ESRF	**Experiment title:** Determination of the charge disproportionation and order sequence in $La_{2-x}Sr_xCoO_4$ ($0.4<x<0.6$) by resonant x-ray scattering.	**Experiment number**: HC1954
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Report:

The coupled order of charge and magnetic degrees of freedom in layered transition-metal oxides have attracted much attention due to its possible important role in their magnetic and electrical properties such as colossal magnetoresistance in manganites, stripe ordering in nickelates and high-temperature superconductivity in cuprates. In analogy with these systems, it appears interesting to investigate the possible existence of stripe ordering phases in $La_{2-x}A_xCoO_4$ with A=Sr or Ca. In the doping range $0.4\leq x\leq 0.6$, charge ordered phases have been reported in $La_{2-x}Sr_xCoO_4$ by neutron scattering at high temperature (~825 K), totally independent of spins, which only orders below 40 K [1]. However, the complete structural and charge disproportionation analysis has not been performed because of the occurrence of broad diffuse superstructure peaks. On the other hand, superstrutcure reflections at (*h*/2, *h*/2, 0) (indexed in the high-temperature tetragonal *I*4/*mmm* phase) were observed in a $La_{1.5}Ca_{0.5}CoO_4$ single crystal with correlation lengths nearly five times longer than those of Sr system by neutron and resonant x-ray scattering (RXS) [2]. Although a full charge disproportionation of Co^{2+} and Co^{3+} within a checkerboard order was concluded, only a qualitative analysis of the RXS data was performed.

We have then performed the complete (energy, azimuth angle and polarization dependencies) RXS study at the Co K-edge in a $La_{1.5}Ca_{0.5}CoO_4$ single crystal and two single crystals of the Sr system ($La_{1.5}Sr_{0.5}CoO_4$ and $La_{1.4}Sr_{0.6}CoO_4$) at room temperature. The main objectives of this study were I) the quantitative characterization of the checkerboard charge ordering in the half-doped cases in order to determine the exact magnitude of the charge disprorportionation between the Co atoms; II) the investigation on the occurrence of anisotropic tensor scattering (ATS) reflections as found in related manganites [3] and III) the determination of the type of commensurate/incommensurate charge ordering that takes place for $x<0.5$ and $x>0.5$.

The two half-doped single crystals show RXS at (3/2, 3/2, 0) and (5/2, 5/2, 0) reflections confirming the presence of an alternating checkerboard pattern in their charge ordered phases. Figure 1 shows the energy depedence of superstructure reflection (3/2, 3/2, 0) for $La_{1.5}Sr_{0.5}CoO_4$ (fig. 1a) and $La_{1.5}Ca_{0.5}CoO_4$ (fig. 1b) as a function of the azimuthal angle, that is a rotation of the sample around the scattering vector. We observe scattered intensity at energies below the Co K edge, which comes from atomic displacements out of the *I*4/*mmm* symmetry (Thomson scattering). Besides, a strong resonance is observed at energies close the Co K

edge in the σ-σ' polarization channel. This enhancement comes from the difference between the anomalous atomic scattering factor of Co atoms located in different crystallographic sites. The azimuthal dependence of the RXS intensity is consistent with the large anisotropy between the *c*-axis and the *ab*-plane, characteristic of these single-layered perovskites. By comparison $La_{1.5}Sr_{0.5}CoO_4$ with $La_{1.5}Ca_{0.5}CoO_4$, we find sharper and more intense peaks for the Ca-doped compound whereas weak diffuse peaks are observed for the Sr-doped one, as shown in the insets of figure 1. This result confirms the long-range chekerboard charge order in $La_{1.5}Ca_{0.5}CoO_4$, while the correlation length is much shorter in $La_{1.5}Sr_{0.5}CoO_4$ suggesting that charge order can be controlled by A site ion radius in layered cobaltates.

