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High-spin and low-spin mixed state in $LaSrCoO_4$: An *ab initio* study

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Spin state is an important issue for many cobaltates, and an intermediate spin (IS) state having a half-filled e_g orbital may well be expected for a Co^{3+} ion in a CoO_6 octahedron with a remarkable tetragonal distortion. Here the single-layered perovskite cobaltate $LaSrCoO_4$, which has a notable tetragonal elongation, is investigated for its spin state and electronic structure, through a set of local-spin-density approximation plus Hubbard U (LSDA+U) calculations including also the multiplet effect and spin-orbit coupling. Counterintuitively, our calculations evidence that the IS state is not the ground state and it would, even if being so, give rise to a wrong ferromagnetic half-metallic solution. We find that a strong band hybridization significantly suppresses a multiplet energy splitting of the IS state. Instead, a high-spin (HS) and low-spin (LS) mixed state turns out to have the lowest total energy among all possibly combined spin states. Moreover, the mixed HS+LS ground state well accounts for the experimental paramagnetic insulating behavior, the effective magnetic moment, and the observed optical spectral features. We also predict that $LaSrCoO_4$ in the mixed HS+LS ground state has a sizeable out-of-plane orbital moment and a local lattice distortion, which would motivate experimental studies.

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I. INTRODUCTION

Spin state is an important topic for many cobaltates, and it strongly affects or even determines their magnetic, electric, transport properties, and so on.[1–19] It can be a low spin (LS), a high spin (HS), or even an intermediate spin (IS) state. This stems from a subtle interplay among the crystal field, Hund exchange, multiplet effect, spin-orbit coupling (SOC), and band hybridization. A Co^{3+} IS state ($S=1, t_{2g\uparrow}^3 e_{g\uparrow}^1 t_{2g\downarrow}^2$) may be stabilized either by a half-filled broad e_g conduction band to gain a lot of kinetic energy or by a Jahn-Teller distortion to form a likely e_g orbital ordering, as suggested by Korotin *et al.* using the local-density approximation plus Hubbard U (LDA+U) band-structure calculations.[7] Search and confirmation of the IS Co^{3+} cobaltates have been of great interest, however, a definite example appears still lacking up to now. Here we are motivated to study the single-layered $LaSrCoO_4$ of the K_2NiF_4-type structure[20,21] (see Fig. 1), which has a notable axial elongation of the CoO_6 octahedra and could thus be a good candidate for an IS Co^{3+} cobaltate.

Among the $La_{2-x}Sr_xCoO_4$ series which received considerable attention very recently,[20–37] $LaSrCoO_4$ was classified as a paramagnetic charge-transfer insulator with an effective magnetic moment of $2.6\mu_B$–$3.0\mu_B$ and an optical gap of 0.95 eV.[22,24,25,38] Indeed, several experimental studies of the structural, electronic, magnetic, and transport properties concluded the IS state of $LaSrCoO_4$ consistently.[21–25] In contrast, Hartree-Fock band-structure calculations by Wang *et al.* inferred the HS and the LS ordered ground state.[26] However, in their calculations of the phase diagram of different spin states, they assumed a cubic ionic crystal field ($10D_q$ only) but neglected the further level splittings due to the realistic strong tetragonal distortion of the CoO_6 octahedra. In view of the controversy, we therefore carried out density-functional calculations, using the experimental structural data[20] (and thus the realistic crystal field) and the local-spin-density approximation plus Hubbard U (LSDA+U) method.[39] Our calculations included also the multiplet effect and spin-orbit coupling, both of which were missing previously in many studies of cobaltates but turn out to be important to gain an insight about the spin state and further to understand the magnetic and electronic properties.[5,36] Counterintuitively, the HS+LS mixed ground state (instead of the IS state) is concluded by the present work. As seen below, this HS+LS ground state well accounts for several experiments and a rational prediction is made.

