

Spin and orbital states in $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$ studied by electronic structure calculationsHua Wu¹ and T. Burnus²¹*II. Physikalisches Institut, Universität zu Köln, Zùlpicher Str. 77, 50937 Köln, Germany*²*Institut für Festkörperforschung, Forschungszentrum Jùlich, 52425 Jùlich, Germany*

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Electronic structure of the layered perovskite $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$ with a checkerboard $\text{Co}^{2+}/\text{Co}^{3+}$ charge order is studied, using the local-spin-density approximation plus Hubbard U calculations including also the spin-orbit coupling and multiplet effect. Our results show that the Co^{2+} ion is in a high spin state (HS, $t_{2g}^5 e_g^2$) and Co^{3+} low spin state (LS, t_{2g}^6). Due to a small Co^{2+} t_{2g} crystal field splitting, the spin-orbit interaction produces an orbital moment of $0.26\mu_B$ and accounts for the observed easy in-plane magnetism. Moreover, we find that the Co^{3+} intermediate spin state (IS, $t_{2g}^5 e_g^1$) has a multiplet splitting of several tenths of eV and the lowest-lying one is still higher than the LS ground state by 120 meV, and that the Co^{3+} HS state ($t_{2g}^4 e_g^2$) is more unstable by 310 meV. Either the IS or HS Co^{3+} ions would give rise to a wrong magnetic order and anisotropy.

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Cobaltates comprise a group of interesting materials which display spectacular properties such as superconductivity,¹ giant magnetoresistance,² and large thermoelectric power.³ One aspect in the physics of cobaltates, which distinguishes them from other transition metal oxides, is the spin state issue, particularly for the Co^{3+} ions. It can be a low spin (LS), a high spin (HS), or even an intermediate spin (IS) state, depending on a subtle interplay among crystal field, Hund exchange, multiplet effects, and spin-orbit coupling (SOC).⁴⁻¹⁷ One prototype material is the perovskite LaCoO_3 , and its temperature-dependent spin state transition has been extensively studied but a consensus has not yet been reached so far: the magnetic excitations at about 100 and 500 K in LaCoO_3 have been ascribed to either an $\text{LS} \rightarrow \text{HS}$ transition,⁴⁻⁹ an $\text{LS} \rightarrow \text{IS}$ transition,¹⁰⁻¹³ or $\text{LS} \rightarrow (\text{LS}+\text{HS}) \rightarrow \text{IS}$ transitions.¹⁴⁻¹⁷

Recently, the single layered perovskite $\text{La}_{2-x}\text{Sr}_x\text{CoO}_4$ received considerable attention for its extremely insulating behavior, peculiar magnetic correlations, and doping-dependent charge/spin superstructures, and its spin state issue becomes a vital topic.¹⁸⁻²⁶ The parent compound La_2CoO_4 has a normal HS Co^{2+} and is an antiferromagnetic insulator with a quite high $T_N=275$ K.²⁷ Upon Sr or Ca doping, Co^{3+} ions are introduced. Measurements of magnetic and transport properties of $\text{La}_{2-x}\text{Sr}_x\text{CoO}_4$ ($0.4 \leq x \leq 0.8$) led Moritomo *et al.* to a conclusion that the Co^{3+} ions undergo a spin state transition from HS ($x \leq 0.6$) to IS ($x \geq 0.8$).²⁸ Neutron scattering measurements of $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$ by Zaliznyak *et al.* showed a checkerboard Co^{2+} - Co^{3+} charge order and a strongly decreasing spin ordering temperature ($T_{SO} \approx 30$ K), and they suggested the Co^{3+} ions to be in an IS but nonmagnetic state quenched by strong planar anisotropy.^{29,30} The Co^{2+} - Co^{3+} charge order was also observed in $\text{La}_{1.5}\text{Ca}_{0.5}\text{CoO}_4$ and the Co^{3+} ions were suggested to be in a mixed IS+HS state.^{31,32} In contrast, a magnetic susceptibility study of $\text{La}_{2-x}\text{Sr}_x\text{CoO}_4$ ($0.3 \leq x \leq 0.8$) and crystal-field model calculations indicated that the Co^{3+} must be in the LS state for $x \geq 0.4$.²¹ In particular, a very recent x-ray absorption spectroscopic study by Chang *et al.* established a picture of HS Co^{2+} and LS Co^{3+} for $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$, and their study well accounts for the extremely insulating nature of the $\text{La}_{2-x}\text{Sr}_x\text{CoO}_4$ series, the high charge ordering temperature and low T_{SO} of $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$.²⁶

It is, however, a bit surprising that this interesting material and the spin state issue received much less theoretical investigation. Previous unrestricted Hartree-Fock calculations showed that there are two spin-state transitions in $\text{La}_{2-x}\text{Sr}_x\text{CoO}_4$ in the doping range of $0 < x < 1.1$, and that $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$ is in the ferromagnetic HS state.³³ In view of the existing controversy, the spin state of the charge ordered $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$ remains to be an open question, and therefore we will shed light on this issue by carrying out a set of density functional electronic structure calculations. Our results show that $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$ is indeed in the HS- Co^{2+} /LS- Co^{3+} ground state, which can explain the experiments as seen below. However, the energetically unfavorable IS or HS Co^{3+} state would have a trouble in such an explanation.

