Spin blockade, orbital occupation and charge ordering in La$_{1.5}$Sr$_{0.5}$CoO$_4$

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Using Co-$L_{2,3}$ and O-$K$ x-ray absorption spectroscopy, we reveal 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. This provides evidence for the spin blockade phenomenon as a source for the extremely insulating nature of the La$_{2-x}$Sr$_x$CoO$_4$ series. The associated $e_g^0$ and $e_g^2$ 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 La$_{1.5}$Sr$_{0.5}$CoO$_4$ is a narrow band material.

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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 manganites and cuprates is the spin state degree of freedom of the Co$^{3+/4+}$ ions: it can be low spin (LS, $S=0$), high spin (HS, $S=2$) and even intermediate spin (IS, $S=1$) [2, 3]. 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 magneto resistance [4, 5], superconductivity [6] and ferro-anti-ferro-magnetic transitions with various forms of charge, orbital and spin ordering [7, 8, 9, 10, 11, 12, 13, 14]. 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 [13]. If true, this would open up new research opportunities since one could envision exploiting explicitly this mechanism in materials design.

Here we focus on the La$_{2-x}$Sr$_x$CoO$_4$ system, which shows quite peculiar transport and magnetic properties [15, 17, 18, 19, 20, 21, 22, 23, 24, 25]. 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 [1, 13, 26]. The commensurate antiferromagnetic (AF) state remains stable up to a surprisingly high value of $x=0.3$ [24, 25]. Charge ordering (CO) and spin ordering (SO) at half doping involve quite different transition temperatures, namely $T_{CO} \sim 750$ K and $T_{SO} \leq 30$ 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 [1, 21, 27].

It was already reported that the SO in the La$_{1.5}$Sr$_{0.5}$CoO$_4$ composition involves non-magnetic Co$^{3+}$ ions with the claim that these Co$^{3+}$ ions are in the IS state and become non-magnetic due to strong planar anisotropy driven quenching of the spin angular momentum below the $T_{SO}$ [21, 22]. Here we go one step further. 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 CO temperature. At the same time, the low SO temperature follows naturally from the presence of the truly non-magnetic ($S=0$) Co$^{3+}$ ions. Single crystals of La$_{1.5}$Sr$_{0.5}$CoO$_4$ have been grown by the travelling floating-zone method and characterized using magnetic and resistivity measurements [23]. The polarization dependent XAS experiments were performed at the Dragon beamline of the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. The Co-$L_{2,3}$ spectra were taken in the total electron yield (TEY) mode and the O-$K$ also in the fluorescence yield (FY) mode with a photon energy resolution of 0.3 and 0.2 eV, respectively. The degree of linear polarization of the incident light was $99\%$. The crystals were mounted with the c-axis perpendicular to the Poynting vector of the light. By rotating the sample around this Poynting vector, the polarization of the electric field can be varied continuously from $E \parallel c$ to $E \perp c$. The crystals were cleaved parallel to the c-axis in a vacuum of $10^{-10}$ mbar.

Fig. 1 depicts the room temperature isotropic Co-$L_{2,3}$ XAS spectra of La$_{1.5}$Sr$_{0.5}$CoO$_4$ together with those of Sr$_2$CoO$_4$Cl, EuCoO$_3$, and CoO serving as the HS-Co$^{3+}$, the LS-Co$^{3+}$, and the HS-Co$^{2+}$ references, respectively [28]. The spectra are dominated by the Co 2$p$ core-hole
spin-orbit coupling which splits the spectrum roughly in two parts, namely the $L_3$ ($h \nu \approx 776$-$784$ eV) and $L_2$ ($h \nu \approx 793$-$797$ eV) white lines regions. The line shape strongly depends 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 sensitive in determining which of the 2$p^53d^{n+1}$ final states can be reached and with what intensity, starting from a particular 2$p^63d^n$ initial state ($n = 6$ for Co$^{3+}$ and $n = 7$ for Co$^{2+}$) [29, 30]. This makes the technique extremely sensitive to the symmetry of the initial state, i.e., the spin, orbital and valence states of the ions.

