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# Possibility for an intermediate-spin ground state in the charge-transfer material $SrCoO_3$

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We discuss the possibility of an intermediate-spin ground state for a $d^5$ ($d^6$) system. The intermediate-spin state is stabilized by the relative stability of the ligand hole state that it hybridizes with. Using atomic multiplet calculations we showed that an intermediate-spin ground state is possible for $Co^{4+}$ ($d^5$) when the $d^6\underline{L}$ state dominates the ground state. From a comparison of the experimental Co $2p$ x-ray absorption spectroscopy spectrum with the calculated one we assume an intermediate-spin ground state for $SrCoO_3$. The intermediate-spin ground state is a highly symmetrical state with high-spin Co $d^6$ ions on each site. Each oxygen then contributes $\frac{1}{3}$ hole which is antiferromagnetically coupled to both neighboring Co ions. In this way the itinerant oxygen holes couple the high-spin Co $d^6$ ions ferromagnetically. With this model of oxygen holes that introduce ferromagnetic correlations we can also explain the spin-glass behavior for slightly doped $LaCoO_3$.

## INTRODUCTION

The electronic properties of $3d$ transition-metal compounds, where electron correlations play an important role have received much attention in recent years, triggered by the discovery of the high-$T_c$ superconductors.[1] In the classification scheme devised by Zaanen, Sawatzky, and Allen[2] transition-metal compounds can be placed either in the Mott-Hubbard regime where the band gap is determined by the $d$-$d$ Coulomb repulsion energy $U$ or in the charge-transfer regime where the band gap is determined by the ligand to metal charge-transfer energy $\Delta$. In an examination of the properties in the $La_{1-x}Sr_xCoO_3$ system which can be placed in the charge-transfer regime[3,4] we encountered many peculiarities and conflicting interpretations of experimental data. Starting with $LaCoO_3$ for which a low-spin to high-spin transition and a semiconductor-to-metal transition have been reported[5–11] there are conflicting arguments with respect to the temperature at which the spin state transition takes place. Recently polarized neutron-scattering experiments[12] firmly supported the spin state transition to take place at about 90 K which is in sharp contrast with the interpretation of x-ray-absorption spectroscopy[13] (XAS) data which indicate the spin state transition in the range 400–650 K coinciding with the gradual semiconductor metal transition. When the $La^{3+}$ is replaced by $Sr^{2+}$ formally $Co^{4+}$ ions are introduced and the remaining $Co^{3+}$ ions are stabilized in the high-spin state because of the larger size of the $Sr^{2+}$ ion. However as Jonker and van Santen[14] showed compounds with $x > 0.15$ in the $La_{1-x}Sr_xCoO_3$ system are ferromagnetic and metallic. These properties which started a lot of research on the system were shown to persist up to $x = 1.0$.[3,15–19] For the metallic $La_{0.5}Sr_{0.5}CoO_3$ Goodenough[20] proposed an intermediate-spin model, which can be rationalized with localized $t_2^5$ configurations on each cobalt and an itinerant $\sigma^*$ band that contains 0.5 electron per Co ion, to account for the ferromagnetism and the observed magnetic moment. Neutron scattering[12] indicates for the low doped $La_{0.92}Sr_{0.08}CoO_3$ the appearance of a spin-glass state and the authors suggested that doping with $Sr^{2+}$ introduced both ferromagnetic and antiferromagnetic interactions in the system. We will now concentrate on the other end member the ferromagnetic metal $SrCoO_3$ a cubic perovskite with $a = 3.836$ Å which can be prepared under high oxygen pressure.[21] This compound which tends to oxygen deficiency has a reported Curie temperature of about 220 K with a magnetic moment of $\mu_{\text{eff}} = 3\mu_B$ and according to most authors the $Co^{4+}$ is in the low-spin state.[17,19] An atomic multiplet calculation for a low spin Co $d^5$ showed discrepancies with the experimental Co $2p$ XAS data.[22] Especially the absence of a prepeak in the experimental spectrum which should appear for a $t_{2g}^5$ low-spin state due to relative stability of the $\underline{p}t_{2g}^6$ final state is a strong indication that the $Co^{4+}$ is not in the low-spin state. Crystal-field theory would then tell you that the $Co^{4+}$ is in the high-spin state. However with $d^5$ ions in a high-spin state one would expect an antiferromagnetic ordering not a ferromagnetic one. Hybridization was not taken into account in the reported calculations. From O $1s$ XAS measurements[23] it is known that the ground state of $SrCoO_3$ has a considerable amount of ligand hole character. The formal $Co^{4+}$ is a high valence state which can be compared to other unusually high valence states such as $Cu^{3+}$, $Ni^{3+}$, and $Fe^{4+}$ in related transition-metal compounds. Materials with these high valence states have ground states which are dominated by the ligand hole character due to small or even negative charge-transfer