We used the structural data of $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$ measured by single-crystal neutron diffraction.³⁴ Our electronic structure calculations were performed by using the full-potential augmented plane waves plus local orbital method.³⁵ The muffin-tin sphere radii are chosen to be 2.5, 2.0, and 1.5 Bohr for La/Sr, Co, and O atoms, respectively. A virtual atom with an atomic number $Z=56.75$ ($0.75Z_{\text{La}}+0.25Z_{\text{Ba}}$) is used for the ($\text{La}_{1.5}\text{Sr}_{0.5}$) sites since La and Sr(Ba) ions are in most cases simply electron donors. The cutoff energy of 16 Ryd is used for plane-wave expansion, and 600 **k** points for integrations over the Brillouin zone. To account for the strong electron correlations, the local-spin-density approximation plus Hubbard U (LSDA+ U) (Ref. 36) calculations were carried out, with $U=5$ eV and Hund exchange of 0.9 eV for the Co 3d electrons.^{37,38} The SOC turns out to be quite important and it is included by the second-variational method with scalar relativistic wave functions.³⁵

Usually, LSDA+ U calculations may yield different orbital-polarized solutions, depending on the initialized occupation number matrix. Talking about the spin state issue, we have done a set of LSDA+ U +SOC calculations which are initialized by assuming the LS, IS, and HS states, respectively. Our results show that while the Co^{2+} ion in $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$ is always stabilized at the normal HS state, the Co^{3+} can be stabilized at the LS, IS, or HS state, as detailed below. It is important to note that the total-energy results reveal the Co^{3+} LS ground state.

Figure 1 shows the density of states in the HS- Co^{2+} /LS- Co^{3+} ground state. The HS Co^{2+} has the $t_{2g}^5 e_g^2$

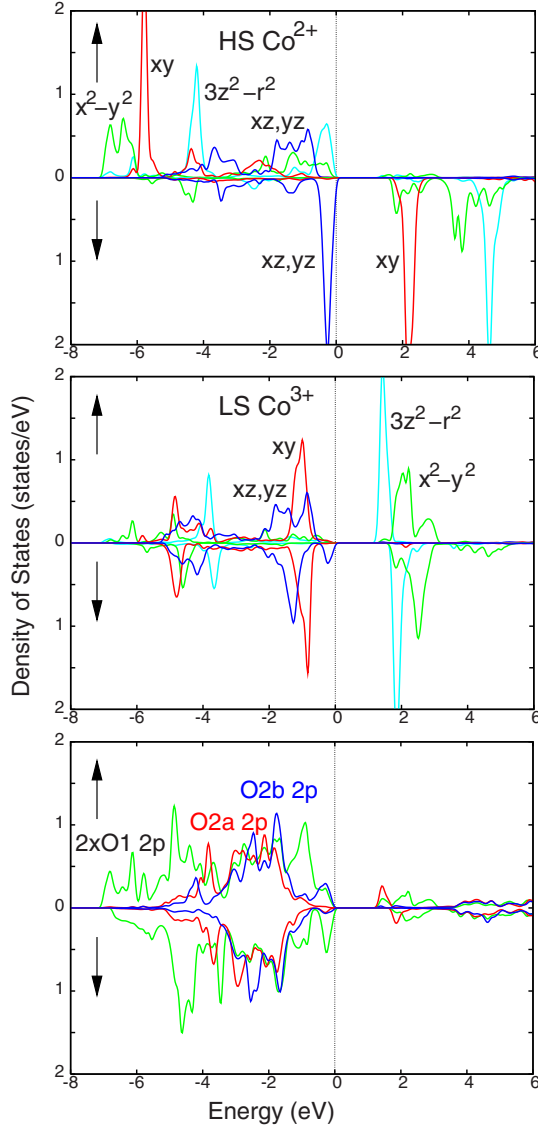


FIG. 1. (Color online) Density of states (DOS) of the HS-Co²⁺/LS-Co³⁺ ground state of La_{1.5}Sr_{0.5}CoO₄ calculated by LSDA+*U*+SOC. The HS Co²⁺ has $t_{2g}^5 e_g^2$ with a t_{2g} hole on the xy orbital, and the LS Co³⁺ closed t_{2g}^6 shell. The 2*p* DOS of the planar O1, Co³⁺-apical O2a, and Co²⁺-apical O2b are also shown. Fermi level is set at zero energy.

