

The Spin State Puzzle in Layered Cobaltates

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. Indeed, giant magneto resistance effects have been observed in the $\text{La}_{1-x}\text{A}_x\text{CoO}_3$ ($A=\text{Ca},\text{Sr},\text{Ba}$) perovskites and $\text{RBaCo}_2\text{O}_{5+x}$ ($R=\text{Eu},\text{Gd}$) layered perovskites. Very recently, also superconductivity has been found in the $\text{Na}_x\text{CoO}_2\cdot y\text{H}_2\text{O}$ material. In fact, numerous one-, two-, and three-dimensional cobalt oxide materials have been synthesized or rediscovered in the last 5 years, with properties that include metal-insulator and ferro-ferri-antiferromagnetic transitions with various forms of charge, orbital and spin ordering. In this report we are questioning the reliability of the spin state assignments in the layered cobaltates as deduced from magnetic, neutron and x-ray diffraction measurements. We determined the spin state of the Co ions using a different technique, namely soft-x-ray absorption spectroscopy (SXAS).

A key aspect of cobalt oxides that distinguish them clearly from the manganese and copper materials, is the spin state degree of freedom of the $\text{Co}^{3+/III}$ ions: it can be low spin (LS, $S=0$), high spin (HS, $S=2$) and even intermediate spin (IS, $S=1$). This aspect comes on top of the orbital, spin (up/down) and charge degrees of freedom that already make the manganite and cuprate systems so exciting. It is, however, also precisely this aspect that causes considerable debate in the literature. For the classic LaCoO_3 compound, for instance, various early studies attributed the low temperature spin state change to be of LS-HS nature, while studies in the last decade put a lot of effort to propose a LS-IS scenario instead.

Figure 1 shows the energetics of three possible $3d^6$ spin states in the simplest ionic picture. In O_H symmetry these are given by $E_{LS} = -24Dq - 6J_H$, $E_{IS} = -14Dq - 7J_H$, and $E_{HS} = -4Dq - 10J_H$. Here $10Dq$ is the crystal field splitting between the t_{2g} and the e_g orbitals of the $3d$ states, and J_H is the Hund's rule exchange interaction that lowers the

energy of each pair of electrons with parallel spin. In the limit of small crystal field splitting, the system will be in the HS state. Upon increasing the crystal field interaction, both the LS and IS states lower their energies faster than the HS state, and at some critical value the HS state will no longer be the ground state. In this model, this will occur for $10Dq = 2J_H$, i.e. about 1.6 eV for a typical value of $J_H \cong 0.8$ eV. The ground state will become LS. Remarkable is that there is no value of $10Dq$ for which the IS state can be the ground state, i.e. the system is either HS or LS, but never IS. In a more accurate energy level scheme which includes the full atomic multiplet theory as outlined in the Sugano, Tanabe and Kamimura textbook, one will find that the HS-LS crossing occurs at $10Dq \cong 2.2$ eV. Also in this more sophisticated ionic picture the ground state of the system is either HS or LS, but never IS.

In the above ionic schemes in O_H symmetry, the IS reaches its minimum energy relative to the HS or LS ground state for the critical $10Dq$ value where the HS-LS crossing occurs, but this minimum energy is still appreciably higher than that of the ground state. *How to stabilize the IS state?* One could envision perhaps two distinctive scenarios. (1) Lowering the local symmetry such that the e_g levels are split: for example, by introducing a strong Jahn-Teller distortion of about 2.4 eV, one indeed can find that the IS state will be the ground state. (2) Band formation: Korotin *et al.* performed LDA+U calculations on LaCoO_3 and obtained a LS-IS crossing instead of a LS-HS one, assuming that both the IS and HS are ferromagnetic insulators. It is clear that it is difficult to find real materials which fulfill the conditions necessary for either of these two scenarios: a Jahn-Teller distortion of 2.4 eV is unrealistically large, and non of the cobaltates are

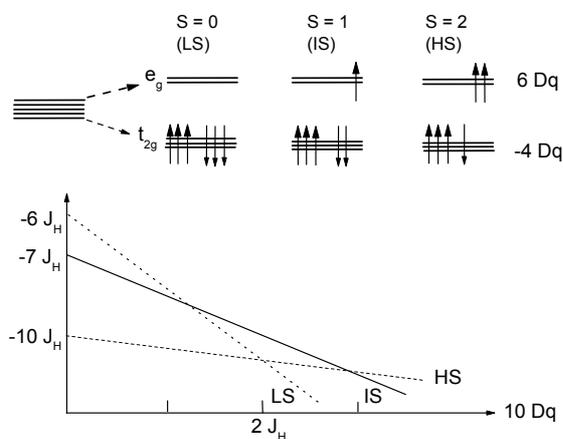


Fig. 1: Simplest ionic energy level diagram for a $3d^6$ system in O_H symmetry.

really insulating when they are in the ferromagnetic phase. Nevertheless, it is tempting to think that perhaps a combination of these two scenarios could help stabilize the IS state. It is therefore not surprising that in the recent literature the IS scenario is often invoked to explain the interesting properties of the newly synthesized layered cobalt perovskites. This even seems to be backed by band structure calculations, although doubts have been raised based on the more precise theoretical work of Wu.