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energies.[24–26] For these compounds it is known that hybridization can change the order of the states in the multiplet. The mechanism for this process is illustrated in Fig. 1,[27] where in an impurity picture the high energy $d^{n-1}$ configurations can cause low-energy bound states to be pushed out of the oxygen band. A nice example are the high-$T_c$ cuprates where the order of the $^1A_{1g}$ and $^3B_{1g}$ configurations in the unhybridized $d^8$ state is inverted in the $d^9\underline{L}$ state[28] and the first ionization states are the famous Zhang-Rice singlets.[29]

We will show using atomic-multiplet calculations, in which the ligand hole states are taken into account, that in a similar way the intermediate-spin state which occurs for $d^5$ ($d^6$) configurations in transition-metal compounds is stabilized when the corresponding $d^{n+1}\underline{L}$ states that it hybridizes with are low in energy. Furthermore with an intermediate-spin ground state we are able to explain the ferromagnetic interactions in the $SrCoO_3$ which could not be accounted for by either high- nor low-spin states. With the intermediate-spin state most of the properties in the $La_{1-x}Sr_xCoO_3$ system such as the spin-glass state and the change in the Curie temperature upon doping can be explained.

## THEORY

If we start from the free ions with $d^5$ and $d^6$ configurations Hund's rule would give the high-spin $^6S$ ($S=5/2$) and a $^5D$ ($S=2$) ground states, respectively. In the solid, however, the introduction of crystal and ligand fields can lead to a low-spin ground state depending on the competition between the cubic crystal field ($10Dq$) and the intra-atomic exchange ($J$). From Fig. 2, where the electron removal energies are presented for $d^5$ and $d^6$ configurations we see that for a $d^6$ compound the low-spin state is more stable than the high-spin state if $10Dq > 2J$. For the $d^5$ configuration the crystal field required to get the low-spin state is even bigger due to the enhanced exchange: $10Dq > 3$ J.

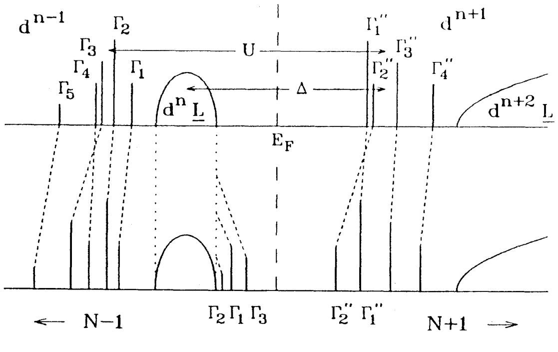

FIG. 1. In an impurity picture high-energy $d^{n-1}$ states can cause low-energy bound states to be pushed out of the oxygen band.

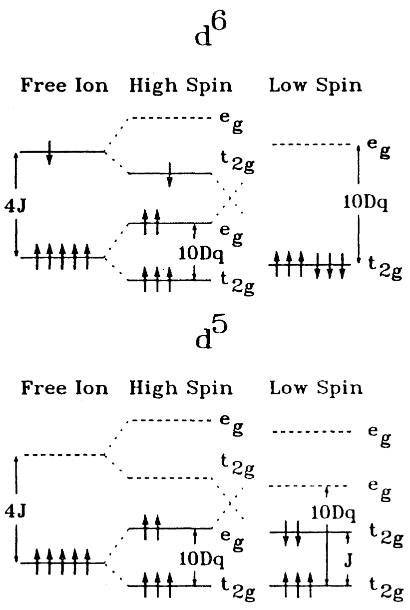

FIG. 2. The schematic electron removal energies for $d^6$ and $d^5$ spin states ranging from the free-ion value on the left via a weak crystal field in the middle to a strong crystal field on the right.