configuration with one t_{2g} hole on the xy orbital. This corresponds to the local crystal field: since the out-of-plane Co²⁺-O2*b* bondlength of 2.192 Å is much bigger than the in-plane Co²⁺-O1 bondlength of 1.955 Å,³⁴ the xy level should be higher than the xz/yz and it is the t_{2g} hole orbital. The t_{2g} crystal field splitting (CFS) and especially electron correlations open a gap between the xz/yz and xy in the down-spin channel. For the LS Co³⁺ ion, it has a closed t_{2g}^6 shell which allows one to calculate the t_{2g} interior small CFS by simply determining the center of gravity of each orbital-resolved density of states. The calculated ionic CFS between the higher xy level and lower xz/yz is 70 meV. However, for the HS Co²⁺ with an open t_{2g} shell, the LSDA self-interaction error of the lower-lying occupied orbital obscures an estimate of a small t_{2g} CFS (For the closed t_{2g}^6 shell, however, the self-interaction errors are common for each t_{2g} orbital and thus counteracted). Instead, we used a $\sqrt{2} \times \sqrt{2} \times 1$ supercell and replaced one Co²⁺ by an immediate neighbor Ni²⁺ ($S=1$, $t_{2g}^6 e_g^2$) which has a closed t_{2g} shell. Thus the Co²⁺ t_{2g} CFS is estimated to be about 30 meV between the xy and xz/yz . Note that the smaller CFS of the Co²⁺ t_{2g} levels than that of the Co³⁺ t_{2g} is consistent with the larger Co-O bondlengths of the former.³⁴ Owing to the small CFS of the open t_{2g} shell at the Co²⁺ site, the SOC is operative and mixes the lower-lying xz/yz with higher xy level and thus produces an in-plane orbital magnetic moment. Our LSDA+*U*+SOC calculations show that La_{1.5}Sr_{0.5}CoO₄ has an easy in-plane magnetism and an orbital moment of $0.26\mu_B$ per Co²⁺ (reduced by Co-O covalent effects), as well as an almost quenched orbital moment of $0.02\mu_B$ at the LS Co³⁺ site due to the closed t_{2g} shell, as seen in Table I. The solution with an easy out-of-plane magnetism was calculated to have a higher energy by 12 meV per Co²⁺ and the corresponding Co²⁺ orbital moment is only $0.01\mu_B$. Thus, our results, based on the HS-Co²⁺/LS-Co³⁺ ground state solution, account for the experimentally observed easy in-plane magnetism of La_{1.5}Sr_{0.5}CoO₄.^{21,28} Moreover, this ground state displays a narrow band insulating behavior with a band gap of 1.2 eV (Fig. 1) which is in agreement with an optical conductivity measurement,³⁹ and the observed spectral peak around 3 eV can be explained as a charge transfer excitation from the in-plane O1 2*p* at about -1 eV to the Co²⁺ xy and Co³⁺ x^2-y^2 both at 2 eV.

TABLE I. Total energies (in unit of meV per 2 f.u.) of La_{1.5}Sr_{0.5}CoO₄ having the LS, IS, or HS Co³⁺ state and a robust HS Co²⁺ calculated by LSDA+*U*+SOC. The HS Co²⁺ configuration is shown only once in the LS-Co³⁺/HS-Co²⁺ ground state. Except for the ground state having an easy in-plane magnetism (the spin and orbital moments in unit of μ_B marked by a subscript “*ab*”), all other solutions have a wrong easy out-of-plane magnetism.

State and configuration	Energy	Co _{spin} ³⁺	Co _{orb} ³⁺	Co _{spin} ²⁺	Co _{orb} ²⁺	Figure
LS Co ³⁺ (t_{2g}^6)/HS Co ²⁺ ($t_{2g}^3 e_g^2 x_z^1 y_z^1 $)	0	0.29 _{ab}	0.02 _{ab}	2.52 _{ab}	0.26 _{ab}	Figure 1
LS Co ³⁺ (t_{2g}^6)/HS Co ²⁺	12	0.29	0.05	2.52	0.01	
IS Co ³⁺ [$t_{2g}^3 (3z^2-r^2) x_z^1 y_z^1 $]/HS Co ²⁺	725	-1.50	0	2.48	0.02	Figure 2(a)
IS Co ³⁺ [$t_{2g}^3 (3z^2-r^2) xy^1 (xz-iyz)^1 $]/HS Co ²⁺	298	-1.52	-1.08	2.51	0	Figure 2(b)
IS Co ³⁺ [$t_{2g}^3 (3z^2-r^2) xy^1 (xz+iyz)^1 $]/HS Co ²⁺	122	2.02	1.30	2.48	0.03	Figure 2(c)
HS Co ³⁺ [$t_{2g}^1 e_g^2 xz-iyz)^1 $]/HS Co ²⁺	311	-2.95	-0.96	2.45	0.02	

