



	<b>Experiment title:</b> Probing the multiferroic nature of $\text{CaBaCo}_4\text{O}_7$ by x-ray absorption spectroscopy.	<b>Experiment number:</b> HC1594
<b>Beamline:</b>	<b>Date of experiment:</b> from: 23/09/2014 to: 28/09/2014	<b>Date of report:</b> 20/02/2015
<b>Shifts:</b>	<b>Local contact(s):</b> Vera Cuartero	<i>Received at ESRF:</i>
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## Report:

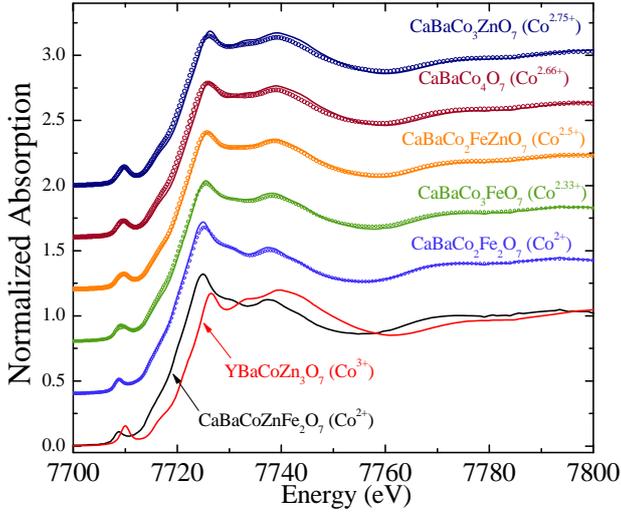
$\text{CaBaCo}_4\text{O}_7$  (CBCO) is an orthorhombic cobaltite (space group  $Pbn2_1$ ), ferrimagnetic below  $T_c=70\text{K}$  [1] and is suggested to be FE below this temperature as well [2]. The mechanism promoting FE has not been fully clarified yet, although a magnetic driven FE is proposed because no structural phase transition is observed across  $T_c$  by neutron diffraction experiments [1]. The crystallographic structure of  $\text{CaBaCo}_4\text{O}_7$  consists of triangular (T) and kagomé (K) layers of  $\text{CoO}_4$  tetrahedra along  $c$  axis. There are four different sites for Co: Co1 stays at the T layer, while Co2, Co3, and Co4 are in the K layers [1].

We have performed XANES and EXAFS measurements as a function of temperature at the Co K edge on this compound and in several doped compounds such as  $\text{CaBaCo}_{4-x}\text{M}_x\text{O}_7$  ( $x=1,2$ ; M: Zn, Fe), aiming to determine whether there is a correlation between magnetoelastic effects and FE in  $\text{CaBaCo}_4\text{O}_7$ . In addition, Fe and Zn K edge spectra were recorded for the doped compositions.

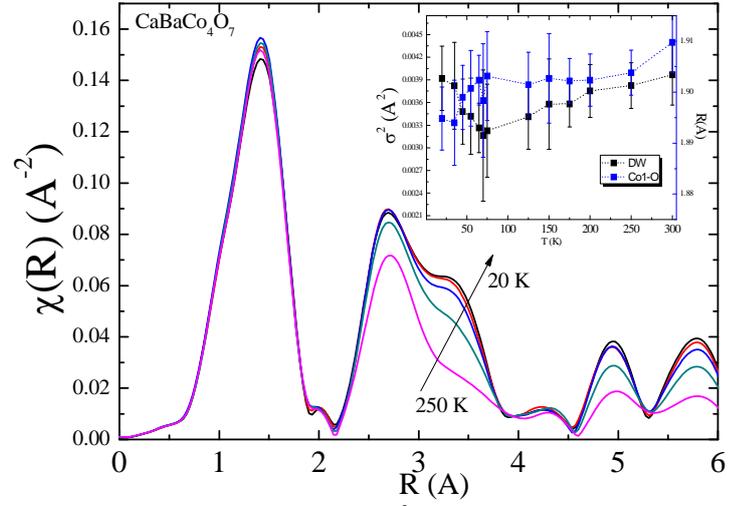
XANES spectra at the Co K edge are shown for all the compositions in figure 1, together with 2 reference spectra for  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$  on a tetrahedral environment. XANES spectra were normalized to unity edge jump using the Athena software from the Demeter package. In order to test the nature of the valence state of Co, a weighted average sum of the reference spectra according to the nominal Co oxidation state is presented on figure 1. The valence state considered for Co is the one obtained by considering the shift of the edge and its linear relation with the chemical shift. The agreement is quite good on the energy range presented, which suggests that a bimodal distribution of  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$  might describe the electronic structure of the compounds. The XANES spectra at the Fe and Zn K edges do not show any shift on the edge (not shown in here), meaning the oxidation state of Fe and Zn is the same along the dilution, being 3+ and 2+ respectively according to the measured references.