For the $d^5$ ($d^6$) configuration there is aside from the high- and the low-spin states the possibility of an intermediate-spin state. In crystal-field theory the intermediate-spin state cannot become the ground state of the system but if hybridization with the oxygen band is taken into account the stability of the ligand hole states has to be accounted for. In the oxygen band the states which hybridize with metal states of $e_g$ symmetry are higher in energy with respect to those that hybridize with states of $t_{2g}$ symmetry because of oxygen-oxygen interactions. This energy difference in a octahedral oxygen cluster is $2(pp\sigma - pp\pi)$ where $pp\pi$ and $pp\sigma$ are the oxygen-oxygen transfer integrals. Therefore oxygen hole states with $e_g$ symmetry are stabilized with respect to oxygen hole states with $t_{2g}$ symmetry by some 1.5–2.0 eV.[30] Besides the difference in energy there is the difference in hybridization strength which is about twice as large for orbitals of $e_g$ symmetry. For simplicity we omit the states of $t_{2g}$ symmetry in the following discussion. However in the calculations they are taken into account.

The $^6A_1$ high-spin ($S=5/2$), the $^4T_1$ intermediate-spin ($S=3/2$), and the $^2T_2$ low-spin ($S=1/2$) states with their charge-transfer states of $e_g$ symmetry only are shown in Fig. 3. The other intermediate-spin state $^4T_2$ is compared to the $^4T_1$ somewhat higher in energy due to a less favorable Coulomb exchange. The $^6A_1$ state hybridizes with ligand hole states of $e_g$ symmetry which have $t_{2g}^3e_g^3$ and $t_{2g}^3e_g^4$ configurations on the metal. These states are $10Dq$ and $20Dq$ higher in energy with respect to the normal high-spin $t_{2g}^4e_g^2$ and $t_{2g}^5e_g^2$ configurations. The low-spin $^2T_2$ hybridizes with a $d^6\underline{L}_{eg}$ state which has the intermediate-spin configuration $t_{2g}^5e_g^1$ and a normal high-spin $t_{2g}^5e_g^2$ configuration for the double ligand hole state. The intermediate spin $^4T_1$ hybridizes with a $d^6\underline{L}_{eg}$ state which has the high-spin $t_{2g}^4e_g^2$ configuration on the metal and a double ligand hole state with the $t_{2g}^4e_g^3$ configuration which is raised in energy by $10Dq$ with respect to the $t_{2g}^5e_g^2$ configuration of the $^2T_2$. The oxygen

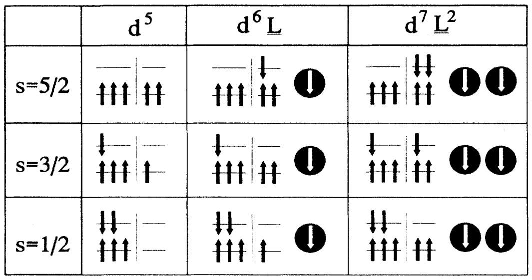

FIG. 3. The $^6A_1$ ($S=5/2$), $^4T_2$ ($S=3/2$), and $^2T_2$ ($S=1/2$) states with their ligand hole states of $e_g$ symmetry.

holes are in all cases antiferromagnetically coupled to the extra $e_g$ electron.

