Ferromagnetic insulating state in tensile-strained LaCoO$_3$ thin films from LDA + U calculations

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With local density approximation+Hubbard U (LDA + U) calculations, we show that the ferromagnetic (FM) insulating state observed in tensile-strained LaCoO$_3$ epitaxial thin films is most likely a mixture of low-spin (LS) and high-spin (HS) Co, namely, a HS/LS mixture state. Compared with other FM states, including the intermediate-spin (IS) state (*metallic* within LDA + U), which consists of IS Co only, and the insulating IS/LS mixture state, the HS/LS state is the most favorable one. The FM order in the HS/LS state is stabilized via the superexchange interactions between adjacent LS and HS Co. We also show that the Co spin state can be identified by measuring the electric field gradient at the Co nucleus via nuclear magnetic resonance spectroscopy.

Perovskite-structure oxides have been proven to be a fertile area in condensed-matter physics. They exhibit interesting properties, including ferroelectricity, ferromagnetism, colossal magnetoresistance (CMR), and multiferroics (simultaneous ferroelectricity and ferromagnetism), as a consequence of their spin, lattice, charge, and orbital degrees of freedom. Advances in thin-film growth techniques have even brought more promising potentials for their future application, as their properties can be engineered via epitaxial strains. A few examples include strontium titanate (SrTiO$_3$), which is ferroelectric in tensile-strained thin film while paraelectric in bulk,[1] lanthanum titanate (LaTiO$_3$), which is conducting in compressive-strained thin film while insulating in bulk,[2] and europium titanate (EuTiO$_3$), in which multiferroics induced by tensile strains has been observed.[3] As to lanthanum cobaltite (LaCoO$_3$), which is a diamagnetic insulator in bulk at low temperatures ($T < 35$ K), a ferromagnetic (FM) *insulating* state has been observed in tensile-strained thin films, e.g., LaCoO$_3$ grown on SrTiO$_3$ or (LaAlO$_3$)$_{0.3}$(Sr$_2$AlTaO$_6$)$_{0.7}$, at $T < 85$ K,[4–13] while the ferromagnetism induced by compressive strains, e.g., LaCoO$_3$ grown on LaAlO$_3$, is not conclusive.[5–7,14] Two questions arise immediately: (1) Given that there are six $3d$ electrons in Co^{3+}, which can thus have a total electron spin $S = 0$, 1, or 2, referred to as low-spin (LS), intermediate-spin (IS), and high-spin (HS) states, respectively, what is the spin state of Co in FM LaCoO$_3$ thin films, in contrast to the LS Co in diamagnetic bulk? (2) What leads to the formation of FM order in LaCoO$_3$ thin films? After all, FM *insulators* are rarely seen. So far, and to the best of our knowledge, all first-principles calculations have only found FM *metallic* LaCoO$_3$ thin films with all Co ions in the IS state,[11,15,16] a prediction clearly inconsistent with transport measurements.[6]

While finite Co spin induced by tensile strains in LaCoO$_3$ thin films has just started to attract attention, finite Co spin induced by thermal excitation in bulk LaCoO$_3$ has been a highly controversial issue for decades.[17,18] With LS Co at $T < 35$ K, bulk LaCoO$_3$ becomes a paramagnetic insulator with a finite Co spin at about 90 K. Such a spin-state crossover in the temperature range of 35–90 K was first suggested to be a LS-HS crossover[19–21] but was later suggested to be LS-IS based on a local density approximation + Hubbard U

(LDA + U) calculation.[22] Since then, both scenarios have received support from various experimental and theoretical works, but, to the best of our knowledge, a consensus has not yet been achieved (see Ref. 23 for a brief review). A study regarding LaCoO$_3$ thin films may also help to understand LaCoO$_3$ bulk from a different perspective. In this Rapid Communication, we investigate the Co spin state in tensile-strained thin films and the formation of FM order via a series of LDA+U calculations. While LDA+U has been frequently used to study cobaltites and the Co spin state, the choice of Hubbard U can be an issue. It has been shown that under the same lattice parameter, the Hubbard U affects the total energy and the determination of the ground state.[16] A well-justified Hubbard U determined by first principles would thus be necessary for finding out the actual ground state. In this Rapid Communication, we compute the Hubbard U parameters of Co in all spin states self-consistently with a linear response approach.[24–26] This method has successfully found the ground state of iron-bearing magnesium silicate (MgSiO$_3$) perovskite at a wide range of pressure.[26] Both the plane-wave pseudopotential (PWPP) method[27] implemented in QUANTUM ESPRESSO codes[28] and the augmented plane wave + local orbitals (APW + lo) method[29] implemented in WIEN2K codes[30] are used. As shall be pointed out later, the orbital occupancies of Co in thin films are different from those in bulk, due to their different symmetries. We therefore compute the electric field gradient (EFG) tensor at the Co nucleus, V_{zz}, with WIEN2K, to see whether the Co spin state in thin films can be identified via EFG, as demonstrated in bulk.[23]

