

Spin Blockade, Orbital Occupation, and Charge Ordering in $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$

Using Co-L_{2,3} and O-K X-ray absorption spectroscopy, we reveal that the charge ordering in $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$ involves high spin ($S=3/2$) Co^{2+} and low spin ($S=0$) Co^{3+} ions. This provides evidence for the spin-blockade phenomenon as a source for the extremely insulating nature of the $\text{La}_{2-x}\text{Sr}_x\text{CoO}_4$ series. The associated e_g^2 and e_g^0 orbital occupation accounts for the large contrast in the Co-O bond lengths and, in turn, the high charge ordering temperature. Yet, the low magnetic ordering temperature is naturally explained by the presence of the non-magnetic ($S=0$) Co^{3+} ions. From the identification of the bands we infer that $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$ is a narrow band material.

Considerable research effort has been put in cobaltate materials during the last decade in search for new phenomena and extraordinary properties. A key aspect of cobaltates, that distinguish them from e.g. the manganates and cuprates, is the spin state degree of freedom of the Co^{3+} 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 manganates and cuprates so exciting. Indeed, numerous cobaltate systems have been discovered with properties that include giant magnetoresistance, superconductivity and ferro-ferri-antiferro-magnetic transitions with various forms of charge, orbital and spin ordering. A new and exciting aspect in here is the recognition that the so-called spin-blockade mechanism could be present and responsible for several of those unusual properties.

Here we focus on the $\text{La}_{2-x}\text{Sr}_x\text{CoO}_4$ system, which shows quite peculiar transport and magnetic properties. This material is extremely insulating for a very wide range of x values with anomalously high activation energies for conductivity, very much unlike the Mn, Ni, or Cu compounds. Charge ordering (CO) and spin ordering (SO) at half doping involve quite different transition temperatures, namely $T_{\text{CO}} \sim 750$ K and $T_{\text{SO}} \leq 30$ K, respectively. This constitutes a ratio of 25, which is extraordinary since it is an order of magnitude larger than in the Mn and Ni materials.

Using soft X-ray absorption spectroscopy (XAS) we are able to show unambiguously that the Co^{3+} ions are in the LS ($S=0$) state, both below and above T_{SO} . Together with the verification that the Co^{2+} ions are HS ($S=3/2$), we establish that the spin-blockade mechanism is active. The highly insulating character of the material over a wide range of temperatures is thus explained. Important is that the associated e_g^0 and e_g^2 orbital occupation ordering leads to a large difference in the Co-O bond lengths and the high T_{CO} . At the same time, the low T_{SO} follows

Beamline

BL11A1 BM-(Dragon) MCD, XAS

Authors

C. F. Chang, Z. Hu, and L. H. Tjeng

II. Physikalisches Institut, Universität zu Köln, Germany



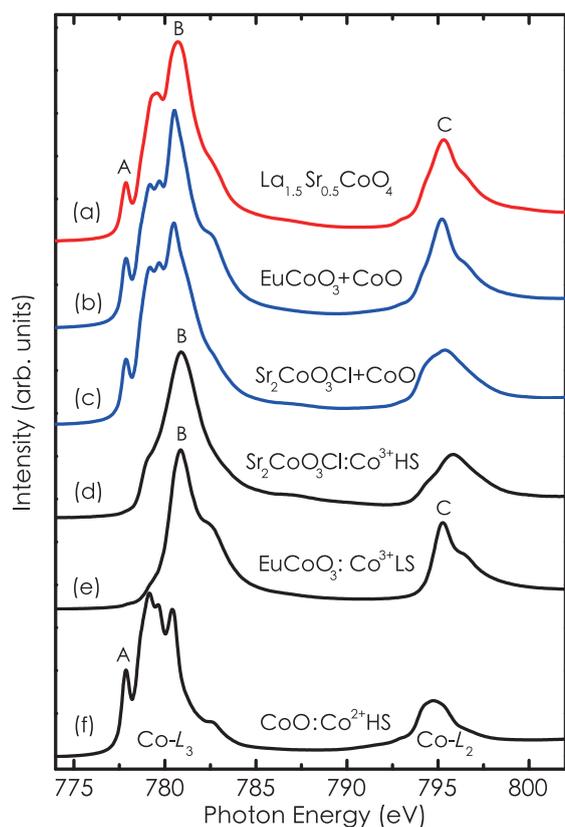


Fig. 1: Isotropic Co- $L_{2,3}$ XAS spectra of (a) $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$, (b) the HS-CoO plus LS- EuCoO_3 scenario, (c) the HS-CoO plus HS- $\text{Sr}_2\text{CoO}_3\text{Cl}$ scenario, (d) $\text{Sr}_2\text{CoO}_3\text{Cl}$, (e) EuCoO_3 , and (f) CoO , all taken at 300 K.