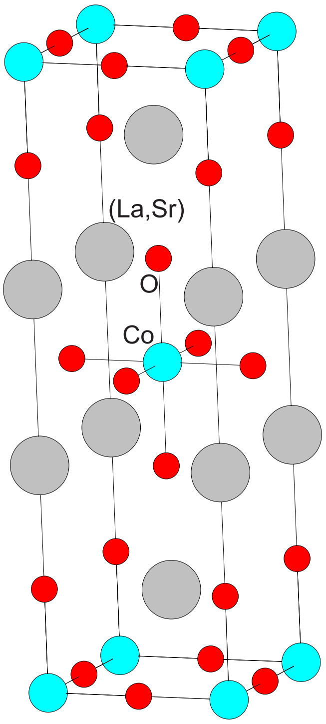

FIG. 1. (Color online) Crystal structure of $LaSrCoO_4$ in the K_2NiF_4 type. The Co-O bond lengths of the tetragonally distorted CoO_6 octahedra are 1.902 Å×4 (in plane) and 2.035 Å×2 (out of plane) after Ref. 20.

TABLE I. Relative total energies (in unit of meV/f.u.), the spin and orbital moments (in unit of μ_B) of $LaSrCoO_4$ in different spin and magnetic states calculated by LSDA+U+SOC. The IS AF, HS AF, and HS+IS FM states are unstable and converge to the IS+LS FM, IS+HS AF, and HS+LS FM states, respectively. Note that the HS+LS mixed state is the ground state.

State and configuration	Energy	m^a_{spin}	m^a_{orb}	m^b_{spin}	m^b_{orb}	Figure
IS FM $[t^3_{2g\uparrow}(3z^2-r^2)^1_{\uparrow}xy^1_{\downarrow}(xz+\mathrm{i}yz)^1_{\downarrow}]$	0	1.93	1.36			Fig. 2
IS FM $[t^3_{2g\uparrow}(3z^2-r^2)^1_{\uparrow}xz^1_{\downarrow}yz^1_{\downarrow}]$	49	1.88	0.02			Fig. 3
IS AF $[t^3_{2g\uparrow}(3z^2-r^2)^1_{\uparrow}xy^1_{\downarrow}(xz+\mathrm{i}yz)^1_{\downarrow}]$						
$\rightarrow$IS$^a[t^3_{2g\uparrow}(3z^2-r^2)^1_{\uparrow}xy^1_{\downarrow}(xz+\mathrm{i}yz)^1_{\downarrow}]$+LS$^b(t^6_{2g})$ FM	22	1.86	1.29	0.31	−0.03	
LS (t^6_{2g})	−57	0	0			
HS AF $[t^3_{2g\uparrow}e^2_{g\uparrow}(xz+\mathrm{i}yz)^1_{\downarrow}]$						
$\rightarrow$IS$^a[t^3_{2g\uparrow}(x^2-y^2)^1_{\uparrow}xz^1_{\downarrow}yz^1_{\downarrow}]$+HS^b $[t^3_{2g\downarrow}e^2_{g\downarrow}(xz-\mathrm{i}yz)^1_{\uparrow}]$ AF	75	1.55	0.04	−2.93	−0.96	Fig. 4
HS $[t^3_{2g\uparrow}e^2_{g\uparrow}(xz+\mathrm{i}yz)^1_{\downarrow}]$+IS$[t^3_{2g\uparrow}(3z^2-r^2)^1_{\uparrow}xy^1_{\downarrow}(xz+\mathrm{i}yz)^1_{\downarrow}]$ FM						
$\rightarrow$HS$^a[t^3_{2g\uparrow}e^2_{g\uparrow}(xz+\mathrm{i}yz)^1_{\downarrow}]$+LS$^b(t^6_{2g})$ FM	−84	2.94	0.89	0.34	0.22	Fig. 5
HS$^a[t^3_{2g\uparrow}e^2_{g\uparrow}(xz+\mathrm{i}yz)^1_{\downarrow}]$+LS$^b(t^6_{2g})$ FM relaxation	−122	2.95	0.90	0.31	0.22	Fig. 7