The pseudocubic lattice parameter of bulk LaCoO$_3$ ($R\bar{3}c$ symmetry) is about 3.81 Å at $T \sim 5$ K.[31,32] To model tensile-strained LaCoO$_3$ thin films via bulk calculations, we constrain the in-plane pseudocubic lattice parameters a_{pc} and b_{pc} of the hypothetical bulk to 3.899 Å (the lattice constant of cubic SrTiO$_3$ at low temperatures),[33] set $\alpha = \beta = \gamma = 90°$, and optimize the out-of-plane pseudocubic lattice parameter (c_{pc}). Due to the lack of accurate information regarding CoO$_6$ octahedral rotation in thin-film LaCoO$_3$ in the low-temperature FM phase, we consider two extreme cases shown in Fig. 1: (a) cube on cube, namely, no CoO$_6$ octahedral rotation degree of
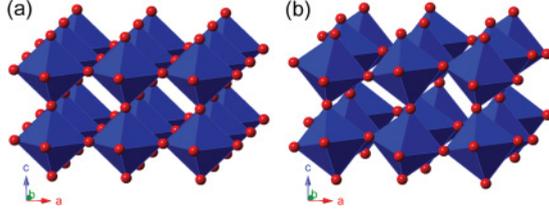
FIG. 1. (Color online) Possible atomic structures of $LaCoO_3$ thin film (La is not shown) subject to constrained in-plane lattice parameters. (a) Cube on cube, no CoO_6 octahedral rotation; (b) full octahedral rotation degree of freedom.
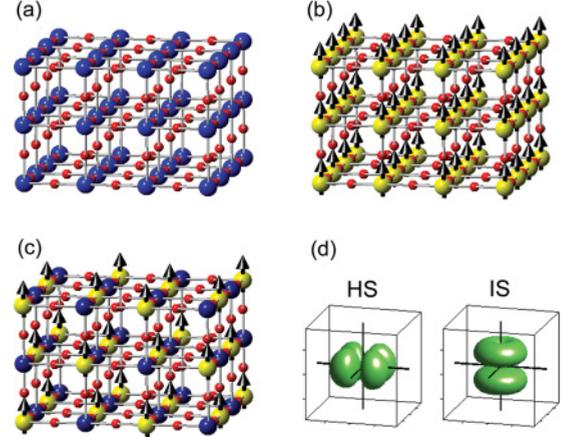

FIG. 2. (Color online) (a)–(c) Possible magnetic configurations in a $LaCoO_3$ epitaxial thin film (La is not shown). The arrows denote nonzero magnetic moments, either IS or HS. (a) LS state; (b) HS or IS state in FM order; (c) HS/LS or IS/LS mixture state in FM order. (d) The $3d$ orbitals occupied by the spin-down electrons of HS and IS Co.