naturally from the presence of the truly nonmagnetic (NM) ($S=0$) Co^{3+} ions.^[1]

Figure 1 depicts the room temperature isotropic Co- $L_{2,3}$ XAS spectrum of $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$ together with those of $\text{Sr}_2\text{CoO}_3\text{Cl}$, EuCoO_3 , and CoO serving as the HS- Co^{3+} , the LS- Co^{3+} , and the HS- Co^{2+} references, respectively^[2]. The spectra of the reference samples show quite different multiplet structures. In particular, the lowest energy peak (A) of the CoO at 777.8 eV is characteristic for an octahedral Co^{2+} . Also very characteristic is the dominant peak (B) at 781 eV of a Co^{3+} ion. Compared to the HS $\text{Sr}_2\text{CoO}_3\text{Cl}$, the LS EuCoO_3 has a higher intensity at the L_2 edge with a rather sharp peak (C) at 795 eV. Focussing now on the $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$ spectrum, one can clearly observe, among others, the low energy peak (A), the dominant peak (B), and the spectral feature (C). This strongly hints towards the presence of not only Co^{2+} and Co^{3+} ions in this material, but especially that the Co^{3+} is LS. To verify this, we have

carried out a simple simulation by making a superposition of CoO and EuCoO_3 spectra and compare the result with the spectrum of $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$. We see from Fig. 1 (b) that the simulation is almost perfect. As a counter check, we also made a superposition of the CoO and $\text{Sr}_2\text{CoO}_3\text{Cl}$ spectra, and find it to be different from the spectrum of $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$, especially in the L_2 edge region.

In order to further confirm that the Co^{3+} ions are in the LS state, we have measured the polarization dependence of the Co- $L_{2,3}$ XAS of $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$ and have simulated the spectra using the successful configuration interaction cluster model that includes the full atomic multiplet theory and the hybridization with the O 2p ligands. The cluster model calculations were done using XTLS 8.3. Figure 2 (a) shows the experimental Co- $L_{2,3}$ XAS of $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$ taken with $E \parallel c$ (red) and $E \perp c$ (black). The experimental linear dichroic (LD) signal, defined as the difference between two polarizations, is displayed in the bottom panel (magenta), together with the simulated LD spectra (black) for the Co^{3+} ion in the (b) LS, (c) HS, and (d) IS state, respectively, while the Co^{2+} ion is kept in the HS. One can observe from the bottom panel that the LS- Co^{3+} scenario nicely reproduces all features of the experimental LD spectrum. In contrast,

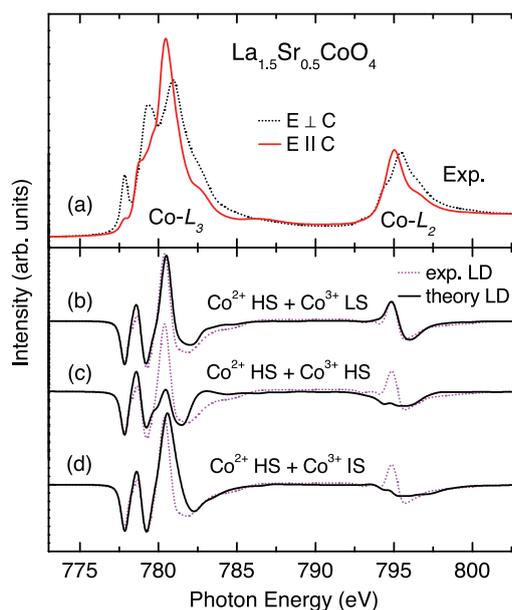


Fig. 2: (a) Experimental polarization-dependent Co- $L_{2,3}$ XAS of $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$ for $E \parallel c$ (red line) and $E \perp c$ (black dotted line); (b), (c), and (d) the experimental linear dichroism (magenta dotted lines) together with the theoretical one (black lines) calculated for scenarios with HS- Co^{2+} and LS-, HS-, or IS- Co^{3+} , respectively.

both the HS-Co³⁺ and the LS-Co³⁺ assumptions would lead to significant discrepancies, not only at the L_3 but also at the L_2 edge.