Comparing the $d^5$ states with their ligand hole states we see that the $^6A_1$ is not so much stabilized by hybridization with the ligand hole states of $e_g$ symmetry whereas the stabilization for the $^4T_1$ state is only large for the first ligand hole state $d^6\underline{L}$. The $^2T_2$ is stabilized extensively by both the $d^6\underline{L}$ and $d^7\underline{L}^2$ states. An impression of the formation of an intermediate-spin ground state is given in Fig. 4, where the $d^5$ states and the $d^6\underline{L}$ states of $e_g$ symmetry that they hybridize with are shown. The picture is drawn for the negative charge-transfer regime where the relative stability of the ligand hole states determine the symmetry of the ground state. The $^4T_1$ intermediate-spin state can become the ground state in a certain crystal field range if the $d^6\underline{L}$ state is low in energy compared to both the $d^5$ and the $d^7\underline{L}^2$ states. The competition between the $d^6\underline{L}$ high-spin $t_{2g}^4e_g^2$ and the $d^6\underline{L}$ intermediate-spin $t_{2g}^5e_g^1$ will then mainly determine the phase diagram. A wide crystal-field range for which the $^4T_1$ becomes the ground state is in this case expected. The parameters needed for a ground state dominated by $d^6\underline{L}$ character are a negative charge-transfer energy and a rather large $d$-$d$ Coulomb repulsion energy $U$.

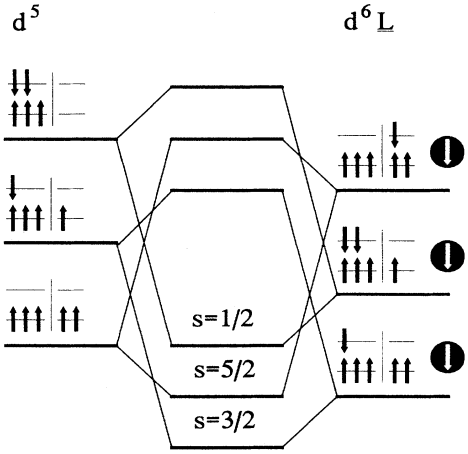

FIG. 4. An impression of the formation of an intermediate-spin around state due to the relative stability of the $d^6\underline{L}_{eg}$ states. The $d^5$ and $d^6\underline{L}_{eg}$ configurations for the three different spin states are indicated.

## RESULTS AND DISCUSSION

For the interpretation of transition-metal $2p$ XAS spectra we compare the experimental results with atomic-multiplet calculations using a program developed by Thole *et al.*,[31] making use of Cowan[32] and Butler[33] computer programs. In these calculations the charge-transfer energy $\Delta$, the $d$-$d$ Coulomb repulsion energy $U$, the core-hole–$d$-electron Coulomb interaction $Q$, the crystal field $10Dq$, and the hybridization $T$ are treated as adjustable parameters. The charge-transfer energy $\Delta$ is by definition, $E[3d^{n+1}\underline{L}]-E[3d^n]=\Delta$ where $E[3d^{n+1}\underline{L}]$ and $E[3d^n]$ denote the configuration averaged energies of the $3d^{n+1}\underline{L}$ and $3d^n$ multiplets, respectively. Just like the charge-transfer energy the $d$-$d$ Coulomb repulsion energy is defined with respect to the configuration averaged energies. For the hybridization we use for the transfer integrals the empirical relation $T_e=-2T_t$. And for the Coulomb interactions we have assumed the relationship $U/Q=0.875$. In the approach the Coulomb interaction, the Co $2p$ spin-orbit coupling and the crystal field act on localized Co $2p$ and $3d$ levels. The Coulomb and exchange parameters are reduced to 80% of their atomic Hartree-Fock values to account for intra-atomic relaxation effects.[32] Hybridization mixes the Co $3d$ orbitals with linear combinations of $p$ orbitals on the six ligand oxygen atoms. In our approximation we took for each Co $d$ orbital just one linear combination of ligand orbitals of the same symmetry. In the calculation these linear combinations are represented by the orbitals of an extra $d$ shell. The fully occupied ligand is represented by a $d^{10}$ configuration so $d^6+d^7\underline{L}$ becomes $d^6d^{10}+d^7d^9$. In addition to the crystal field acting on the Co $3d$ orbitals we introduced a crystal field acting on the ligand orbitals simulating the splitting of the $e_g$ and $t_{2g}$ levels in the oxygen band.