II. CALCULATIONS AND DISCUSSION

We used the structural data of $LaSrCoO_4$ measured by powder x-ray diffraction.[20] Our electronic-structure calculations were performed by using the full-potential augmented plane waves plus local-orbital method.[40] A virtual atom with an atomic number $Z=56.5$ $(0.5Z_{\text{La}}+0.5Z_{\text{Ba}})$ is used for the (LaSr) sites since La and Sr(Ba) ions are in most cases simply electron donors. The cutoff energy of 16 Ry is used for plane-wave expansion and 600 **k** points for integrations over the Brillouin zone. Besides the pure LS, IS, or HS state, all possible combinations of the ordered spin states were also studied, using a doubled $\sqrt{2}\times\sqrt{2}\times 1$ supercell. The muffin-tin sphere radii are chosen to be 2.5, 2.0, and 1.5 bohrs for La/Sr, Co, and O atoms, respectively. The Co sphere is, to a good approximation, big enough to include all the localized Co 3d electrons: each fully occupied 3d orbital in various spin states is found to have an occupation number bigger than 0.9e. The self-interaction corrected LSDA+U functional[39] in a strongly atomic limit should reasonably well describe the ground-state property of this Mott insulator having a charge-transfer gap. Moreover, a technical advantage is that the constrained LSDA+U calculations allow us to readily access different spin and orbital states by initializing their corresponding occupation number matrix, and thus to study their relative stability and electronic/magnetic structures, etc. Our LSDA+U calculations were carried out by using the typical value of $U=5$ eV and Hund exchange of 0.9 eV to account for the strong correlation of the Co 3d electrons.[41,42] Using of that U value is also justified by the calculated band gap of 0.9 eV in the predicted HS+LS mixed ground state (being very close to the experimental one of 0.95 eV). As seen below, the HS+LS mixed ground-state solution well accounts for several experiments. Note that $U\leq 4$ eV (≥ 6 eV) gives a band gap of ≤ 0.5 eV (≥ 1.2 eV) for the HS+LS mixed ground state, which remains to be more stable than the concerned IS state by 87 (38) meV/Co for the $U=4$ eV (6 eV). In addition, selectively for the HS+LS mixed state and the IS state, both of the most concern in this work, we also applied the PBE0 hybrid functional (but only to the Co 3d electrons which are poorly treated by LSDA), which mixes 1/4 Fock exact exchange into the PBE exchange functional.[43,44] Our PBE0 calculations, confirming the LSDA+U results, show that the HS+LS mixed state is insulating and the IS state is half metallic, and that the former is more stable than the latter by 68 meV/Co. In the present study, the SOC turns out to be quite important and it is included in all our calculations by the second-variational method with scalar relativistic wave functions.[40]

We first study the IS state which might be intuitively expected to be the ground state. In a c-axis elongated CoO_6 octahedron as in $LaSrCoO_4$, the one-electron crystal field levels order, from low to high, (xz,yz), xy, $3z^2-r^2$, and x^2-y^2. The atomic configuration of the IS state, $t^3_{2g\uparrow}e^1_{g\uparrow}t^2_{2g\downarrow}$, would be $t^3_{2g\uparrow}(3z^2-r^2)^1_{\uparrow}xz^1_{\downarrow}yz^1_{\downarrow}$ in a one-electron picture as usually adopted. However, taking into account the multiplet effect and SOC, the lowest-energy state is $t^3_{2g\uparrow}(3z^2-r^2)^1_{\uparrow}xy^1_{\downarrow}(xz+iyz)^1_{\downarrow}$. This is because in a many-body picture, there is a weaker Coulomb repulsion between the $3z^2-r^2$ and xy electrons than between $3z^2-r^2$ and (xz,yz), and then the SOC lifts the double degeneracy of (xz,yz) which is half filled. Starting from this $t^3_{2g\uparrow}(3z^2-r^2)^1_{\uparrow}xy^1_{\downarrow}(xz+iyz)^1_{\downarrow}$ IS state, we calculated both ferromagnetic (FM) and antiferromagnetic (AF) coupled IS states. The IS FM state is stabilized as it is and taken as the total-energy reference zero but the IS AF state is unstable and converges to an IS+LS state, see Table I. This IS+LS state is a half metal (not shown here) and lies higher in total energy than the IS FM state by 22 meV/Co. Here the stable IS FM solution is discussed, see