The SAXS spectroscopy has been developed in the last 15 years into one of the most powerful techniques to investigate the local electronic properties of strongly correlated systems. Unique to SXAS is that the dipole selection rules are very effective in determining which of the final states can be reached and with what intensity, starting from a particular initial state. This makes the technique extremely sensitive to the symmetry of the initial state, i.e. the valence, orbital, and spin state of the ion.

In the last two years, we have carried out extensive experiments on a large variety of layered cobaltate materials. One of the most decisive measurements was the one on $\text{Sr}_2\text{CoO}_3\text{Cl}$. This is a relatively simple model compound, in which there are no spin state transitions present and in which there is only one kind of Co^{3+} coordination. Important is that this coordination is identical to the pyramidal CoO_5 present in the heavily debated layered perovskites. The claim made in the literature so far is that such pyramidal Co^{3+} ions are in the IS state, thought to be the result of the stabilization due to the combination of band formation and the presence of a strong low symmetry (Jahn-Teller) crystal field splitting associated with the pyramidal-coordination. However, the outcome of our measurements on this model system, as we will describe

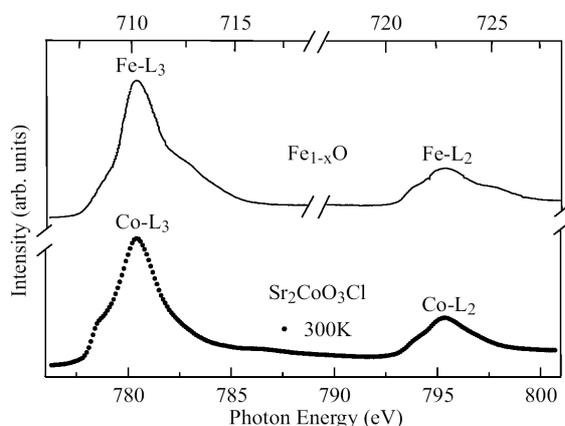


Fig. 2: $\text{Co-L}_{2,3}$ XAS spectrum of $\text{Sr}_2\text{CoO}_3\text{Cl}$ measured at 300 K. The $\text{Fe-L}_{2,3}$ XAS spectrum of Fe_{1-x}O ($x \leq 0.05$) reproduced from the thesis of J.-H. Park.

below, is quite different, and from this we infer that the spin states and their temperature dependence in layered cobalt perovskites may be very different in nature from those proposed in the recent literature.

Figure 2 shows the $\text{Co-L}_{2,3}$ SXAS spectrum of $\text{Sr}_2\text{CoO}_3\text{Cl}$ taken at room temperature. It is dominated by the Co 2p core-hole spin-orbit coupling which splits the spectrum roughly in two parts. 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. Utilizing the sensitivity of the spectra to the symmetry of the initial state, we compare the $\text{Co-L}_{2,3}$ SXAS spectrum of $\text{Sr}_2\text{CoO}_3\text{Cl}$ to that of another $3d^6$ compound, namely Fe_{1-x}O ($x \leq 0.05$), reproduced from the thesis of J.-H. Park. Except for the different photon energy scale and the smaller 2p core-hole spin-orbit splitting, the Fe_{1-x}O spectrum as shown in Fig. 2 is essentially identical with that of $\text{Sr}_2\text{CoO}_3\text{Cl}$. From this we can immediately conclude that the Co^{3+} ions in $\text{Sr}_2\text{CoO}_3\text{Cl}$ are in the HS state, since the Fe^{2+} ions are also unambiguously HS. Our conclusion contradicts clearly the IS assignment commonly made in the literature so far.