First we calculated $d^5$ spectra without hybridization with the crystal field $10Dq$ as the only free parameter as a function of which the spectra change gradually until the ground state becomes low spin giving rise to a completely different spectrum. In Fig. 5 the experimental spectrum (obtained from Ref. 23) is shown with the calculated spectra for high spin and low spin at crystal fields of $10Dq=3.3$ eV and $10Dq=3.6$ eV, respectively. The spectrum for the high-spin $t_{2g}^3e_g^2$ state ($S=5/2$) which is shown in Fig. 5 shows an $L_2$ edge which is completely different from the experimental spectrum. The spectrum of the $^2T_2$ low-spin state in Fig. 5 shows a peak about 6 eV in front of the main peak which can be attributed to the $\underline{p}t_{2g}^6$ final state which is energetically favorable. In the experimental spectrum this peak is clearly absent. So the experimental spectrum cannot be explained when hybridization is not taken into account.

When the hybridization is switched on three extra parameters are introduced: the transfer integral $T_e$, the charge-transfer energy $\Delta$, and the $d$-$d$ Coulomb repulsion energy $U$. (The transfer integral $T_t$ and the core-hole–$d$-electron interaction $Q$ are related to $T_e$ and $U$, respectively). The values were roughly estimated from the reported parameters of the related compounds $LaFeO_3$ and $SrFeO_3$ (Ref. 34), $T_e=2$ eV, $U=7$ eV, and $\Delta=-5$ eV

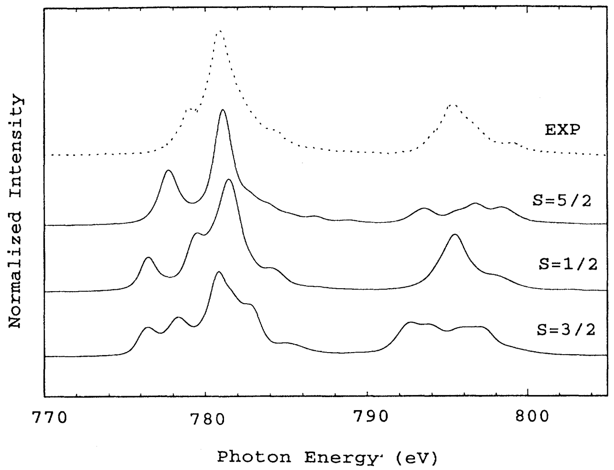

FIG. 5. The experimental $SrCoO_3$ spectrum (dotted line) together with the calculated spectra for high spin ($S=5/2$) at $10Dq=3.3$ eV, low spin at $10Dq=3.6$ eV ($S=1/2$), and we show also the intermediate-spin ($S=3/2$) spectrum at $10Dq=3.3$ eV where it lies about 1 eV above the high-spin ground state.

($U_{\text{eff}}=13$ eV and $\Delta_{\text{eff}}=-2$ eV). The splitting of the $e_g$ and $t_{2g}$ levels in the oxygen band was taken 1.8 eV.[30] With these parameters the relative stability of the different spin states was calculated as a function of the crystal field as is shown in the phase diagram in Fig. 6. As expected the low-spin state and to a lesser extent the intermediate-spin state are lowered in energy when the crystal field is increased. The intermediate-spin state becomes the ground state for values of the crystal field between 0.6 and 1.1 eV. The spectra for the high-spin, the intermediate-spin, and the low-spin states at crystal fields of, respectively, 0.3, 1.0, and 1.2 eV are shown in Fig. 7 with the experimental spectrum. We note that the shape of the spectrum depends mainly on the spin state and does not change dramatically with the crystal field.