freedom, and (b) full CoO_6 rotation degree of freedom subject to the above-mentioned constraints. We also consider several magnetic configurations shown in Fig. 2: (a) all Co ions in LS state, (b) all Co ions have the same magnetic moment aligned in FM order, and (c) a mixture state with LS Co surrounded by magnetic Co (and vice versa) aligned in FM order. The configuration shown in Fig. 2(c) is a legitimate postulate, as the observed magnetization in $LaCoO_3$ thin films rarely exceeds $0.85\mu_B$/Co.[4–11] For the configuration in Fig. 2(b), a convergent wave function for HS state cannot be obtained; only an IS state can be found. For the configuration in Fig. 2(c), both HS/LS and IS/LS mixture states can be obtained. The self-consistent Hubbard U parameters (U_{sc}) of LS and IS Co are both 7.0 eV, while the HS/LS state has $U_{sc}^{(HS)} = 5.4$ and $U_{sc}^{(LS)} = 7.2$ eV.[34] The dependence of U_{sc} on c_{pc} is negligible. To demonstrate how the choice of Hubbard U can affect the determination of the ground state, we also present the result obtained using a constant $U = 7$ eV for all Co in our PWPP calculations. In tensile-strained $LaCoO_3$ thin films, CoO_6 octahedra possess tetragonal symmetry, namely, a longer Co-O distance on the xy plane, regardless of CoO_6 rotation. In tetragonal symmetry (D_{4h}), the spin-down electron of HS Co occupies d_{xy} orbital, and the spin-down electrons of IS Co occupy d_{xz} and d_{yz} orbitals, as shown in Fig. 2(d). Such orbital occupancies are very different from those in bulk $LaCoO_3$, in which the CoO_6 octahedra have a trigonal symmetry (D_{3d}), with the [111] direction being the high-symmetry axis. In bulk $LaCoO_3$, the spin-down electron of HS Co occupies the d_{z^2}-like orbital oriented along the [111] direction, and the IS Co spin-down electrons occupy the doublet with threefold rotation symmetry about the [111] direction.[23]

The optimized out-of-plane pseudocubic lattice parameter (c_{pc}) of each FM state and associated relative energy (ΔE) and band gap (E_{gap}) are listed in Tables I and II. Regardless of

CoO_6 rotation, the HS/LS mixture state (with U_{sc}) is the most stable FM state given by the PWPP method (Table I).[35] While the choice of $U = 7.0$ eV makes the HS/LS state less favorable in PWPP calculations, APW + lo calculations still find HS/LS the most stable FM state (Table II). Both PWPP and APW + lo methods open an energy gap for the HS/LS state, consistent with transport measurements.[6] Also, the presence of HS Co is consistent with recent x-ray magnetic circular dichroism (XMCD) and x-ray absorption spectroscopy (XAS) spectra.[9,10] In contrast, the IS state is never the most favorable FM state, regardless of the computation method and CoO_6 rotation. Its partially filled bands formed by partially occupied d_{z^2} and $d_{x^2-y^2}$ orbitals in IS Co lead to a nonzero density of state at the Fermi level. When the IS Co concentration is reduced to 50%, an energy gap is opened in APW + lo calculations (Table II), while PWPP calculations still give a conducting IS/LS state (Table I). Such a difference is likely to result from the way that the Hubbard U is applied. In PWPP, the Hubbard U is applied to the projection of the total wave function onto Co $3d$ orbitals;[24] in APW + lo, the Hubbard U is directly applied to the $3d$ orbitals within the muffin-tin radius of Co (1.9 bohrs). Insulating or not, the IS/LS state is highly unlikely; its energy is even higher than that of the IS state. It is worth mentioning that the Co-O distance (d_{Co-O}) and Co-O-Co angle obtained in our calculation are different from those estimated in Ref. 5, where a

TABLE I. Optimized out-of-plane pseudocubic lattice parameter (c_{pc}) and associated relative energy (ΔE) and energy gap (E_{gap}) of each FM state in tensile-strained $LaCoO_3$ thin film (PWPP method).

	No CoO_6 rotation			Full CoO_6 rotation		
	c_{pc} (Å)	ΔE (eV/f.u.)	E_{gap} (eV)	c_{pc} (Å)	ΔE (eV/f.u.)	E_{gap} (eV)
LS	3.865	0.35	0.54	3.660	0.32	1.24
IS	3.785	0.20	Metal	3.785	0.19	Metal
IS/LS	3.720	0.35	Metal	3.680	0.29	Metal
HS/LS (U_{sc})	3.685	0.00	0.92	3.680	0.00	0.90
HS/LS ($U = 7$ eV)	3.700	0.29	1.12	3.695	0.29	0.90

TABLE II. Optimized c_{pc} and associated ΔE and E_{gap} of each FM state (APW + lo method, with CoO_6 rotation).

	c_{pc} (Å)	ΔE (eV/f.u.)	E_{gap} (eV)
LS	3.660	0.37	1.72
IS	3.741	0.18	Metal
IS/LS	3.672	0.29	0.59
HS/LS ($U = 7$ eV)	3.686	0	1.52