Since the Co^{2+} ion is always stabilized at the HS state as described above, in the following the spin state and electronic structure of the Co^{3+} ion only are further discussed. From the middle panel of Fig. 1, it can be seen that the $3z^2-r^2$ level is lower than the x^2-y^2 by 0.7 eV, in good agreement with an x-ray absorption spectroscopic study.²⁶ When a Co^{3+} IS state is realized, most probably one t_{2g} electron will be promoted to the $3z^2-r^2$ level rather than the much higher x^2-y^2 . Simply according to the crystal field level diagram, it is the xy electron which will be promoted to the $3z^2-r^2$, as seen in Fig. 2(a). It is, however, important to note that the IS state has a significant multiplet effect. Because the $3z^2-r^2$ electron density has a bigger overlap and thus a stronger Coulomb repulsion with xz and yz than with xy ,²¹ Coulomb interaction will strongly favor a promotion of one xz/yz electron, instead of the naively expected xy electron, to the $3z^2-r^2$ level. Indeed, this solution [see Fig. 2(b) and Table I] turns out to have a much lower total energy than the former [Fig. 2(a)] by about 430 meV per Co^{3+} , through our LSDA + U + SOC calculations for the antiferromagnetically coupled IS- Co^{3+} /HS- Co^{2+} states. Such a significant multiplet effect, which has been often omitted in *ab initio* electronic structure calculations, should be taken good care of when studying the intriguing spin state issue of cobaltates.⁸

As seen in Table I, the Co^{3+} IS state with one xz/yz hole lies higher in energy than the LS ground state by 298 meV and has a large out-of-plane orbital moment of $-1.08\mu_B$ (parallel to the spin moment of $-1.52\mu_B$) which consists of $-0.8\mu_B$ from the complex orbital $xz-iyz$ (namely, Y_{2-1} or d_{-1}) and $-0.28\mu_B$ from the $xy+i(x^2-y^2)$ (Y_{2-2} or d_{-2}) due to the Coulomb interaction adjusted electron occupation.⁴⁰ Moreover, the IS Co^{3+} ion having an empty x^2-y^2 orbital and HS Co^{2+} having a singly occupied x^2-y^2 are expected to be ferromagnetically coupled in the *ab* basal plane, according to Goodenough-Kanamori-Anderson superexchange rules. This is supported by our result that the ferromagnetic IS- Co^{3+} /HS- Co^{2+} state is lower than the antiferromagnetic state by 176 meV (Table I), giving a strong in-plane ferromagnetism which is however in disagreement with the observed low $T_{\text{SO}} \approx 30$ K. Furthermore, this lowest-lying Co^{3+} IS state [Fig. 2(c)] out of its multiplet is still higher than the LS ground state by 122 meV, and it has again a huge out-of-plane orbital moment of $1.3\mu_B$ [$0.8\mu_B$ from $xz+iyz$ (Y_{21} or d_1) and $0.5\mu_B$ from $xy-i(x^2-y^2)$ (Y_{22} or d_2)], in contradiction with the observed easy in-plane magnetism. This supports an analysis of magnetic anisotropy by Hollmann *et al.*²¹

It might be a bit surprising that the Co^{3+} ion in $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$ with a large distortion of the CoO_6 octahedron does not have the IS as its ground state. We note that the large difference of the Co^{3+} -O bondlengths, $1.888 \text{ \AA} \times 4$ vs $2.077 \text{ \AA} \times 2$,³⁴ does not signal a strong Jahn-Teller (JT) distortion which may stabilize the IS state with a half-filled e_g orbital, since in the isostructural La_2NiO_4 the non-JT ion Ni^{2+} has also very different bondlengths, $1.95 \text{ \AA} \times 4$ vs $2.22 \text{ \AA} \times 2$.⁴¹ The out-of-plane elongation of the CoO_6 and NiO_6 octahedra may well be a consequence of the reduction of internal strains in the single-layered perovskites. Although the large distortion of the CoO_6 octahedron yields a pronounced e_g splitting of 0.7 eV as discussed above, it is far less than the required huge e_g splitting of about 2 eV via a JT