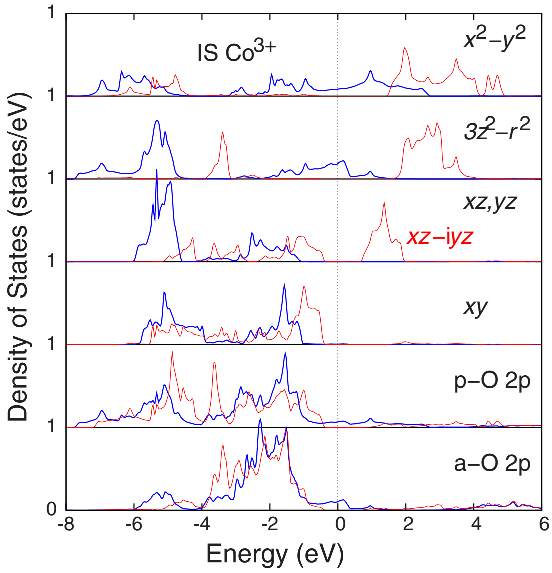

FIG. 2. (Color online) Orbitally resolved Co $3d$ density of states (DOS), the planar-O (p-O) and apical-O (a-O) $2p$ DOS of LaSrCoO$_4$ in the IS FM state with the formal configuration $t^3_{2g\uparrow}(3z^2-r^2)^1_\uparrow xy^1_\downarrow(xz+iyz)^1_\downarrow$ calculated by LSDA+U+SOC. Blue (bold) lines refer to the up spin, and red (thin) lines the down spin. Fermi level is set at the zero energy. It is a half metal with a broad x^2-y^2 conduction band. The (xz,yz) orbitals are 3/4 occupied with a hole in the $xz-iyz$ (i.e., d_{-1}) complex orbital.

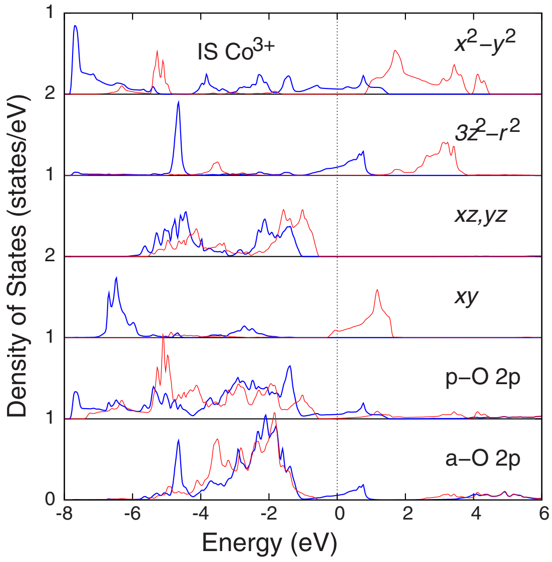

FIG. 3. (Color online) The Co $3d$, the planar-O and apical-O $2p$ DOS of LaSrCoO$_4$ in the IS FM state with the formal configuration $t^3_{2g\uparrow}(3z^2-r^2)^1_\uparrow xz^1_\downarrow yz^1_\downarrow$. See the main text and Table II for a comparison with those results shown in Fig. 2.