TABLE III. Fully optimized pseudocubic lattice parameters of each FM state at the volume as in Table I (with CoO_6 rotation).

	a_{pc}, b_{pc} (Å)	c_{pc} (Å)	c_{pc}/a_{pc}
IS	3.848	3.893	1.012
IS/LS	3.847	3.778	0.982
HS/LS (U_{sc})	3.863	3.745	0.969
HS/LS ($U = 7$ eV)	3.865	3.757	0.972

constant $d_{Co-O} = 1.93$ Å is assumed (regardless of compressive or tensile strains), and a Co-O-Co angle of $176°$ is estimated for $LaCoO_3$ grown on $SrTiO_3$. In our PWPP calculation with U_{sc} and CoO_6 rotation, the HS/LS state has $d_{Co(HS)-O} = 2.015$ and 1.872 Å, $d_{Co(LS)-O} = 1.922$ and 1.886 Å, and Co-O-Co angles of $163.8°$ and $156.6°$, on the xy plane and along the z axis, respectively. Even for the IS state suggested by Ref. 5, we have $d_{Co(IS)-O} = 1.973$ and 1.939 Å, and Co-O-Co angles of $162.3°$ and $154.9°$, on the xy plane and along the z axis, respectively.

Other than the total energy, structural properties can be a useful criterion to determine which FM state favors tensile strains ($c_{pc}/a_{pc} < 1$). Starting with the structures listed in Table I with CoO_6 rotation, we perform a full structural optimization (at constrained volume) via variable cell-shape damped molecular dynamics.[36] All lattice parameters, including α, β, and γ, are optimized, so the final structures only experience hydrostatic pressures. With α, β, and γ slightly deviated from $90°$, the IS state has $c_{pc}/a_{pc} > 1$, while all other states remain $c_{pc}/a_{pc} < 1$ (but the IS/LS state still has a c_{pc}/a_{pc} larger than that of the HS/LS state), as shown in Table III. The larger c_{pc}/a_{pc} ratio associated with IS Co is a direct consequence of its occupied d_{xz} and d_{yz} orbitals (by spin-down electrons), which elongate the Co-O distance along the z direction. In contrast, the fully optimized HS/LS state has $c_{pc}/a_{pc} = 0.969$, in excellent agreement with $c_{pc}/a_{pc} = 0.967$ observed in experiments.[6]

A significant part of the cobalt-spin controversy arises from the difficulty in directly measuring the total electron spin of Co. Such a difficulty, also appearing in other spin systems, can be resolved by comparing the calculated and measured EFGs.[23,26,37] So far, the insulating FM state has been observed in $LaCoO_3$ thin films with a_{pc} ranging from 3.84 to 3.90 Å.[5,8] In these thin films, the magnetic Co concentration and Co-O distance may be different, which can lead to slightly different EFGs for Co in the same spin state. To find out the possible upper and lower limits of HS and IS Co EFGs, we compute them in two extreme cases: (1) thin films with $a_{pc} = 3.899$ Å and 50% of magnetic Co, namely, the HS/LS and IS/LS states listed in Tables I and II, and (2) a single isolated HS or IS Co in an array of LS Co in a fully relaxed structure with $a_{pc} \sim 3.81$ Å, where the orbital occupancies of isolated HS and IS Co are maintained in tetragonal symmetry [Fig. 2(d)]. In these APW + lo calculations, IS Co does not lead to a metallic state, in contrast to bulk $LaCoO_3$ (D_{3d} symmetry).[23] Different choices of Hubbard U have been adopted as well (5 eV, 7 eV, and U_{sc}). The results of all these calculations show that the EFG mainly depends on the spin state: $14.7 < V_{zz}^{(HS)}/(10^{21}$ V/m$^2) < 19.9$ and $-14.6 < V_{zz}^{(IS)}/(10^{21}$ V/m$^2) < -8.0$.

The quadrupole frequency $\nu_Q \equiv 3eQ|V_{zz}|/2I(2I - 1)h$ can thus be easily predicted, with $Q = 0.42 \times 10^{-28}$ m^2 and $I = 7/2$ for the ^{59}Co nucleus. Based on the range of $V_{zz}^{(HS)}$ and $V_{zz}^{(IS)}$, we conclude that in insulating $LaCoO_3$ thin films, a measured ν_Q via nuclear magnetic resonance (NMR) spectroscopy within $\sim 8.2 \pm 2.4$ MHz can be strong evidence for IS Co, and a measured ν_Q within $\sim 12.6 \pm 1.9$ MHz should indicate HS Co.

