A different look at the spin state of Co$^{3+}$ ions in CoO$_3$ pyramidal coordination

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Using soft-x-ray absorption spectroscopy at the Co-$L_{2,3}$ and O-$K$ edges, we demonstrate that the Co$^{3+}$ ions with the CoO$_3$ pyramidal coordination in the layered Sr$_2$CoO$_3$Cl compound are unambiguously in the high spin state. Our result questions the reliability of the spin state assignments made so far for the recently synthesized layered cobalt perovskites, and calls for a re-examination of the modeling for the complex and fascinating properties of these new materials.

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The class of cobalt-oxide based materials has attracted considerable interest in the last decade because of expectations that spectacular properties may be found similar to those in the manganites and cuprates. In fact, all possible spin states have been claimed for each of the different Co sites present. There is no consensus in the predictions from band structure calculations $^{[27, 28, 29]}$. We carried out a test experiment using a relatively simple model compound, namely Sr$_2$CoO$_3$Cl, in which there are no spin state transitions present and in which there is only one kind of Co$^{3+}$ ion coordination $^{[9]}$. Important is that this coordination is identical to the pyramidal Co$_3$O$_5$ present in the heavily debated layered perovskites $^{[2, 3, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22]}$. Using a spectroscopic tool, that is soft x-ray absorption spectroscopy (XAS), we demonstrate that pyramidal Co$^{3+}$ ions are not in the often claimed LS state but unambiguously in a HS state. This outcome suggests that the spin states and their temperature dependence in layered cobalt perovskites may be rather different in nature from those proposed in the recent literature.

Bulk polycrystalline samples of Sr$_2$CoO$_3$Cl were prepared by a solid state reaction route $^{[8]}$. The magnetic susceptibility is measured to be very similar to the one reported by Loureiro et al. $^{[9]}$. We find that up to 600 K the susceptibility does not follow a Curie-Weiss behavior, making a simple determination of the spin state impossible. Spectroscopic measurements were carried out using soft x-rays in the vicinity of the Co-$L_{2,3}$ ($h\nu \approx 780$-800 eV) and O-$K$ ($h\nu \approx 528$-535 eV) absorption edges. The experiments were performed at the Dragon beamline at the NSRRC in Taiwan, with a photon energy resolution of about 0.30 eV and 0.15 eV, respectively. Clean sample surfaces were obtained by scraping in-situ with a diamond file, in an ultra-high vacuum chamber with a pressure in the low $10^{-9}$ mbar range. The Co-$L_{2,3}$ XAS spectra were recorded in the total electron yield mode by measuring the sample drain current, and the O-$K$ XAS spectra by collecting the fluorescence yield to minimize background signal and maximize bulk sensitivity. A single crystal of EuCoO$_3$ is included as an unambiguous reference for a LS Co$^{III}$ system $^{[30]}$.

In this manuscript we are questioning the reliability of the spin states as obtained from magnetic, neutron and x-ray diffraction measurements for the newly synthesized layered cobalt perovskites $^{[2, 3, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22]}$. We

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Fig. 1 shows the Co-L$_{2,3}$ XAS spectrum of Sr$_2$CoO$_3$Cl taken at room temperature. It is dominated by the Co 2p core-hole spin-orbit coupling which splits the spectrum roughly in two parts, namely the L$_3$ (h$_\nu$ $\approx$ 780 eV) and L$_2$ (h$_\nu$ $\approx$ 796 eV) white lines regions. The line shape of the spectrum depends strongly on the multiplet structure given by the Co 3d-3d and 2p-3d Coulomb and exchange interactions, as well as by the local crystal fields and the hybridization with the O 2p ligands. Unique to soft x-ray absorption is that the dipole selection rules are very effective in determining which of the 2p$^5$3d$^{n+1}$ final states can be reached and with what intensity, starting from a particular 2p$^6$3d$^n$ initial state (n=6 for Co$^{3+}$) [31, 32]. This makes the technique extremely sensitive to the symmetry of the initial state, i.e. the valence [33], orbital [34, 35], and spin [36-38, 39] state of the ion.

Utilizing this sensitivity, we compare the Co-L$_{2,3}$ XAS spectrum of Sr$_2$CoO$_3$Cl to that of another 3d$^5$ compound, namely FeO, reproduced from the thesis of J.-H. Park [40]. This spectrum was taken at room temperature. Except for the different photon energy scale and the smaller 2p core-hole spin-orbit splitting, the FeO spectrum as shown in Fig. 1 is essentially identical with that of Sr$_2$CoO$_3$Cl. From this we can immediately conclude that the Co$^{3+}$ ions in Sr$_2$CoO$_3$Cl are in the HS state, since the Fe$^{2+}$ ions are also unambiguously HS.