Fig. 2. It is also a half metal (in disagreement with the experimental paramagnetic insulating behavior). This is because the formally unoccupied x^2-y^2 level becomes a broad antibonding band with a bandwidth of about 5 eV, and it strides over the Fermi level and gets partially occupied. The x^2-y^2 band effect helps to gain a lot of kinetic energy, stabilizing the FM half-metallic state. In contrast, this band effect is strongly suppressed in the AF state (due to exchange splitting), and thus the AF IS state becomes unstable. For the stable IS FM state, the Co^{3+} ion has a local spin moment of $1.93\mu_B$ (within the muffin-tin sphere) out of the total integer spin moment of $2\mu_B$ for this half-metallic state. Moreover, it has a big out-of-plane orbital moment of $1.36\mu_B$, of which $0.81\mu_B$ is contributed by the $xz+iyz$ (i.e., d_1) complex orbital and $0.55\mu_B$ by the $xy-i(x^2-y^2)$ (i.e., d_2).

To demonstrate the multiplet effect, we also calculated the IS FM state with $t^3_{2g\uparrow}(3z^2-r^2)^1_\uparrow xz^1_\downarrow yz^1_\downarrow$. Its total energy is calculated to be higher by 49 meV/Co and it is nearly a half metal, as seen in Table I and Fig. 3. This is unlike the metastable IS Co^{3+} in an insulating solution of La$_{1.5}$Sr$_{0.5}$CoO$_4$ in which the corresponding multiplet splitting is more than 400 meV/Co.[36] Here the much reduced multiplet splitting is simply due to a nearly equal occupation of the e_g orbitals, see Table II. For the above-discussed IS FM reference state $t^3_{2g\uparrow}(3z^2-r^2)^1_\uparrow xy^1_\downarrow(xz+iyz)^1_\downarrow$, the formally unoccupied up-spin x^2-y^2 orbital has now the occupation number of $0.64e$ due to the band hybridization effect, and it is not much different from the occupation number of $0.87e$ for the formally fully occupied up-spin $3z^2-r^2$ orbital. Note that this x^2-y^2 orbital couples with the xy orbital via the SOC and then contributes to the above orbital moment by $0.55\mu_B$. For the IS state $t^3_{2g\uparrow}(3z^2-r^2)^1_\uparrow xz^1_\downarrow yz^1_\downarrow$, the occupation number of the two e_g orbitals is just reversed, $0.65e$ for $3z^2-r^2$ and $0.85e$ for x^2-y^2. The partial depletion of the $3z^2-r^2$ orbital (and the more x^2-y^2 occupation) is due to the stronger (weaker) Coulomb repulsion by the fully occupied xz and yz orbitals. In contrast, the formal e_g occupation $(3z^2-r^2)^1(x^2-y^2)^0$ turns out by our previous calculations to be approximately the case $[(3z^2-r^2)^{0.95}(x^2-y^2)^{0.35}]$ for the IS Co^{3+} ions in La$_{1.5}$Sr$_{0.5}$CoO$_4$.[36] In the sense, the band effect of the IS FM half metallic state strongly suppresses the multiplet splitting in LaSrCoO$_4$. Note also that in this higher-lying IS state, there is no orbital degeneracy present, and thus the orbital moment should quench and the calculated value is only $0.02\mu_B$ as expected.

Now we turn to the LS state. It is an insulator with a band gap of about 0.7 eV which lies between the occupied $pd\pi$ antibonding bands of the t_{2g} orbitals and the unoccupied $pd\sigma$ antibonding bands of the e_g orbital (not shown here). Somewhat counterintuitively, this LS state is calculated to be more stable than the above lowest-energy IS multiplet state by 57 meV/Co. In other word, the present results suggest the IS state not to be the ground state as previously concluded.[21–25] This suggestion is supported by more results as seen below. Note, however, that the LS state cannot account for the observed effective magnetic moment of $\mu_{eff}=2.6\mu_B-3.0\mu_B$, and it may not be the ground state either.