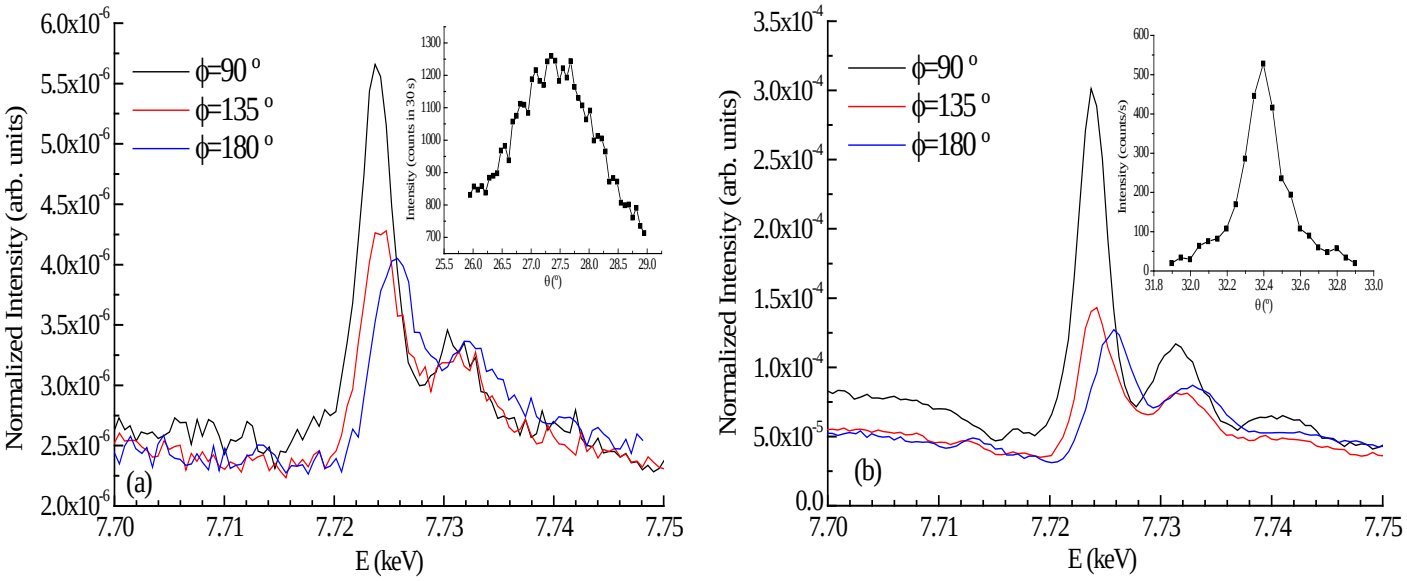

Figure 1. Energy dependence of the RXS intensity of the (3/2, 3/2, 0) reflection in the σ-σ' polarization channel for different azimuthal angles in (a) $La_{1.5}Sr_{0.5}CoO_4$ and (b) $La_{1.5}Ca_{0.5}CoO_4$. The insets show the longitudinal scans of the (3/2, 3/2, 0) reflection at the Co K edge for the Sr and Ca single crystals, respectively.

The complete RXS study has been then carried out in the $La_{1.5}Ca_{0.5}CoO_4$ sample. First, we also observe RXS intensity at the (3/2, 3/2, 1) reflection, indicating that our crystal has the twin structure in the low temperature orthorhombic phase, the orthorhombic *a* and *b* axes are superposed. We have searched for forbidden (*h*/4, *h*/4, 0) reflections but they were not detected in either the σ-σ' or the σ-π' polarization channels. In contrast to the single-layered $La_{1.5}Sr_{0.5}MnO_4$ manganite [3], no strong local anisotropy of the CoO_6 octahedron is expected. In order to determine the magnitude of the charge disproportionation between the two distinct Co sites, the calculation of the energy dependence of the structure factors for the various observed resonant reflections is in progress. We recall here that a reliable calculation implies the use of correct Thomson terms fixed by the distortions of low temperature orthorhombic phase.

Finally, we have searched for the corresponding charge order peaks in the $La_{1.4}Sr_{0.6}CoO_4$ single crystal. Neither commensurate (*h*/2, *h*/2, 0) peaks nor incommensurate (*h*/2±0.1, *h*/2±0.1, 0) peaks were detected. The fact that we were unsuccesful in detecting resonant superstructure peaks in $La_{1.4}Sr_{0.6}CoO_4$ can be understood in terms of the weak diffuse scattering already observed in $La_{1.5}Sr_{0.5}CoO_4$ and taking into account that the correlation lengths for concentrations away from half-doping are even more reduced. To clarify this point, the future study of the charge ordered phases in both, underdoped (x<0.5) and overdoped (x>0.5) $La_{2-x}Ca_xCoO_4$ single crystals by resonant x-ray scattering at the Co K-edge is planned.

References

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