To find further support for our conclusion, we also compare the Co-L$_{2,3}$ XAS spectrum of Sr$_2$CoO$_3$Cl with that of EuCoO$_3$, which is known to be a LS system [30]. From Fig. 2 one can now clearly see large discrepancies between the spectra of the two compounds. Not only are the line shapes different, but also the ratios of the integrated intensities of the L$_3$ and L$_2$ regions. In comparison with Sr$_2$CoO$_3$Cl, the LS EuCoO$_3$ has relatively less intensity at the L$_3$ and more at the L$_2$, characteristic for a spin state difference [32, 33, 34]. Fig. 2 thus demonstrates that Sr$_2$CoO$_3$Cl is definitely not a LS system.

It would have made our case even easier to prove, if we could have excluded experimentally the IS scenario for Sr$_2$CoO$_3$Cl by comparing the spectrum to that of a known Co$^{3+}$ IS reference system. However, there is to date no consensus for such an oxide reference system. Nevertheless, the spin state can also be deduced from theoretical simulations of the experimental spectra. To this end, we use the successful configuration interaction cluster model that includes the full atomic multiplet theory and the hybridization with the O 2p ligands [31, 32, 41]. We have carried out the calculations for a Co$^{3+}$ ion in the CoO$_5$ pyramidal cluster as present in Sr$_2$CoO$_3$Cl and for the ion in the CoO$_6$ octahedral cluster found in EuCoO$_3$. We use parameter values typical for a Co$^{3+}$ system [26]. The Co 3d to O 2p transfer integrals are adapted for the various Co-O bond lengths according to Harrison’s prescription [42, 43]. This together with the crystal field parameters determines whether the Co$^{3+}$ ion is in the
HS or LS state \[23\]. The results are shown in Fig. 2 and one can clearly see that the calculated spectrum of the HS pyramidal CoO\(_3\) cluster reproduces very well the experimental Sr\(_2\)CoO\(_3\)Cl spectrum, and that the calculated LS octahedral CoO\(_6\) spectrum matches nicely the experimental EuCoO\(_3\) spectrum. This demonstrates that our spectroscopic assignments are firmly founded.

More spectroscopic evidence for the HS nature of the Co\(^{3+}\) in the pyramidal CoO\(_3\) coordination can be found from the O K XAS spectrum as shown in Fig. 3. The structures from 528 to 533 eV are due to transitions from the O 1s core level to the O 2p orbitals that are mixed into the unoccupied Co 3d \(t_{2g}\) and \(e_g\) states. The broad structures above 533 eV are due to Sr 4d, Co 4s and Cl 3p related bands. For comparison, Fig. 3 also includes the spectrum of the LS EuCoO\(_3\), and clear differences can be seen in the line shapes and energy positions of the Co 3d - O 2p derived states. This again is indicative that Sr\(_2\)CoO\(_3\)Cl is not a LS system. To interpret the spectra, we also have carried out full-potential band structure calculations \[27\] for Sr\(_2\)CoO\(_3\)Cl in the local density approximation with correction for electron correlation effects (LDA+U) \[14\]. We find the ground state of the system to be an antiferromagnetic insulator with a band gap of 1.3 eV and a magnetic moment of 3.2 \(\mu_B\). Although less than 4\(\mu_B\), this indicates that the Co is in the HS state since in an antiferromagnet the moment is reduced due to covalency. The calculated unoccupied O 2p partial density of states (DOS) are depicted in Fig. 3, and good agreement with the experimental spectrum can be observed.

It is now interesting to look with more detail into the character of the states relevant for the O K XAS spectra. For the LS EuCoO\(_3\) with the 3d \(t_{2g}\) configuration, the lowest energy structure in the spectrum at about 529.5 eV is due to transitions into the unoccupied Co 3d \(e_g\) states. The fact that Sr\(_2\)CoO\(_3\)Cl has a lower energy structure thus indicates that transitions to the lower lying \(t_{2g}\) are allowed, i.e. that the \(t_{2g}\) states are not fully occupied. In other words, Sr\(_2\)CoO\(_3\)Cl is in the HS \(t_{2g}e_g^2\) or IS \(t_{2g}e_g^2\) state. At first sight, one might then expect a much larger spectral weight for the higher lying \(e_g\) level, since the hybridization with the O 2p is larger for the \(e_g\) than for the \(t_{2g}\). However, our LDA+U calculations in which we find the HS ground state, indicate that, because of the missing apical oxygen in the CoO\(_5\) coordination, the unoccupied 3\(z^2\)-\(r^2\) level is pulled down by 1.6 eV from the \(x^2\)-\(y^2\) level, and comes close to the unoccupied \(t_{2g}\). Moreover, because of the large displacement (0.33 Å) of the Co ion out of the O\(_4\) basal plane of the pyramid \[3\], the hybridization of the \(x^2\)-\(y^2\) with the O 2p ligands is strongly reduced. Therefore, the dominant lower energy structure at 528.3 eV consists of the unoccupied minority \(t_{2g}\) (dashed line in Fig. 3) and minority \(3z^2\)-\(r^2\) (dashed dotted line) levels, and the shoulder at 530.4 eV of the minority \(x^2\)-\(y^2\) (dotted line).