Here the HS state is studied. The HS state would yield a strong AF coupling as in the parent compound La$_2$CoO$_4$ having the HS Co^{2+} ions and a quite high $T_{\mathrm{N}}=275$ K.[45] However, the HS AF state is calculated to be unstable but converges to an IS+HS AF state, which has a higher total energy than the reference IS FM state by 75 meV/Co and is thus not the ground state at all. Moreover, this IS+HS AF state has a much smaller insulating gap of only 0.2 eV (see Fig. 4) and a strong AF coupling, both of which are in disagreement with the observed paramagnetic insulating behavior with a band gap of 0.95 eV.[25,38]

TABLE II. Spin-resolved Co $3d$ orbital occupation in the two IS FM states of LaSrCoO$_4$ calculated by LSDA+U+SOC. The formally unoccupied x^2-y^2 orbital gets more than half filled due to a strong band hybridization and to a weaker Coulomb repulsion by the xz and the yz electrons than by the xy electrons.

		$3z^2-r^2$	x^2-y^2	xy	xz,yz	Figure
Nominal IS $[t^3_{2g\uparrow}(3z^2-r^2)^1_{\uparrow}xy^1_{\downarrow}(xz+\mathrm{i}yz)^1_{\downarrow}]$	$\uparrow$	0.87	0.64	0.92	1.86	Fig. 2
	$\downarrow$	0.23	0.24	0.89	1.01	
Nominal IS $[t^3_{2g\uparrow}(3z^2-r^2)^1_{\uparrow}xz^1_{\downarrow}yz^1_{\downarrow}]$	$\uparrow$	0.65	0.85	0.94	1.84	Fig. 3
	$\downarrow$	0.19	0.23	0.14	1.82	

Now attention is paid to the HS+LS state and HS+IS FM state. The HS+LS FM state is stabilized as it is (see Fig. 5) but the HS+IS FM state is unstable and converges exactly to the HS+LS state. So far, all the possible spin states have been studied, and the total-energy results show that the HS+LS state is the ground state, as seen in Table I. Moreover, a stripe AF structure of the HS Co^{3+} ions in the HS+LS ground state is calculated to be slightly more stable than the FM state by only about 3 meV/Co. Considering four nearest neighbors and four next-nearest neighbors of the HS Co^{3+} sublattice (see Fig. 6), the small AF exchange constant is thus estimated to be only about 0.1 meV. This is apparently due to a dilution of the magnetic lattice by the formally nonmagnetic LS Co^{3+} ions. The weak AF couplings and a magnetic frustration most probably explain the observed paramagnetic[25] (or spin-glassy[24]) state of LaSrCoO$_4$. As seen in Table I, the HS Co^{3+} has a spin moment of 2.94μ_B which is reduced (by about 1/4) from its formal $S=2$ by covalency, and it has also a big out-of-plane orbital moment of 0.89μ_B carried mostly (0.75μ_B) by the $xz+iyz(d_1)$ orbital. The formal LS Co^{3+} has a finite induced spin moment of 0.34μ_B due to the band effect and also an orbital moment of 0.22μ_B. As concluded previously,[22,24,25] an IS state ($S=1$) yields a $\mu_{eff}=\sqrt{4S(S+1)}\approx 2.8\mu_B$ and accounts well for the measured $\mu_{eff}=2.6\mu_B-3.0\mu_B$. Alternatively, using the picture of the HS+LS ground state (one half $S=2$ and the other half $S=0$) and assuming a covalency reduction by about 1/4, we estimate $\mu_{eff}\approx(1-1/4)\sqrt{1/2\times(4\times 2\times 3+1\times 2)}\approx 2.7\mu_B$ by including approximately a contribution of the above formal $L=1$ orbital moment. As seen in Fig. 5, this HS+LS ground state has a band gap of about 0.9 eV, which agrees well with the measured optical gap of 0.95 eV. Furthermore, the observed optical-absorption peaks at about 2 and 3 eV (with an electric field $E\parallel ab$)[38] can well be explained as a charge-transfer excitation from the planar-O $2p$ at about -1 eV to the HS Co^{3+} xy at about 0.9 eV, and to the LS Co^{3+} x^2-y^2 at about 2 eV, respectively. A presence of the single xy hole of the HS Co^{3+} and double x^2-y^2 holes of the LS Co^{3+} also accounts for the observed optical spectral intensity rate of 1:2.[38] In a word, the mixed HS+LS state has been found to be the ground state of LaSrCoO$_4$, and it well explains several experiments.