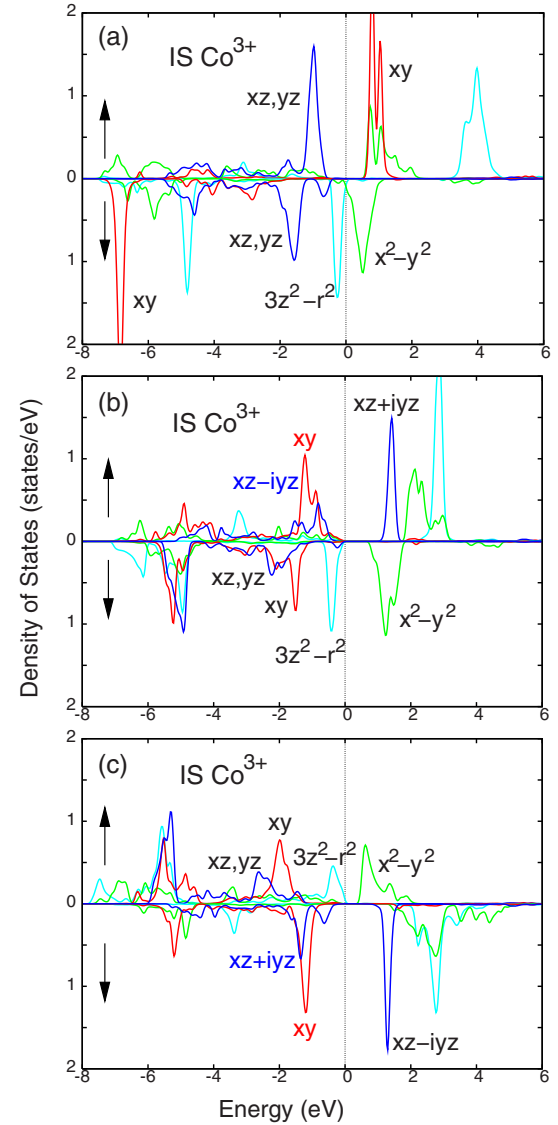


FIG. 2. (Color online) Density of states of the IS Co^{3+} ion in different configurations: (a) $t_{2g}^3(3z^2-r^2)^1xz^1yz^1$, (b) $t_{2g}^3(3z^2-r^2)^1xy^1(xz-iyz)^1$, and (c) $t_{2g}^3(3z^2-r^2)^1xy^1(xz+iyz)^1$. The corresponding multiplet splitting is calculated to be several tenths of eV (see Table I). Note that the most favorable IS Co^{3+} state [configuration (c)], being ferromagnetically coupled with the robust HS Co^{2+} (not shown here but refer to Fig. 1), is still higher in energy than the LS Co^{3+} ground state by 122 meV and has a wrong easy out-of-plane magnetism (see Table I and main text).

distortion to stabilize the IS state as ground state.⁴⁰ In this sense, a stabilization of the IS state via the JT effect may need an astonishingly large distortion which seems however hardly to reach in real materials.

Now we turn to a possible Co^{3+} HS state. We first note that the HS Co^{3+} would have a strong antiferromagnetic coupling with the HS Co^{2+} as in the parent compound La_2CoO_4 with a quite high T_N of 275 K, in contrast to the low $T_{\text{SO}} \approx 30$ K of $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$. This already infers that a HS Co^{3+} state is quite unlikely. Indeed, our calculations show that the HS Co^{3+} state is higher in energy than the LS ground state by 311 meV and that it has a big out-of-plane orbital

moment of $-0.96\mu_B$ (parallel to its spin moment of $-2.95\mu_B$, see Table I) being again in disagreement with the observed easy in-plane magnetism.

To conclude, we confirm that the checkerboard charge order in $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$ consists of the HS Co^{2+} and LS Co^{3+} , through a set of LSDA+ U band structure calculations including the spin-orbit coupling and multiplet effect. This solution accounts for the optical spectra. The small $\text{Co}^{2+} t_{2g}$ crystal field splitting makes the spin-orbit coupling operative, which produces the observed easy in-plane magnetism.

In contrast, either the higher-lying IS or highest HS Co^{3+} states would yield a wrong easy out-of-plane magnetism. Moreover, the IS (HS) Co^{3+} would have strong ferromagnetic (antiferromagnetic) coupling with the robust HS Co^{2+} , both in disagreement with the low spin-ordering temperature of $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$. Finally we note that the multiplet effect of the IS state is significant and should be taken good care of.

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