We have also verified that this LS ($S=0$) state is stable below T_{50} by using yet another spectroscopic method, namely the O-K XAS. The top panel of Fig. 3 (a) displays the isotropic spectra of $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$ taken at 300 K and 18 K. One can clearly see that the lineshape of the 529.5 eV pre-edge feature at both temperatures is very similar to that of EuCoO_3 , a reliable LS-Co³⁺ reference [2]. The temperature dependence, if any, is only a slight broadening.

The presence of LS-Co³⁺ ions provides a natural explanation for the rapid lowering of the T_{50} when doping La_2CoO_4 with Sr. The number of paths with strong superexchange interactions between the HS-Co²⁺ ions is simply reduced when NM Co³⁺ ions are introduced. It should therefore be of no surprise that the T_{50} drops from 275 K for La_2CoO_4 to only 30 K for $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$ in which the Co²⁺/Co³⁺ ions are checkerboard ordered.

The presence of LS-Co³⁺ ions in between HS-Co²⁺ is also exciting since it gives a beautiful explanation for the highly insulating behavior in $\text{La}_{2-x}\text{Sr}_x\text{CoO}_4$ despite the heavy doping. If one considers a pair of neighboring HS-Co²⁺ ($S=3/2$) and LS-Co³⁺ ($S=0$) ions, one can directly see that the hopping of a charge carrier will not result in an identical pair with just the charges interchanged. Instead, the pair created will have a completely different spin state configuration. Although such a hopping does not involve the Coulomb energy U , it does cost a significant amount of energy since the energy difference between a HS- and LS-Co²⁺ as well as between a LS- and IS-Co³⁺ could amount to several tenths of an eV. The hopping of charge carriers between these two types of Co ions is thus severely suppressed. This type of suppression of the conductivity is known as spin-blockade. We note that the spin-blockade mechanism is effective in $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$ both below and above the T_{50} since the LS state of the Co³⁺ is independent of the SO. This explains why the activation energies for the conductivity remain high even at elevated temperatures.

The spin state contrast, which goes along with the Co²⁺/Co³⁺ charge state, has also consequences for the stability of the CO. The orbital occupation of the HS-Co²⁺ is predominantly $t_{2g}^5 e_g^2$ while that of the LS-Co³⁺ is mainly $t_{2g}^6 e_g^0$, as we have verified from our cluster calculations. There is thus also an extremely strong e_g orbital occupation contrast. With the e_g orbitals pointing towards the oxygens and the t_{2g} in between this leads to significant differences in the local Co-O distances for the two different ions. This in turn causes strong localization and stabilization of the charge contrast, thereby explaining the very high $T_{\text{CO}} \sim 750$ K in $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$.

There is yet another aspect which makes this system to be highly insulating. For this we look in more detail at the energetics of the unoccupied states of the Co³⁺. Figure 3 (b) shows the polarization dependence of the O-K XAS. These interested states are located in the so-called pre-edge region between 528-531 eV. Using $E \parallel c$ light (solid line) we can reach the unoccupied O-2p_{xy}--Co-3d_{3z²-r²} hybridized band, and found it to be peaked at 529.3 eV. With $E \perp c$ light (dotted line), we see that the peak of the mixed O-2p_{xy}--Co-3d_{x²-y²} band lies 0.7 eV higher, at 530.0 eV. The lowest energy states at 528.5 eV are of almost pure 3z²-r² nature. These assignments are very well supported by the LDA+U calculations as shown with blue curves in Fig. 3 (b).