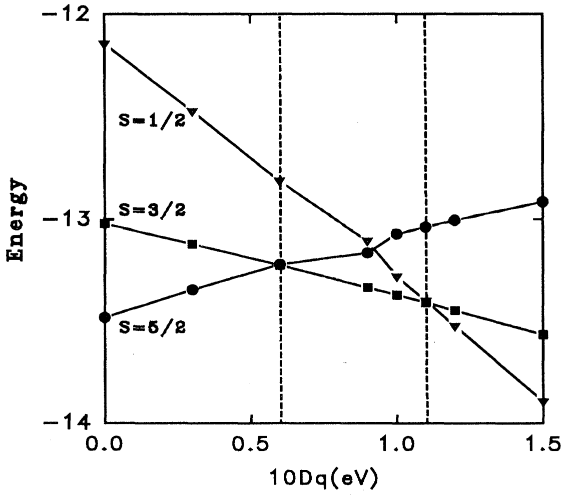

FIG. 6. Energy differences (eV) between the ${}^2T_2$, the ${}^4T_1$, and the ${}^6A_1$ as a function of the crystal field.

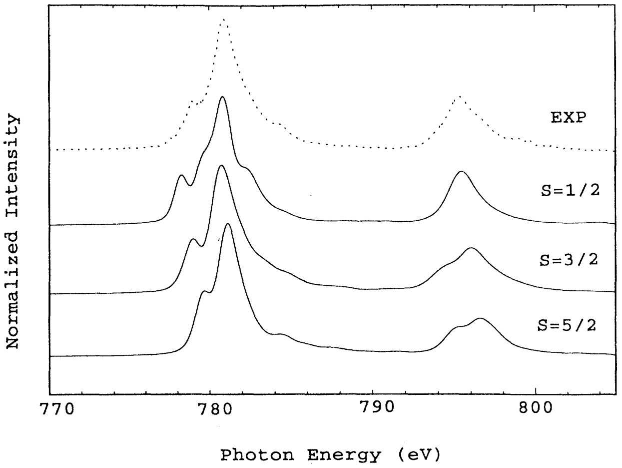

FIG. 7. The experimental $SrCoO_3$ spectrum (dotted line) compared with calculated spectra for the parameter values $T_e=2$ eV, $U=7$ eV, and $\Delta=-5$ eV. The spectrum for the low-spin ground state ($S=1/2$) at $10Dq=1.2$ eV, the intermediate-spin ground state ($S=3/2$) at $10Dq=1.0$ eV, and the high-spin spectrum ($S=5/2$) at $10Dq=0.3$ eV.

The resemblance of the intermediate-spin spectrum which has a ground state consisting of 8% $d^5$, 67% $d^6\underline{L}$, and 25% $d^7\underline{L}^2$ character with the experimental spectrum is quite good especially at the $L_3$ edge. In the $L_2$ edge the positions of the calculated poles correspond to the features in the experimental spectrum but the intensities of the poles are somewhat different. For the low-spin spectrum the main difference is still in the presence of the prepeak, although it has shifted towards the main peak with respect to the calculation without hybridization, we have not been able to improve its position any further and therefore we exclude the low-spin state for $SrCoO_3$. The general features of the high-spin spectrum are identical to the intermediate-spin spectrum. However the splitting of the main peak and the prepeak is rather small in the high-spin spectrum. The comparison of the experimental Co $2p$ XAS spectrum with the calculated ones indicates that $SrCoO_3$ can best be described with an intermediate-spin ground state and that the low-spin state can be excluded. The value for the charge-transfer energy $\Delta$ used in the calculations is rather small when we compare it with the reported values on the related $LaCoO_3$ of $\Delta_{\text{eff}}=4$ eV (Refs. 4 and 35) taking into account that $\Delta$ decreases by some 3 eV when the cation valence is increased by one. However, the reported value of $\Delta_{\text{eff}}$ for $LaCoO_3$ is based on cluster calculations for $LiCoO_2$.[36] And since the changes in the parameter values have little effect on the low-spin cluster calculation the estimated $\Delta_{\text{eff}}=4$ eV is rather arbitrary and very close to $\Delta_{\text{eff}}=5.5$ eV for CoO.[36] An estimation of $\Delta_{\text{eff}}$ by extrapolating values obtained for related compounds gave $\Delta_{\text{eff}}=1$ eV for the low-spin $LaCoO_3$ (Ref. 4) which is in good agreement with the $\Delta_{\text{eff}}=-2$ eV for $SrCoO_3$ that we used in the multiplet calculations. A somewhat less negative value for $\Delta_{\text{eff}}$ does not change the spectrum from the multiplet calculation very much when the ground state remains dominated by the $d^6\underline{L}$ character. We obtained a very rough estimate of $\Delta_{\rm eff}$ by relating changes in the charge-transfer energies to changes in the Madelung potentials using the values tabulated by Torrance *et al.*[37] going from $LaCoO_3$ to $SrCoO_3$:

$$\Delta(\mathrm{SrCoO_3})-\Delta(\mathrm{LaCoO_3})=-V_M(\mathrm{Co}^{4+})+V_M(\mathrm{Co}^{3+}) \\ -U(\mathrm{Co}^{3+}) \ ,$$

where $U$ is the bare on site Coulomb repulsion. Even with the large value $\Delta(\mathrm{LaCoO_3})=4$ eV we obtained $\Delta(\mathrm{SrCoO_3})=-4.5$ eV and although it is a very rough estimate a negative value for $\Delta(\mathrm{SrCoO_3})$ is not out of place.

As in $SrFeO_3$ but also, e.g., $LiNiO_3$ and $NaCuO_2$, the ground state in $SrCoO_3$ is dominated by a ligand hole. In charge-transfer transition-metal compounds the bandgap is determined by the magnitude of the charge-transfer energy $\Delta$. In $SrCoO_3$ with its negative $\Delta$ charge fluctuations of the type $d^{n+1}\underline{L}d^{n+1}\underline{L} \rightarrow d^{n+1}d^{n+1}\underline{L}^2$ are expected. For $NaCuO_2$ a gap was reported to open as a result of the geometrical arrangement.[25] The copper-oxygen-copper bond angle is 90°, leading to strong intracluster and weak intercluster interactions. In this view $LaCuO_3$ with 180° bond angles would be metallic contrary to recent band-structure calculations.[38] A somewhat different description was given by Sarma *et al.*[26] who used Hartree-Fock calculations to predict insulating verus metallic behavior for negative-$\Delta$ compounds. $SrCoO_3$ has an ideal perovskite structure with Co-O-Co bond angles of 180° giving rise to a strong overlap between nearest-neighbor clusters. With $\frac{1}{3}$ of a hole on each oxygen and an on-site Coulomb repulsion energy of $U_p=6$ eV we estimate the effective Coulomb interaction $U_{\rm eff}=U_p/3=2$ eV which compared with an oxygen bandwidth of about $W_p=4$ eV is not in conflict with the experimentally reported metallic state.[21]

The intermediate-spin state can be visualized as high-spin Co $d^6$ ions ($S=2$) with a hole antiferromagnetically coupled in a linear combination of oxygen $\sigma$ orbitals which hybridize with the $d$ electrons of $e_g$ symmetry resulting in a total spin $S=1.5$. In order for an oxygen hole of $e_g$ symmetry to hybridize with both adjacent Co ions the spin of the $e_g$ electrons on both Co ions should be parallel. Looking at an $CoO_6$ cluster and knowing that there is $\frac{1}{3}$ hole per oxygen we conclude that the two holes on the six oxygens must be of different $e_g$ symmetry in order for both holes to hybridize with the central Co ion. So all oxygens are equivalent with $\frac{1}{6}$ hole of $x^2$-$y^2$ symmetry and $\frac{1}{6}$ hole of $3z^2$-$r^2$ symmetry on each oxygen both of which hybridize with both Co ions. As a result a ferromagnetic ground state for the itinerant $SrCoO_3$ can be explained very similar to the Zener double exchange mechanism.[39,40] The mobile oxygen holes couple the $S=2$ moments on the cobalt ions ferromagnetically when their spins are conserved during transport.

