



	Experiment title: Reaction mechanism of the oxygen intercalation in SrCoO_{2.5} by in situ XAFS techniques	Experiment number: CH-1492
Beamline: BM29/BM01B	Date of experiment: from: 23/04/2003 to: 25/04/2003 from: 26/06/2003 to: 01/07/2003	Date of report: 03/03/2004
Shifts: 15 + 6	Local contacts: Simone De Panfilis and Wouter van Beek	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

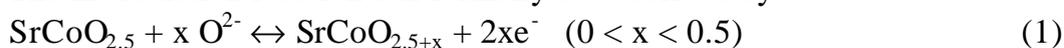
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We have investigated the intercalation of oxygen into SrCoO_{2.5} with brownmillerite type structure on BM 29 and BM01B. One aim was to follow the evolution of the Co oxidation state as a function of the charge transfer. The reaction has been carried out *in situ* in an electrochemical cell operating with extremely thin SrCoO_{2.5} working electrodes under galvanostatic conditions. To optimise the EXAFS signal, collected in transmission mode, special extra thin (less than 30 μm) working electrodes have been ad hoc prepared and tested in our lab prior to the experiment at the ESRF. In this regard we kindly thank Simone De Panfilis who allowed us to do a first test 4 weeks before the experiment. The intercalation reaction can formally be described by:



The Co is purely Co³⁺ for the starting compound whereas Co⁴⁺ is achieved for the final reaction product. The reaction has been followed in situ by XAS techniques, as shown in Fig.1a for the FT of the EXAFS signal. The EXAFS and XANES spectra of the starting (x = 0) and final (x = 0.5) phases has been optimized first. Then each intermediate spectrum has been reconstructed as a linear combination of the two defined phases, without fixing the sum of the phases to 1.0. The results are reported in Fig.1b (left axis), while Fig.1c shows that the sum of the phases lies within 0.98 and 1.02, with the only exceptions of three points which are related to the filling of the electrolyte (which implies an abrupt increase of the overall absorption of the sample). The right axis of Fig.1b reports the shift of the edge position, which correlates well with the evolution of the oxidized fraction as estimated by both XANES and EXAFS data. A close inspection of the data of Fig.1b, does not show a continuous evolution of the Co oxidation state but two different steps were observed. The first covers the continuous formation from SrCoO_{2.5} to SrCoO_{2.7} while the second starts from SrCoO_{2.8} to give the fully oxidized SrCoO₃ phase. Around SrCoO_{2.75 ± 0.05} a plateau is observed leading to the assumption that around this charge transfer a “stand-by” of the Co oxidation takes place. From parallel in situ neutron diffraction on D20 (ILL, Grenoble) we know that for this charge transfer region an ordered intermediate phase occurs yielding weak superstructure reflections due to oxygen ordering [1-3]. This intermediate phase, which has been supposed to be a deficient cubic perovskite phase, could be identified on BM01B (ESRF) to be weakly tetragonal. This fact, most evidenced by the splitting of the (h00) reflections (see Fig.2 for h=2), has been extremely important for developing a model concerning the intercalation reaction mechanism. On

this basis we were able to develop a structural model for $\text{SrCoO}_{2.75}$ with tetragonal symmetry, which consists in the formation of CoO_6 bi-pyramidal units interconnected by a common oxygen atom in the native CoO_4 tetrahedral layers. From the analyzed EXAFS/XANES spectra (Fig.1b) we may now conclude that the oxidation state of the bridging oxygen atom of the bi-pyramidal units is not O^{2-} but is somehow shifted towards O. This would imply that, for stoichiometries around $x = 0.25$, a charge transfer to the oxygen and not to the cobalt conduction band occurs during the electrochemical oxidation. A feature that, in turns, would imply that this oxygen sub-band is energetically higher than the cobalt band, in the $\text{SrCoO}_{2.75}$ intermediate phase. A complete paper reporting diffraction (both neutrons and x-rays) and absorption (both XANES and EXAFS) data has recently been submitted [3]. Ab initio simulations with periodic codes have been started.