An analysis of electronic structures can help in developing a physical understanding of the FM order in the HS/LS state, whose projected density of states (PDOS) is shown in Fig. 3. The case with $U = 7$ eV and no CoO_6 rotation is presented, as the main features in the PDOS are not sensitive to the choice of U and CoO_6 rotation. Extracted from Fig. 3(a), both HS and LS Co have a nonzero magnetic moment: $2.97\mu_B$ and $0.56\mu_B$, respectively. The FM order is established via the superexchange interaction between HS and LS Co, as described by the Goodenough-Kanamori rule,[17,38–40] which states that the superexchange interaction between two cations (with or without a shared anion) is ferromagnetic if the electron transfer is from a filled to a half-filled orbital or from a half-filled to an empty orbital. Indeed, for the HS/LS state, electrons transfer from the filled d_{xz} and d_{yz} orbitals of LS Co to the half-filled d_{xz} and d_{yz} orbitals of HS Co via the
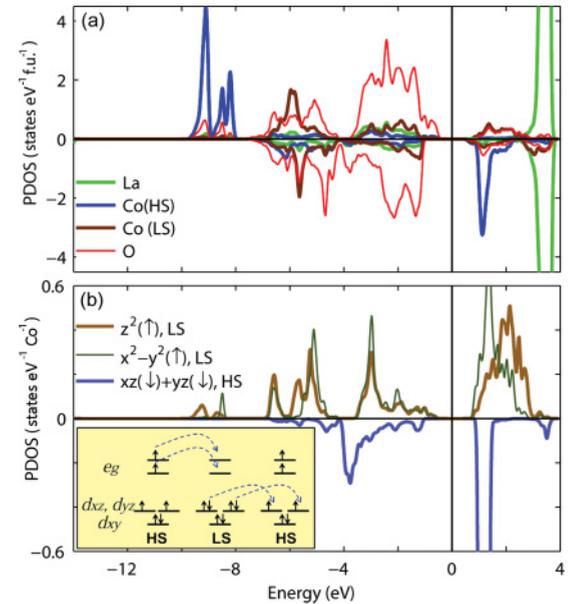

FIG. 3. (Color online) Projected density of states of a ferromagnetic HS/LS state (no CoO_6 rotation, $U = 7$ eV) onto (a) each atomic site, and (b) some of the Co 3d orbitals. The inset in (b) shows the electron transfer between HS and LS Co.
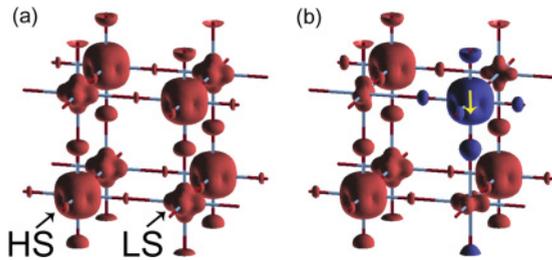
FIG. 4. (Color online) Spin density $s(\mathbf{r})$ of a HS/LS state (no CoO_6 rotation, $U = 7$ eV) with (a) all HS Co magnetic moments aligned, and (b) one HS Co magnetic moment flipped downward (indicated by the arrow). The isosurface values are 0.02 (red/dark gray) and -0.02 (blue/light gray).

oxygen in between, and also from the half-filled e_g (d_{z^2} and $d_{x^2-y^2}$) orbitals of HS Co to the empty e_g orbitals of LS Co, as depicted in the inset of Fig. 3(b). The PDOS shown in Fig. 3(b) confirms this model: the finite spin-up e_g electrons localized at the LS Co site (transferred from the HS Co site) and the finite spin-down d_{xz} and d_{yz} electrons localized at the HS Co site (transferred from the LS Co site). Such electron transfers have been described also via a *configuration fluctuation* model,[20,21] which further suggests that the interchange of spin states (without net transfer of charge) led by electron transfers stabilizes the FM order in the HS/LS state.