With this model we are able to understand the behavior of $SrCoO_3$ upon doping with electrons by replacing Sr with La. Electron doping has both a positive and a negative effect on the ferromagnetic exchange. The electrons reduce the number of holes in the oxygen band which are responsible for the ferromagnetic interaction in the first place. However, the effective magnetic moment on the Co sites is enhanced stabilizing the ferromagnetic state. So if the number of holes is sufficiently large upon electron doping the Curie temperature is expected to increase. Magnetic data[17] confirm this and show a maximum Curie temperature in the $La_{1-x}Sr_xCoO_3$ system around $x=0.7$. Other evidence is found in the $SrCo_{1-x}Fe_xO_3$ system where the Co ($S=2$) is replaced with Fe ($S=5/2$). The $Fe^{4+}$ and $Co^{4+}$ have almost identical ground states with just one $t_{2g}$ electron less for the Fe. The moment on the metal is increased upon Fe doping but the number of holes is not reduced and $T_C$ is reported to increase all the way up to $x=0.8$ (Ref. 41) after which the screw spin structure of $SrFeO_3$ is formed.

Recently from a neutron-scattering study, Asai *et al.*[12] suggested that the magnetic correlations in undoped $LaCoO_3$ are weakly ferromagnetic and from the appearance of a spin-glass state in $La_{0.92}Sr_{0.08}CoO_3$ they conclude that the introduction of $Sr^{2+}$ brings about not only ferromagnetic interactions but also antiferromagnetic interactions.

In our model a low concentration of localized holes gives rise to two different oxygen ions oxygens with and without a hole. In this case there are two different interactions between the high-spin Co ions. The interaction via an oxygen ion without a hole gives rise to a normal Anderson[42] superexchange interaction which is strong and negative as is reported for well known $G$-type antiferromagnet $SrCoO_{2.5}$.[43] When there is a hole on the oxygen the interaction is ferromagnetic because the hole wants to hybridize with both Co neighbors as was discussed above. The introduction of holes bring about only ferromagnetic interactions between high-spin Co ions. However, the undoped $LaCoO_3$ has a low-spin ground state which is almost degenerate with the high-spin state and replacing the $La^{3+}$ with the larger $Sr^{2+}$ then apart from introducing holes stabilizes the high-spin state of $Co^{3+}$ with respect to its low-spin state.

The intermediate-spin ground state can also be realized for $d^6$ compounds. The high-spin $t_{2g}^4e_g^2$ is not so much stabilized by $e_g$ hybridization since the $t_{2g}^4e_g^3$ and $t_{2g}^4e_g^4$ configurations are raised in energy by 10 and $20Dq$, respectively. The low-spin $t_{2g}^6$ configuration is stabilized by both $t_{2g}^6e_g^1$ and $t_{2g}^6e_g^2$ the single and double ligand hole states. The intermediate-spin $t_{2g}^5e_g^1$ is mainly stabilized by the $t_{2g}^5e_g^2$ single ligand hole state. In case the $d^7\underline{L}$ configuration dominates the ground state the competition between the high-spin $t_{2g}^5e_g^2$ and the low-spin $t_{2g}^6e_g^1$ will determine the symmetry of the ground state. So an $^3T_1$ intermediate-spin configuration is theoretically possible but when compared to the intermediate spin for $d^5$ compounds using the same parameters, the crystal-field range in which it is stabilized is much narrower.

## SUMMARY AND CONCLUSIONS

With atomic-multiplet calculations we showed that for a negative charge-transfer $d^5$ compound the intermediate-spin state can become the ground state of the system due to the relative stability of the ligand hole state of $e_g$ symmetry that it hybridizes with. From the comparison of the Co $2p$ XAS spectrum of $SrCoO_3$ with the experimental spectrum a low-spin ground state can be excluded. The intermediate-spin state gives the best fit of the experimental spectrum. This intermediate-spin state should be visualized as a state with $Co^{3+}$ high spin at the metal sites and a hole antiferromagnetically coupled to the electrons of $e_g$ symmetry. The hybridization of an oxygen hole with both neighboring Co ions causes a ferromagnetic interaction. When the number of holes is reduced and they are no longer itinerant the experimentally observed spin-glass state results from the two types of interactions in the system: the ferromagnetic $Co^{3+}$-O-$Co^{3+}$ interaction via an oxygen with a hole and the double exchange via an oxygen without a hole, which is strong and negative.

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