From the LDA+U calculations, we have found that the IS state \[23\] is unstable with respect to HS ground state for the real crystal structure of Sr\(_2\)CoO\(_3\)Cl. We have also found nevertheless, that the IS state can be stabilized by artificially moving the Co ion into the O\(_4\) basal plane of the CoO\(_5\) pyramid. For the latter, however, the calculated unoccupied O 2p partial DOS does not reproduce the experimental O-K XAS spectrum that well, as one can see from the discrepancies in the 531-532 eV range in Fig. 3. What happens is that the \(x^2\)-\(y^2\) level is pushed up by the increased hybridization with the O 2p ligands, since the Co ion is within the O\(_4\) basal plane in this artificial crystal structure. Moreover, the up-rising majority \(x^2\)-\(y^2\) becomes unoccupied, resulting in the IS state. Apparently, the actual large base corrugation of the CoO\(_5\) pyramid helps to stabilize the HS state \[27\], a trend that should not be overlooked if one is to understand the real spin state of CoO\(_5\) pyramids. We find from our LDA+U calculations that the HS is more stable than the IS for out-of-basal-plane Co displacements larger than a critical value of about 0.15 Å.
Having established that the pyramidal coordinated Co$^{3+}$ ions in Sr$_2$CoO$_3$Cl are in the HS state, we now turn our attention to other layered cobalt materials that have the same structural units. Neutron diffraction experiments on RBaCo$_2$O$_{5.0}$ ($R$ = rare earth) have revealed the existence of alternating Co$^{2+}$ and Co$^{3+}$ ions, both in pyramidal CoO$_5$ coordination. The magnetic structure is G-type antiferro with moments of 2.7 and 4.2 $\mu_B$ [11], or 2.7 and 3.7 $\mu_B$, respectively [12,13]. For the R=Nd compound, charge ordering was not observed, but an average moment of 3.5 $\mu_B$ was measured [14,15]. These studies suggested two possible scenarios for the Co$^{3+}$ ions, namely either HS with spin-only moments or IS with orbital moment. Our findings based on Sr$_2$CoO$_3$Cl on the other hand, strongly suggest the HS state of such pyramidal Co$^{3+}$ ions. Here we keep in mind that the out-of-plane Co displacements of the pyramids in R BaCo$_2$O$_{5.0}$ are larger than 0.35 Å [11,13,14], i.e. much larger than the above mentioned 0.15 Å critical value. The first scenario is thus favored, with the remark that neutron diffraction techniques tend to observe smaller magnetic moments due to the Co-O covalency, which is responsible for the antiferromagnetic superexchange interactions present in these materials.

The experimental situation for the R BaCo$_2$O$_{5.5}$ system is more complicated. Neutron and x-ray diffraction measurements indicate the presence of all Co$^{3+}$ ions in alternating pyramidal CoO$_5$ and octahedral CoO$_6$ units [14,15,16,17,18,19,20,22]. The magnetic structure is most likely not a simple G-type [20,21], and depending on the model, values between 0.7 and 2.0 $\mu_B$ have been extracted for the pyramidal Co$^{3+}$ [20,22]. The IS state is thus proposed, and in fact most other studies also assume this starting point [11,13,14], i.e. much larger than the 0.15 Å critical value. We therefore infer that also in these systems suggested two possible scenarios for the Co$^{3+}$ ions affecting the various exchange interactions in the compounds in which the pyramidal Co$^{3+}$ remains HS.

Summarizing, we have found an overwhelming amount of evidence for the HS nature of the pyramidal coordinated Co$^{3+}$ ions in Sr$_2$CoO$_3$Cl: (1) the Co $L_{2,3}$ spectrum has essentially an identical line shape as the Fe $L_{2,3}$ in FeO; (2) the Co $L_{2,3}$ spectrum can be reproduced to a great detail by model calculations with the Co ion in the HS state; (3) the O K spectrum can be well explained by LDA+U calculations with the Co in the HS state, but not with the Co in the IS state; and (4) LDA+U calculations yield the HS ground state and no stable IS state for the real crystal structure. With other newly synthesized layered cobalt oxides having very similar pyramidal Co$_3$O$_5$ units, we infer that those Co$^{3+}$ ions must also be in the HS state, contradicting the assignments made so far. It is highly desirable to investigate the consequences for the modeling of the properties of these new materials.

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