The spectra of the reference samples show quite different multiplet structures with peaks at quite different energies. In particular, the lowest energy peak (A) of the CoO at 777 eV can be taken as a characteristic for the presence of an octahedral Co$^{3+}$ ion since it has an energy well below that of any Co$^{3+}$ or Co$^{4+}$ (not shown here) features. Also very characteristic is the dominant peak (B) at 781 eV of a Co$^{2+}$ ion. In comparing the spectrum of EuCoO$_3$ with that of Sr$_2$CoO$_3$Cl, one can, for example, notice that the LS Co$^{3+}$ ion has a higher intensity at the $L_2$ edge with a rather sharp peak (C) at 795 eV. Focussing now on the La$_{1.5}$Sr$_{0.5}$CoO$_4$ spectrum, one can clearly observe, among others, a low energy peak (A) at 777 eV, a dominant peak (B) at 781 eV, and a sharply peaked $L_2$ edge (C) at 795 eV. 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 the as-measured CoO and EuCoO$_3$ spectra and compare the result with the spectrum of La$_{1.5}$Sr$_{0.5}$CoO$_4$. We see from Fig. 1 that the simulation is almost perfect. As a counter check, we also made a superposition of the CoO and Sr$_2$CoO$_3$Cl spectra, and observe noticeable discrepancies between this superposition and the spectrum of La$_{1.5}$Sr$_{0.5}$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 La$_{1.5}$Sr$_{0.5}$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$^{3+}$ and LS-, HS-, or IS-Co$^{3+}$, respectively. The calculated linear dichroism for the HS-Co$^{2+}$, LS-, HS-, and IS-Co$^{3+}$ is also shown individually in (e), (f), (g), and (h).
O 2p transfer integrals were adapted for the various Co-O bond lengths [37] according to Harrison’s prescription [38]. The crystal field parameters were determined from constrained density-functional calculations using the linearized augmented plane wave plus local orbital method [39] and the electron-correlation corrected local-density-approximation (LDA+U) [40]. The cluster model calculations were done using XTLS 8.3 [30].

The top panel of Fig. 2(a) shows the experimental Co-K-edge XAS of La$_{1.5}$Sr$_{0.5}$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 middle 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 middle panel that the LS-Co$^{3+}$ scenario nicely reproduces all features of the experimental LD spectrum. In contrast, the HS-Co$^{3+}$ assumption would lead to significant discrepancies, not only at the L$_3$ but also at the L$_2$ edge. Also the IS-Co$^{3+}$ scenario gives less than satisfactory fit to the experimental spectrum; the L$_2$ edge structure cannot be reproduced at all. More insight can be gained from the lower panel of Fig. 2 in which the calculated LD spectra are individually depicted. The Co$^{2+}$ LD spectrum (e) shows only a modest modulation at the L$_2$ edge, and so does the HS-Co$^{3+}$ (g) and the IS-Co$^{3+}$ (h) as well. Only the LS-Co$^{3+}$ (f) displays the strong LD modulation as experimentally observed for the L$_2$ region.

So far the spin-state issue in the La$_{2-x}$Sr$_x$CoO$_4$ system has been addressed using magnetic susceptibility [16, 17, 18, 23] or NMR measurements [20], with conflicting results: all three possible scenarios (HS, IS, LS) have been proposed for the Co$^{3+}$ ion. Interestingly, neutron scattering experiments have revealed the presence of non-magnetic Co ions in the SO state of La$_{1.5}$Sr$_{0.5}$CoO$_4$ [21]. Yet it was claimed that these Co$^{3+}$ ions are in the LS state and that they become non-magnetic as a result of the quenching of the spin angular momentum due to the strong planar anisotropy in the SO state [21, 22].

Our XAS data yield new and crucial information. The Co$^{3+}$ ions are indeed non-magnetic, but because of a completely different reason: they are in the LS (S=0) state. The XAS data were taken at room temperature, i.e. above $T_{SO}$. We expect that this LS (S=0) state is also stable below $T_{SO}$. We have verified this using yet another spectroscopic method, namely the O-K XAS. The top panel of Fig. 3(a) displays the isotropic spectrum of La$_{1.5}$Sr$_{0.5}$CoO$_4$ taken at 300 K and 18 K. These spectra were taken in the FY method to avoid charging problems which otherwise could occur at low sample temperatures when using the TEY. 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-Co$^{3+}$ reference [28]. The temperature dependence, if any, is only a slight broadening with increasing temperature, and certainly not the massive change of the spectral lineshape (over a range of $\approx 1$ eV) as reported for LaCoO$_3$ in going from the low-temperature non-magnetic to the high-temperature paramagnetic state [31].

The presence of LS-Co$^{3+}$ ions provides a natural explanation for the rapid lowering of the $T_{SO}$ when doping La$_2$CoO$_4$ with Sr. The number of paths with strong superexchange interactions between the HS-Co$^{2+}$ ions are simply reduced when non-magnetic Co ions are introduced. It should therefore be of no surprise that the $T_{SO}$ drops from 275 K for La$_2$CoO$_4$ to a low 30 K for La$_{1.5}$Sr$_{0.5}$CoO$_4$ in which the Co$^{2+}$/Co$^{3+}$ ions are checkerboard ordered.

