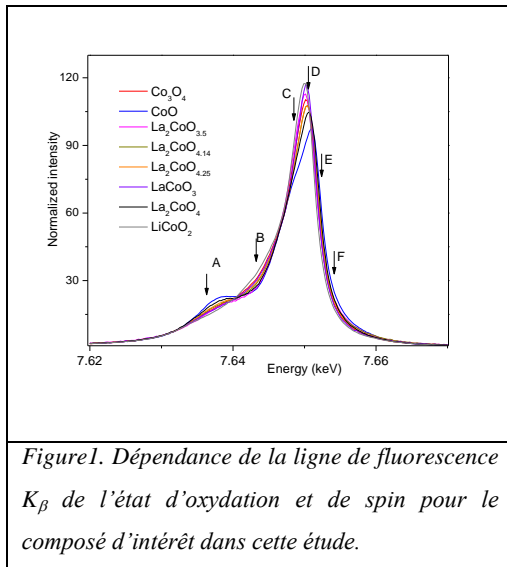


Spin selective EXAFS study of $\text{La}_2\text{CoO}_{4.25}$ by the use of fluorescence high resolution energy detection

In the wide range of stoichiometry shows that the series $\text{La}_2\text{CoO}_{4+\delta}$ the compound with maximum oxidation ($\delta = 0.25$) has a special role from a structural and magnetic point of view.



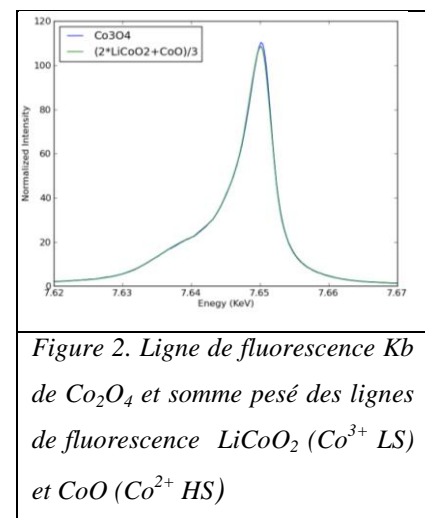
In order to obtain structural information on the local distortions induced by doping, we selectively studied the local structure of atoms Co^{3+} and Co^{2+} using the chemical sensitivity of high-energy resolution fluorescence detection (HERFD) at emission line K_β . Indeed HERFD detection of K_β line fluorescence showed a clear dependence on the oxidation states and spin of 3d transition metals, which allows the study of inorganic compounds (Fig. 1)

For the mixed valence compound $\text{La}_2\text{CoO}_{4.25}$, the emission line K_β can be reasonably represented by the sum of two emission lines of two reference compounds, representing both sites correctly.

For cobalt can be seen in Figure 2 that the two main effects on the shape and position of the transmission line is the oxidation state and spin while the local structure is negligible.

This stoichiometry corresponds to the presence in the crystal $\text{Co}^{3+}(d^6)$ in configuration $S=0$ non-magnetic low-spin (LS) and $\text{Co}^{2+}(d^7)$ in configuration $S=3/2$ and at high spin (HS).

Although both Cobalt ions are very different, oxygen doping does not produce two distinctly different crystallographic sites. The two oxidation states of Co are available on the same crystallographic sites which makes it indistinguishable from the effects of oxygen doping on the local structure of Co atoms hosting an interstitial oxygen in their coordination spheres.



The emission line K_b Co_2O_3 (composed by 2/3 of sites by octahedral Co^{3+} LS and a third of sites tetrahedral Co^{2+} HS) is in very good agreement with the weighted sum of the two compound with a octahedral local environment: LiCoO_2 Co^{3+} LS and CoO (Co^{2+} HS).

Thus recording EXAFS spectra for different positions of the emission line (positions A, B, C, D, E, F of Figure 1) we have obtained spectra more or less sensitive to species Co^{2+} or Co^{3+} . With the information of contrasts between the two sites, obtained by refinement of the emission line by mathematical convolution, we reconstructed the spectra for both components (Fig. 3).

Although the mathematical model of reconstruction is still not perfect for the amplitudes at low energy, a first qualitative analysis gives reasonable informations, the ions Co^{2+} (spin up) have an average distance larger than the Co^{3+} ions and a minor number of oxygen in their coordination sphere. More surprisingly the second coordination sphere of Co^{3+} ion is more distorted than commonly thought in the literature showing a strong distortion of the local structure by oxygen doping. These results are important to understand the chemical origin of superlattice peaks found in diffraction experiments on single crystals

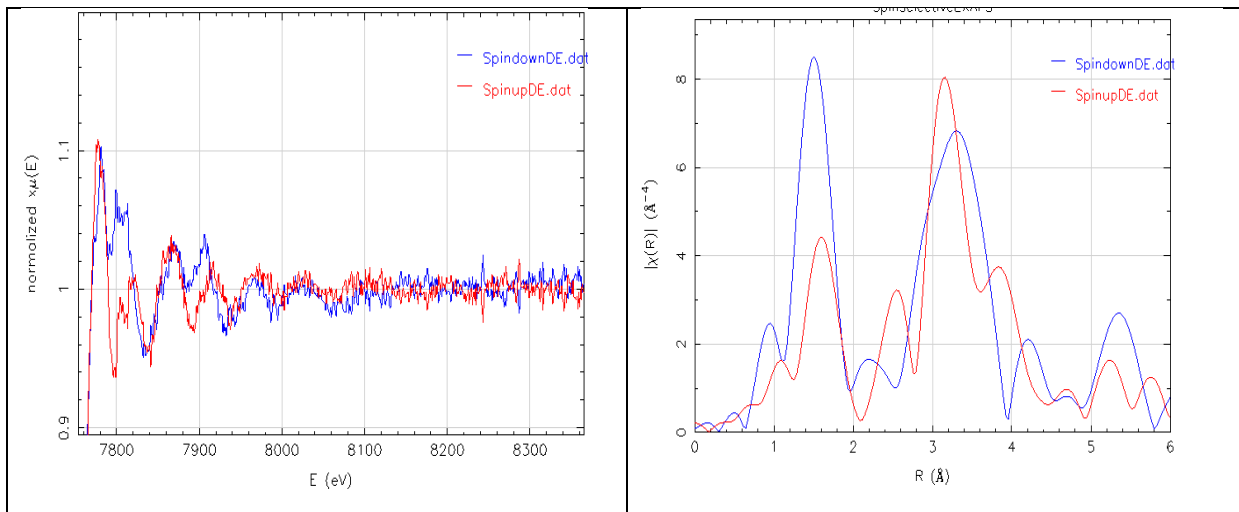


Figure 3. Spin sélective EXAFS obtenu entre le couple de points DE de la Fig. 3 (à gauche le signal brut et à droite la transformée de Fourier). En rouge les lignes correspondent au spin up et en bleu au spin down.