

Title: Charge superstructure in single-layered $\text{La}_{2-x}\text{Ca}_x\text{CoO}_{4+\delta}$ ($0.4 \leq x \leq 0.7$) studied by resonant x-ray scattering

Joaquín García (1), Gloria Subías (1), Javier Blasco (1), M. Concepción Sánchez (1) and Guillaume Beutier (2)

(1) Instituto de Ciencia de Materiales de Aragón, CSIC-Universidad de Zaragoza, Zaragoza, Spain

(2) Université Grenoble Alpes, CNRS, Grenoble INP, SIMAP, Grenoble (France)

jgr@unizar.es

Hole-doped $\text{La}_{2-x}\text{Ca}_x\text{CoO}_{4+\delta}$ single-layered perovskites undergoes structural phase transitions with decreasing temperature due to the rich interplay between charge, spin, orbital and lattice degrees of freedom. These structural transitions are coupled to an electronic localization due to the nominal fractional valence of the Co atoms resulting in charge superstructure. In this work, we propose a model for the Co charge superstructure in the single-layered $\text{La}_{2-x}\text{Ca}_x\text{CoO}_{4+\delta}$ ($0.4 \leq x \leq 0.7$) perovskites based on the photon energy, azimuth angle and polarization dependence of the scattered intensity of selected reflections measured in a resonant x-ray scattering experiment.

Room temperature resonant x-ray experiments at the Co K-edge we carried out at the BM02-D2AM beam line at the ESRF. Single crystals were cut with the surface perpendicular to the $[1, 1, 0]_t$ direction for $\text{La}_{2-x}\text{Ca}_x\text{CoO}_{4+\delta}$ (0.4, 0.5 and 0.6) whereas $\text{La}_{1.3}\text{Ca}_{0.7}\text{CoO}_{3.9}$ was cut along the $[0, 0, 1]_t$ direction. An empirical analysis of the resonant data, once corrected for self-absorption, was carried out by the experimental determination of the resonant atomic scattering factor tensor. Theoretical simulations of the resonant reflections were also carried out by the FDMNES code to estimate the magnitude of the local structural distortions associated with the charge disproportionation.

Tetragonal superlattice ($h/2, h/2, l$)-type reflections were detected for all the samples independently from the Ca content in agreement with a checkerboard ordering of two different Co sites. The corresponding average charge disproportionation results in about $0.5 \pm 0.1 e^-$. No forbidden ($h/4, h/4, l$)-type reflections were observed at room temperature indicating the lack of any local anisotropy ordering in contrast with the behavior found in the single-layered manganites. Finally, we found the pattern of small distortions ($\sim 0.05 \text{ \AA}$) of the alternating expanded and compressed CoO_6 octahedra compatible with the resonant x-ray scattering results. The symmetry of this displacement pattern is consistent with the $A2mm$ (or $Ammm$) orthorhombic structure of the ordered phase and the structural transition is accounted for by the condensation of two soft modes $-X_1^+(B_{2u})$ and $X_1^+(A_1)$ — acting on the oxygen atoms.

Thus, the single-layered $\text{RE}_{1.5}\text{A}_{0.5}\text{TMO}_4$ (RE=rare earth, A=Ca, Sr and TM=Mn, Ni, Co) perovskites show a common checkerboard ordering of two non-equivalent TM atoms associated to two distinct valence states. However, compared to $\text{La}_{1.5}\text{Sr}_{0.5}\text{MnO}_4$, where the maximum charge disproportionation is about $0.15 e^-$, the charge disproportionation (or the compression/expansion of the oxygen octahedra) in the single-layered cobalt oxides is relatively high ($\sim 0.5 e^-$). This is understood by the fact that charge superstructures (driven by concomitant structural transitions) appears at much higher temperatures (well above room temperature) in the layered cobalt oxides than in the layered manganites ($T_{\text{CO}} \sim 230 \text{ K}$).