The presence of LS-Co$^{3+}$ ions in between HS-Co$^{2+}$ is also exciting since it gives a beautiful explanation for the highly insulating behavior in La$_{2-x}$Sr$_x$CoO$_4$ despite the heavy doping. If one considers a pair of neighboring HS-Co$^{2+}$ (S=3/2) and LS-Co$^{3+}$ (S=0) ions, then 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: the hopping of a spin 1/2 particle will produce a IS-Co$^{3+}$ (S=1) and LS-Co$^{2+}$ (S=1/2) final state. 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-Co$^{2+}$ as well as between a LS- and IS-Co$^{3+}$.
could amount to several tenths of an eV [2]. The hopping of charge carriers between these two types of Co ions is thus severely suppressed. This type of suppression of the conductivity, known as spin-blockade, has been proposed to explain the thermoelectric power of HoBaCo$_2$O$_{5.5}$ [13]. We note that the spin-blockade mechanism is effective in La$_{1.5}$Sr$_{0.5}$CoO$_4$ both below and above the $T_{SO}$ since the LS state of the Co$^{3+}$ 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 Co$^{2+}$/Co$^{3+}$ charge state, has also consequences for the stability of the CO. The orbital occupation of the HS-Co$^{2+}$ is predominantly $t_{2g}^2e_{g}^2$ while that of the LS-Co$^{3+}$ is mainly $t_{2g}^0e_{g}^0$, as we have verified from our cluster calculations. There is thus also an extremely strong $e_g$ orbital occupation contrast, even when taking into account that the LS-Co$^{3+}$ is more covalent than the HS-Co$^{2+}$ [11]. 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, as indeed revealed by diffraction experiments [21, 24, 25]. This in turn causes strong localization and stabilization of the charge contrast, thereby explaining the very high $T_{CO} \sim 750$ K in La$_{1.5}$Sr$_{0.5}$CoO$_4$.

There is yet another aspect which makes this system to be highly insulating. For this we look in more detail to the energetics of the unoccupied states of the Co$^{3+}$. The bottom panel of Fig. 3(b) shows the polarization dependence of the O-K XAS. Here we are mainly interested in the lowest lying states, i.e. the unoccupied states of the Co$^{3+}$ which can be reached when an electron is transferred from a neighboring Co$^{2+}$. These states are located in the so-called pre-edge region between 528-531 eV [31]. Using $E || c$ light (solid line) we can reach the unoccupied O-2$p_{x,y}$-Co-3$d_{x^2,y^2}$ 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-2$p_{x,y}$-Co-3$d_{x^2,y^2}$ band lies 0.7 eV higher, at 530.0 eV. The lowest energy states at 528.5 eV are of almost pure $3z^2-r^2$ nature. These assignments are very well supported by the LDA+U calculations: not only the larger intensity of the $3z^2-r^2$ (solid line) in comparison to that of the $x^2-y^2$ state (dotted line) is reproduced but also the relative energy positions.

This is an important finding since it establishes that the band available for conduction, namely the one with the lowest energy, is of $3z^2-r^2$ origin. This is very different from the cuprate, nickelate and manganate systems, where the relevant band is formed out of the $x^2-y^2$ orbital. The consequences are obvious: with the $3z^2-r^2$ orbital having much smaller overlap with the in-plane O-2$p_{x,y}$ 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 with the charge/spin state of the Co ions become the dominant interactions to make La$_{2-x}$Sr$_x$CoO$_4$ highly insulating over a wide range of $x$.

We note that the observed and calculated 0.7 eV energy shift between the $3z^2-r^2$ (solid line) and the $x^2-y^2$ (dotted line) states in Fig. 3(b) reflects the large tetragonal distortion of about 10% [37]. This large crystal field splitting in the $e_g$ orbital is in fact the cause for the strong modulation in the LD spectrum at the $L_2$ edge for the LS-Co$^{3+}$ ion as depicted in the bottom panel of Fig. 3 curve (f): without such an energy splitting which is felt by the electron promoted from the Co 2$p$ core, one would not observe any dichroism in the otherwise highly symmetric, closed-shell $t_{2g}^2$ ground state.

To summarize, we find using soft x-ray absorption spectroscopy at the Co-$L_{2,3}$ and O-$K$ edges 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 $T_{CO}$.

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