The above-mentioned superexchange interaction can be visualized via electron spin density $s(\mathbf{r}) \equiv \rho_\uparrow(\mathbf{r}) - \rho_\downarrow(\mathbf{r})$, where $\rho_\uparrow(\mathbf{r})$ and $\rho_\downarrow(\mathbf{r})$ are the spin-up and spin-down electron densities, respectively. Figure 4(a) shows $s(\mathbf{r})$ corresponding to the configuration with all HS Co magnetic moments aligned (the same as the configuration in Fig. 3). The nonzero magnetic moments localized at the LS Co sites (with e_g character), aligned with the HS Co magnetic moments, are consistent with the PDOS shown in Fig. 3. When the magnetic moment of one HS Co in a 40-atom supercell is flipped [Fig. 4(b)], the alignment of magnetic moments is altered, and so is the condition that allows configuration fluctuation [inset of Fig. 3(b)]. The spin density at the surrounding LS Co sites is thus significantly affected. One flipped HS Co spin (in a 40-atom cell) increases the total energy by 195 meV/supercell. Flipping one more HS Co spin, so the total magnetization per supercell becomes zero, further increases the total energy by

78 meV/supercell. With CoO_6 rotation, the energy increases associated with one and two flipped HS Co spins are 96 and 34 meV/supercell, respectively. These results indicate that the magnetic moment of HS Co in the HS/LS state should align at low temperatures.

While our calculations have shown that the HS/LS state is the most favorable state among the ferromagnetic states being considered, the magnetic state in actual $LaCoO_3$ thin films can be more complicated. The magnetization observed in experiments rarely exceeds $0.85\mu_B/Co$,[4–11] smaller than that of the HS/LS mixture ($2\mu_B/Co$). Such a magnetization suggests that the HS Co population should be smaller than 50%. In fact, XAS spectra combined with atomic multiplet calculations have suggested that a $LaCoO_3$ thin film on $SrTiO_3$ consists of about 64% of LS Co and 36% of HS Co.[10] Given that the FM order is achieved via the superexchange interaction within the HS-LS-HS Co configuration shown in Fig. 2(c), one can thus expect that the ferromagnetic HS/LS domain and nonmagnetic LS domain coexist in tensile strained thin films, as observed using magnetic force microscopy (MFM).[7] Also, since the HS/LS state favors a larger in-plane lattice parameter, thin films with larger in-plane lattice parameters can be expected to have a larger HS/LS domain, and thus larger magnetization, consistent with the increase of magnetization with lattice parameter observed in experiment.[5]

In summary, we use LDA $+ U$ calculations to show that the ferromagnetic insulating state in tensile-strained $LaCoO_3$ thin films is most likely a mixture of HS and LS Co. Among all the ferromagnetic states studied in this Rapid Communication (HS/LS, IS/LS, and IS), the insulating HS/LS mixture state is the most favorable one, energetically and structurally. Its FM order is established via the superexchange interaction between LS and HS Co. We also show that cobalt spin states in $LaCoO_3$ thin films could be identified via NMR spectroscopy.

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[32]While $LDA + U$ gives a pseudocubic lattice parameter of about 3.78 Å for bulk $LaCoO_3$ (see 27), inclusion of zero point motion energy can improve this 1% underestimate, and better agreement with experiments can be achieved, as reviewed by R. M. Wentzcovitch *et al.*, Rev. Min. Geochem. **71**, 59 (2010).

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[34]In this Rapid Communication, U_{sc} is extracted from a series of $LDA + U$ ground states associated with different trial U's, as detailed in the Supplemental Material of Ref. 26 [http://link.aps.org/supplemental/10.1103/PhysRevLett.106.118501]. In our earlier work on LS $LaCoO_3$ (Ref. 27), the Hubbard U for LS Co ($\sim$8.3 eV) was extracted from the LDA ground state, as detailed in Ref. 24.

[35]In our calculations with constrained in-plane lattice parameters ($a_{pc} = b_{pc} = 3.899$ Å), a HS state with G-type antiferromagnetic (AFM) order can be obtained, and its energy is lower than that of the HS/LS state. Given the neglect of finite thickness, the possible uncertainty of energy given by the $LDA + U$ method, and the fact that an AFM thin film is not observed in experiments, we limit our discussions on the available FM states (IS, IS/LS, and HS/LS).

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