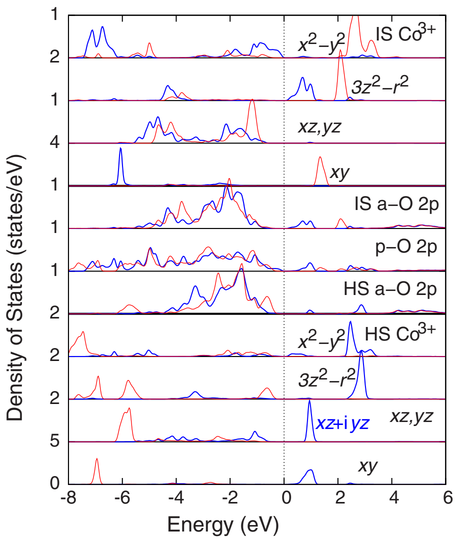

FIG. 4. (Color online) The IS Co^{3+} $3d$ DOS, $2p$ DOS of the apical-O of the IS Co^{3+} ion (IS a-O), planar-O $2p$ DOS, $2p$ DOS of the apical-O of the HS Co^{3+} ion (HS a-O), and the HS Co^{3+} $3d$ DOS of LaSrCoO$_4$ in the IS+HS AF state.

Note that the mixed HS+LS ground state is most probably subject to a local lattice distortion due to the different

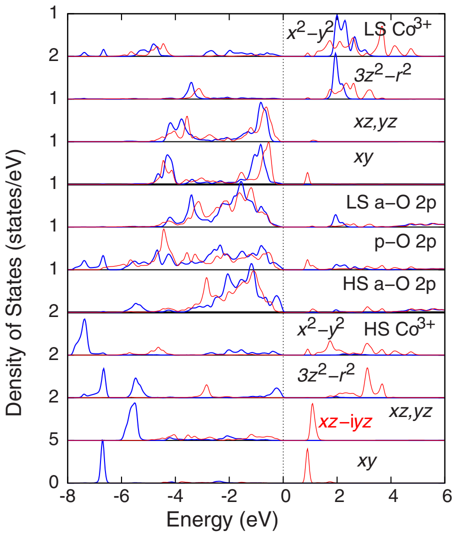

FIG. 5. (Color online) The LS Co^{3+} $3d$ DOS, $2p$ DOS of the apical-O of the LS Co^{3+} ion (LS a-O), planar-O $2p$ DOS, $2p$ DOS of the apical-O of the HS Co^{3+} ion (HS a-O), and the HS Co^{3+} $3d$ DOS of LaSrCoO$_4$ in the HS+LS FM state. This is the ground-state solution and it well explains several experiments. See the main text for discussion.

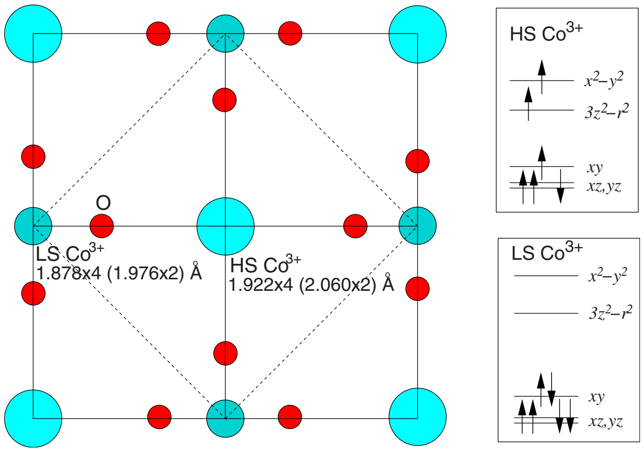

FIG. 6. (Color online) The ideal HS+LS checkerboard order of LaSrCoO$_4$ in the *ab* basal plane, marked with the theoretically optimized in-plane (out-of-plane) Co-O bond lengths, and the corresponding energy-level diagrams of the HS and LS Co^{3+} ions as well.