The extraction of the  $\chi(k)$  signals were also performed using Athena program, and R-space EXAFS spectra were obtained by calculating the Fourier Transform (FT) of the  $k^2\chi(k)$  signals in the  $(2.5-14.5) \text{ \AA}^{-1}$   $k$ -range. Figure 2 shows the FT of the  $k^2$ -weighted EXAFS signals of the parent compound CBCO, at selected temperatures, above and below the transition temperature ( $T_c=70\text{K}$ ). The magnitude of the FT spectra of all samples show a main peak at  $\sim 1.4 \text{ \AA}$  corresponding to the first (Co-O) coordination shells without phase

shift correction. The intensity of this peak slightly increases when lowering the temperature down to  $\sim 70$  K. Below that temperature, the first peak is less intense when decreasing temperature, indicating that there might be structural local changes below  $T_c$  on Co-O distances.



**Fig. 1.** Comparison between the measured spectra (points) and the calculated weighted average spectra of  $\text{Co}^{3+}$  ( $\text{YBaCoZn}_3\text{O}_7$ ) and  $\text{Co}^{2+}$  ( $\text{CaBaCoZnFe}_2\text{O}_7$ ) according to the nominal oxidation state (column 1 on table I) (lines). The reference spectra are plotted on the bottom part of the graph.



**Fig. 2.** Fourier transform of the  $k^2$  weighted EXAFS signal at  $T=250, 125, 70, 45$  and  $20$  K. Inset: temperature evolution of  $\sigma^2$  and Co1-O distance.

The spectra were fitted on the R-space using a sine window between 1 and 2 Å ( $\delta R=0.3$ ). Four Co-O distances were considered for each Co site on the 1<sup>st</sup> shell, considering then 4 crystallographic sites for Co (4 FEFF calculations). The inset of Fig. 2 plots  $\sigma^2(T)$  (Co-O peak) as a function of temperature,  $\sigma$  the width of the Co-O pair distribution function, together with one of the Co-O distances, which shows the same evolution as the other three distances (not shown here). There is a progressive decrease of  $\sigma^2$  with temperature down to approximately  $T_c=70\text{K}$ , mainly attributed to the decrease of thermal disorder. Below  $T_c$ ,  $\sigma^2$  shows a clear increase, pointing to a possible scenario where local symmetry-breaking distortions can be present in every unit cell above  $T_c$ , but randomly oriented, whereas below  $T_c$  the distortions order so that the average Co-O distances are no longer regular, but coherently distorted. Besides, all Co-O mean distances show a contraction below  $T_c$ , coinciding with the  $\sigma^2$  increase, as shown on the inset of figure 2.

In addition, there are noticeable changes on the intensity of the peaks corresponding to further shells, corresponding to Co-Co, Co-O, Co-Ba and Co-Ca, so that the influence of Co-Ba/Co-Ca distances needs to be considered for further more detailed analysis.

## References.

- [1] V. Caignaert et al., Phys Rev. B **81**, 094417 (2010).