More spectroscopic evidence for the HS nature of the Co^{3+} in the pyramidal CoO_5 coordination can be found from the O K SXAS 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, La 5d, Co 4s and Cl 3p related bands. Fig. 3 also includes the O-K SXAS spectrum of LaCoO_3 at 20 K, i.e. in the LS state. One can see clearly that the spectrum of $\text{Sr}_2\text{CoO}_3\text{Cl}$ is different from that of LS LaCoO_3 , proving that $\text{Sr}_2\text{CoO}_3\text{Cl}$ is not a LS system. The LaCoO_3 spectrum also reveals significant changes with temperature which is due to the gradual crossover from a LS state to a IS or HS state at higher temperatures. This high sensitivity of the O-K SXAS to the spin state can be explained as follows. At low temperatures, the LS Co^{3+} has its t_{2g} shell completely occupied, so that only transitions to the higher lying empty e_g states are possible (see Fig.1 for a schematic energy level diagram). At higher temperatures, with part of the Co ions in the IS or HS state, the t_{2g} states becomes partially unoccupied, so that also transitions with lower energies are allowed. Thus the fact that $\text{Sr}_2\text{CoO}_3\text{Cl}$ has a lower energy structure indicates that it is in the HS $t_{2g}^4 e_g^2$ or IS $t_{2g}^5 e_g^1$ state.

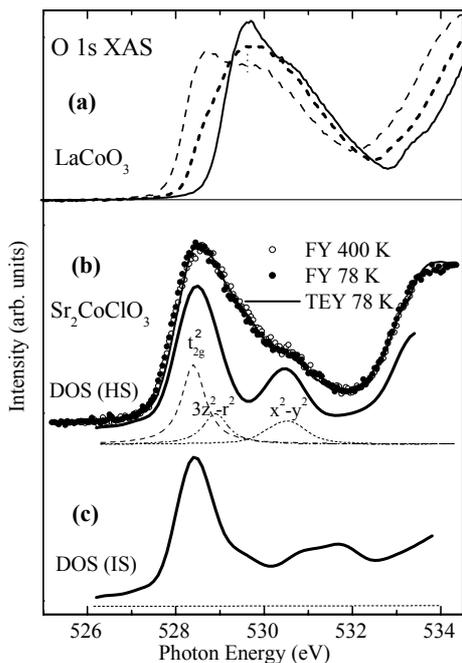


Fig. 3: (a) O-K XAS spectra of LaCoO_3 taken at 20 K (solid line); 300 K (short-dashed line) and 650 K (dashed line). (b) The $\text{Sr}_2\text{CoO}_3\text{Cl}$ spectra taken at 78 K (filled circles), 400 K (open circles). The solid line below the experimental curves of $\text{Sr}_2\text{CoO}_3\text{Cl}$ depict the LDA+U calculated unoccupied O 2p partial DOS for $\text{Sr}_2\text{CoO}_3\text{Cl}$ in the real crystal structure with the HS state. (c) The calculated unoccupied O 2p partial DOS in the IS state stabilized using an artificial crystal structure as described in the text.

To interpret the spectra, we have carried out LDA+U band structure calculations for $\text{Sr}_2\text{CoO}_3\text{Cl}$. 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(b), and good agreement with the experimental spectrum can be observed. From the calculations, we have found that the IS state is unstable with respect to HS ground state for the real crystal structure of $\text{Sr}_2\text{CoO}_3\text{Cl}$. 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 SXAS spectrum that well, as one can see from the discrepancies in the 531-532 eV range in Fig. 3(c). 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 about 0.33 \AA for the CoO_5 pyramid helps to stabilize the HS state, 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 \AA .

This HS finding is very important for the spin state issue in the newly synthesized layered cobaltates which show giant magnetoresistance, metal-insulator transition (MIT), spin-state transition, and orbital-ordering phenomena, since it was always assumed that the pyramidal coordinated Co^{3+} ions in these materials are in the IS state. More spectroscopic studies are underway and, in fact, have already revealed also surprises about the spin state of Co^{3+} ions in different local coordinations. The conclusion is certain that we have to go back to the drawing board to find a new explanation for the fascinating properties of these new layered cobaltates.

We greatly acknowledge the NSRRC staff for their continuous support and for providing us with a very stable beam. The research in Köln is supported by the Deutsche Forschungsgemeinschaft through SFB 608.

BEAMLINE

11A Dragon beamline

EXPERIMENTAL STATION

XAS chamber of the Universität zu Köln, Germany

AUTHORS

Z. Hu and L. H. Tjeng
II. Physikalisches Institut, Universität zu Köln,
Germany

H. Wu
Max-Planck-Institut für Physik Komplexer Systeme,
Dresden, Germany

H. H. Hsieh, H.-J. Lin, and C. T. Chen
National Synchrotron Radiation Research Center,
Hsinchu, Taiwan

PUBLICATIONS

• Z. Hu, H. Wu, M. W. Haverkort, H. H. Hsieh, H.-J. Lin, T. Lorenz, J. Baier, A. Reichl, I. Bonn, C. Felser, A. Tanaka, C. T. Chen, and L. H. Tjeng, Phys. Rev. Lett. **92**, 207402 (2004).

CONTACT E-MAIL

tjeng@ph2.uni-koeln.de