke, P. Schiffer, A. Soukiassian, M. Warusawithana, L. Maritato, and D. G. Schom, Appl. Phys. Lett. 92, 112508 (2008).
7 H. B. Zhao, K. J. Smith, Y. Fan, G. Lüpfke, A. Bhattacharya, S. D. Bader, M. Warusawithana, X. Zhai, and J. N. Eckstein, Phys. Rev. Lett. 100, 117208 (2008).
8 A. Bhattacharya, S. J. May, S. G. E. Te Velthuis, M. Warusawithana, X. Zhai, B. Jiang, J. Zuo, M. R. Fitzsimmons, S. D. Bader, and J. N. Eckstein, Phys. Rev. Lett. 100, 257203 (2008).
9 A. Perucchi, L. Baldassarre, A. Nucara, P. Calvani, C. Adamo, D. G. Schom, P. Orgiani, L. Maritato, and S. Lupi, Nano Lett. 10, 4819 (2010).
10 A. Galki, C. Aruta, P. Orgiani, C. Adamo, V. Bisogni, N. B. Brookes, G. Ghiringhelli, D. G. Schom, P. Thakur, and L. Maritato, Phys. Rev. B 85, 125129 (2012).
11 S. Dong, R. Yu, S. Yunoki, G. Alvarez, J.-M. Liu, and E. Dagotto, Phys. Rev. B 78, 201102(R) (2008).
12 B. R. K. Nanda and S. Satpathy, Phys. Rev. B 79, 054428 (2009).
13 A. Bhattacharya, X. Zhai, M. Warusawithana, J. N. Eckstein, and S. D. Bader, Appl. Phys. Lett. 90, 222503 (2007).
14 S. J. May, P. J. Ryan, J. L. Robertson, J. Kim, T. S. Santos, E. Karapetrova, J. L. Zarestky, X. Zhai, S. G. E. Te Velthuis, J. N. Eckstein, S. D. Bader, and A. Bhattacharya, Nature Mater. 8, 892 (2009).
15 G. Kresse and J. Hafner, Phys. Rev. B 47, 558 (1993).
16 G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996).
17 P. E. Blöchl, Phys. Rev. B 50, 17953 (1994).
18 G. Kresse and D. Joubert, Phys. Rev. B 59, 1758 (1999).
19 S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, and A. P. Sutton, Phys. Rev. B 57, 1505 (1998).
20 V. Anisimov, F. Aryasetiawan, and A. Lichtenstein, J. Phys.: Condens. Matter. 9, 767 (1997).
21 P. E. Blöchl, O. Jepsen, and O. K. Andersen, Phys. Rev. B 49, 16223 (1994).
22 E. O. Wollan and W. C. Koehler, Phys. Rev. 100, 545 (1955).
23 R. H. Mitchell, A. R. Chakhmourov and P. M. Woodward, Phys. Chem. Minerals 27, 583 (2000).
24 A. Nakayama, K. Ohtaka, H. Arima, N. Nakayama and T. Mizota, Acta Crystallogr. E 61, 148 (2005).
25 Note that with the GGA+U scheme a Stoner type ferromagnetic state is expected stable for large values of $U_{eff}$.
26 Z. Fang, I. V. Solovyev, and K. Terakura, Phys. Rev. Lett. 84, 3169 (2000).