size of the LS (0.545 Å) and HS (0.61 Å) Co^{3+} ions. This will help to gain an elastic energy. Our calculations completing a structural optimization show that indeed the HS Co^{3+} has longer Co-O bond lengths (in-plane 1.922 Å × 4 and out-of-plane 2.060 Å × 2, see Fig. 6) than the LS Co^{3+} (1.878 Å × 4 and 1.976 Å × 2), lowering the total energy further by 38 meV/Co, as seen in Table I. In contrast, the above IS FM half-metallic state prefers a regular CoO$_2$ basal plane to maximize the band kinetic energy, and our calculations show that the measured homogeneous Co-O lattice[20] is just an equilibrium state of the calculated IS FM state. Note that the predicted local lattice distortion in the HS+LS ground state makes insignificant changes in the electronic state, spin, and orbital moments as seen in Fig. 7 and Table I. Thus, the above discussion and conclusion about the mixed HS+LS ground state remain unchanged. Note also that so far only the homogeneous Co-O lattice has been observed.[20–25] A long-range HS+LS order may indeed be hard to establish since the involved ions (the octahedral Co^{3+} ions only) are the identical element and have the same valence state and coordination. However, a short-range HS+LS order and a local lattice distortion may well be the case, which calls for experimental studies.

III. CONCLUSION

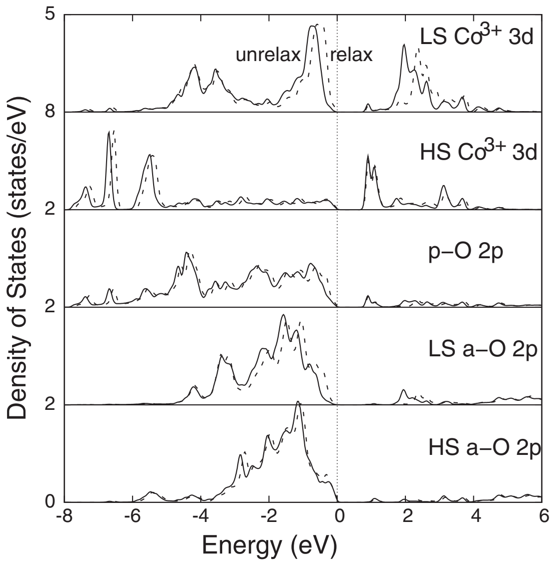

FIG. 7. DOS of LaSrCoO$_4$ in the mixed HS+LS ground state without/with (solid/dashed lines) a structural optimization. There are no significant changes in the electronic structure. See Fig. 5 for other notations.

We studied the electronic and magnetic structures of the layered perovskite LaSrCoO$_4$ using the LSDA+U+SOC calculations including also the multiplet effect. Our calculations show that the IS state would be a FM half metal (which is in disagreement with the experiments) and is not the ground state as *a priori* expected for this cobaltate having a notable tetragonal distortion of the constituent CoO$_6$ octahedra. We found that the strong band hybridization of the x^2-y^2 orbital significantly suppresses the multiplet energy splitting of the IS state. Instead, the HS+LS mixed state has the lowest total energy among all the possible ordered spin-state combinations. Moreover, this HS+LS mixed state well accounts for the observed paramagnetic insulating behavior of LaSrCoO$_4$, its effective magnetic moment, and the optical-absorption spectra. We therefore conclude the HS+LS mixed ground state in LaSrCoO$_4$. Furthermore, we predict that LaSrCoO$_4$ has a big out-of-plane orbital moment and thus an easy out-of-plane magnetization, and that it has a local lattice distortion which would facilitate a likely short-range HS+LS order. The prediction calls for experimental studies.

ACKNOWLEDGMENT

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