This is an important finding since it establishes that the conduction-band bottom is of 3z²-r² origin. The

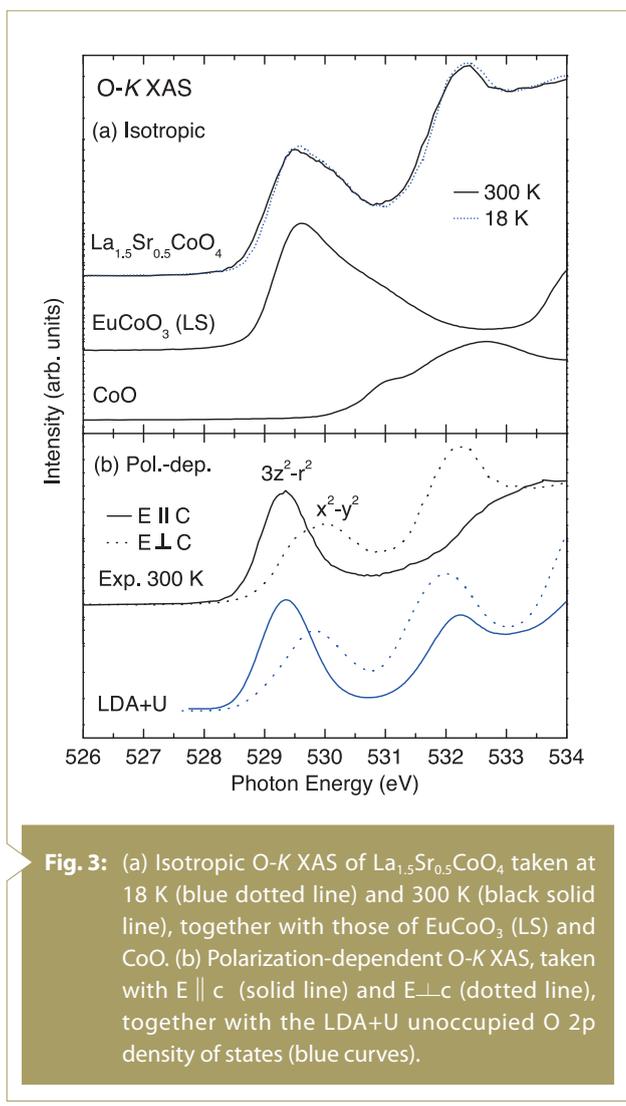


Fig. 3: (a) Isotropic O-K XAS of $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$ taken at 18 K (blue dotted line) and 300 K (black solid line), together with those of EuCoO_3 (LS) and CoO. (b) Polarization-dependent O-K XAS, taken with $E \parallel c$ (solid line) and $E \perp c$ (dotted line), together with the LDA+U unoccupied O 2p density of states (blue curves).

consequences are obvious: with the $3z^2-r^2$ orbital having much smaller overlap with the in-plane $O-2p_{x,y}$ ligands than the x^2-y^2 , the conduction band gets much narrower, with the result that the spin-blockade effect together with the strong coupling of the Co-O distances become the dominant interactions to make $La_{2-x}Sr_xCoO_4$ highly insulating over a wide range of x .

To summarize, we find using the Co- $L_{2,3}$ and O-K XAS that the charge ordering in $La_{1.5}Sr_{0.5}CoO_4$ involves high spin ($S=3/2$) Co^{2+} and low spin ($S=0$) Co^{3+} ions. We infer that the spin blockade mechanism is active here and that there is a strong coupling between the local Co-O distances and the charge/spin state of the ions. The crystal field scheme for the Co^{3+} ion caused by the tetragonal distortion makes the conduction band extremely narrow. All these factors provide an explanation for the highly insulating properties as well as for the very low T_{SO} and the exceptionally high T_{CO} .

This study has been done in collaboration with Hua Wu, T. Burnus, N. Hollmann, M. Benomar, T. Lorenz, A. Tanaka, H.-J. Lin, H. H. Hsieh, and C. T. Chen.

Experimental Station

X-ray Absorption Spectroscopy end station

Publications

1. C. F. Chang, Z. Hu, Hua Wu, T. Burnus, N. Hollmann, M. Benomar, T. Lorenz, A. Tanaka, H.-J. Lin, H. H. Hsieh, C. T. Chen, and L. H. Tjeng, Phys. Rev. Lett. **102**, 116401 (2009).
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Contacted E-mail

chang@ph2.uni-koeln.de