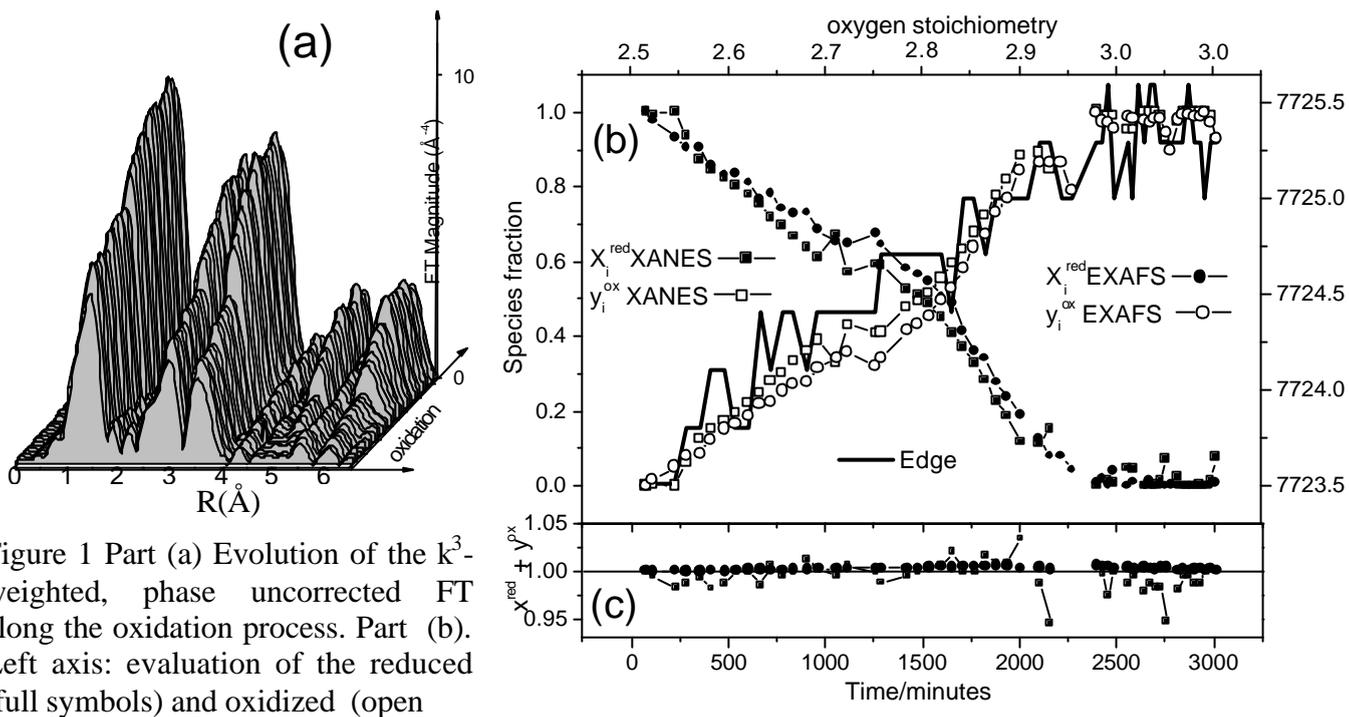


Figure 1 Part (a) Evolution of the k^3 -weighted, phase uncorrected FT along the oxidation process. Part (b). Left axis: evaluation of the reduced (full symbols) and oxidized (open

symbols) phases as obtained from the XANES (squares) and EXAFS (circles) data analysis. Right axis: shift of the edge position, which correlates well with the evolution of the oxidized fraction as estimated by XANES and EXAFS data. Part (c) sum of the oxidized and reduced fractions (symbols as in part b).

[1] R. Le Toquin, W. Paulus, A. Cousson, ILL 5-25-70 experimental report.

[2] R. Le Toquin, W. Paulus, A. Cousson, W. Treutmann, O. Hernandez, award for the best contribution in chemistry/physics at the Colloque de Association Française de la Cristallographie, Caen 7-10 July 2003.

[3] R. Le Toquin, W. Paulus, A. Cousson, C. Prestipino, C. Lamberti, J. Am. Chem. Soc. (2004) submitted.

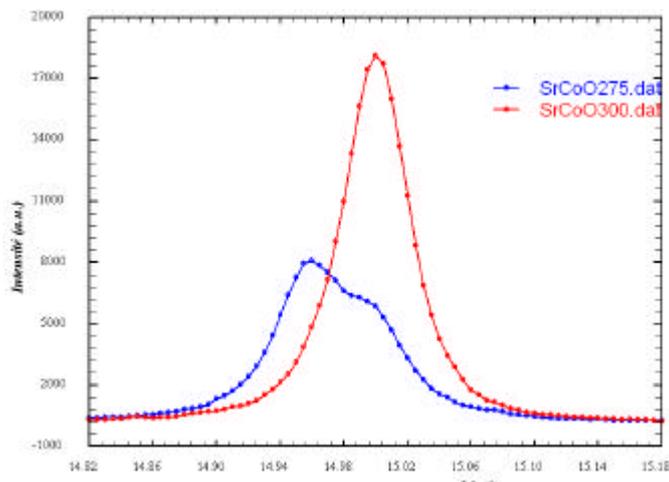


Figure 2: (200) reflection obtained on BM01B for the $\text{SrCoO}_{3.0}$ cubic and $\text{SrCoO}_{2.75}$ phases. The splitting of the (200)/(020) and (002) reflections reflects the lowering of the symmetry in the $\text{SrCoO}_{2.75}$ case.