

Title: Charge and magnetic orders in single-layer transition-metal oxides: an insight from XAS, XES and REXS

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Complex transition-metal oxides belong to the class of multifunctional materials with coupled magnetic, structural, orbital and charge orderings giving rise to unconventional properties. Among them, insulator-to-metal transitions continue to be a challenging subject, especially when electronic correlations are strong and the transition-metal atom has a mixed valence state. This is the case of $\text{La}_{2-x}\text{A}_x\text{BO}_4$ (A=Sr or Ca, B=Mn, Co, Ni, Cu) Ruddlesden-Popper perovskites (RPP). All of them crystallize in the tetragonal $I4/mmm$ symmetry but different properties are observed depending on the mixed valence transition-metal atom. The Mn-based RPP also exhibit charge ordered (CO) phases with enhanced complexity due to the orbital degrees of freedom of Mn^{3+} ions in their antiferromagnetic phases whereas in the Co-based RPP, the observed charge and spin orderings were determined to be related to the spin state of the Co^{3+} ions.

Experimentally, the doping-induced electronic changes can be examined by means of x-ray absorption spectroscopy (XAS) and resonant elastic x-ray scattering (REXS) at the transition-metal K edges, which probe the unoccupied 3d states indirectly via the 4p states but are also sensitive to structural distortions. Complementary to these techniques, K-shell x-ray emission spectroscopy (XES) provides access to the occupied density of electronic states.

In this talk, we present our research on the CO phases in the isostructural $\text{La}_{1-x}\text{Sr}_{1+x}\text{MnO}_4$ ($x \leq 0.5$) and $\text{La}_{2-x}\text{Ca}(\text{Sr})_x\text{CoO}_4$ ($0 \leq x \leq 1$) series by a combination of the above mentioned synchrotron radiation techniques. In the Mn-based RPP, the CO phase for $x \leq 0.5$ is well described by a bimodal distribution of $\text{Mn}^{3.5-\delta}$ and $\text{Mn}^{3.5+\delta}$ ions with the charge disproportionation $\delta = 0.15 e^-$ [1, 2] while for $x > 0.5$, an incommensurate sinusoidal charge-density-wave is obtained [3]. Polarization-dependent XAS study at the Mn K-edge shows that the Mn local structure is anisotropic according to the tetragonal distortion of the MnO_6 octahedron in the layered structure. This anisotropy is also observed in the appearance of linear dichroism of the Mn $K\beta$ main lines that is strongest for $x=0$ and decreases with increasing hole doping joint to an inversion of the spectral line shape [4]. However, the Mn $K\beta$ main lines of polycrystalline samples remain almost unchanged upon hole doping. We thus conclude that the total charge and spin density on Mn atoms change very little so the holes are mainly localized on the oxygen lattice and the hole doping causes a spatial redistribution of the 3d electron density from the c-axis into the ab-plane. On the other hand, the same checkerboard ordering of only two

Co sites is maintained for $0.4 \leq x \leq 0.7$ in the Co-based RPP and the average charge disproportionation is relatively high ($\sim 0.5 e^-$) [5]. Polarization-dependent XAS study at the Co K-edge also shows an anisotropic Co local structure according to the tetragonal layered structure similar to the Mn-based compounds but in this case, a very weak linear dichroism has been found in the Co K β main lines for all samples. The Co K β main lines of polycrystalline samples also changes very little for $x \leq 0.7$. We thus conclude that the total charge and spin density at the Co sites change very little with hole doping and the 3d electron density is rather symmetric with respect to the *ab*-plane and *c*-axis because the average Co valence is modulated by the oxygen stoichiometry.

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