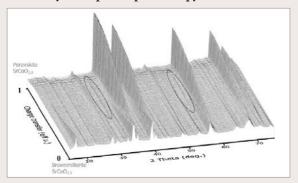
[C5. R. Le Toquin] Time-resolved in situ studies of oxygen intercalation into SrCoO_{2.5}, performed by neutron diffraction and X-ray absorption spectroscopy



Evolution of the neutron powder diffraction pattern obtained in situ during the electrochemical oxidation of $SrCoO_{2.5}$ vs charge transfer. The diffractogram of the brownmillerite $SrCoO_{2.5}$ is represented at the bottom, whereas that of the perovskite $SrCoO_{3.00}$ is shown at the top. The dotted ellipsoids show the positions of the superstructure reflections.

Electrochemical oxidation of the antiferromagnetically ordered $SrCoO_{2,5}$, with brownmilleritetype structure, to the cubic ferromagnet SrCoO₃, with perovskite structure, has been investigated in situ by neutron diffraction as well as by X-ray absorption fine structure (XAFS) spectroscopy in specially designed electrochemical cells. The neutron diffraction experiments were performed twice, using two different wavelengths of 1.2921(2) and 4.74 Å, in order to better discriminate structural and magnetic changes as functions of the charge transfer. From the neutron diffraction experiments, two intermediate phases, SrCoO_{2.75} and SrCoO_{2.82}(0.07), were characterized. No superstructure reflections were observed for the corresponding SrCoO_{2.75} phase. Instead we observed here, for the first time, 3D oxygen ordering during an oxygen intercalation reaction, as established for $SrCoO_{2.82}(0.07)$, which can be described as a tetragonal unit cell, related to the perovskite cell by a = 2(ax2) and c = 2a. The structure of this intermediate phase confirms the strongly topotactic character of the oxygen intercalation reaction. We were also able to prove, from in situ XAFS spectroscopy at the Co absorption edge, that the evolution of the Co valence state from formally +3 for $SrCoO_{25}$ to +4 for the final

reaction product $(SrCoO_{3.0})$ does not proceed continuously but gives evidence for the formation of O- species for stoichiometries corresponding to $SrCoO_{2.82}(0.07)[1]$. The use of neutrons (vs X-rays) in the diffraction experiments and the choice of the transmission (vs fluorescence) mode in the XAFS experiment guarantee that the obtained data well represent bulk and not just surface properties.

[1] R. Le Toquin, W. Paulus, A. Cousson, C. Prestipino, C. Lamberti, JACS 128 (2006) 13161-13174

[Collaboration : R. Le Toquin, W. Paulus, Université de Rennes 1, A. Cousson, LLB, C. Prestipino, C. Lamberti, Université de Turin]

[C6. V. Paul-Boncour] Structural and magnetic properties of RMn2D6 compounds (R=Y, Dy, Er) synthesized under high deuterium pressure

Hydrogen absorption in RMn₂ Laves Phases (R= Rare Earth) modifies significantly their magnetic properties. For x £ 4.5, the RMn₂H_x hydrides crystallize in a structure derived from that of the parent intermetallic, with H atoms in tetrahedral interstitial sites. Applying a hydrogen pressure of several MPa to YMn₂ led to the formation of YMn₂H₆ [1]. According to X-ray (XRD) and neutron powder (NPD) diffraction experiments, YMn₂D₆ crystallizes in a disordered fluorite structure (K₂PtCl₆ type) with a =6.709(1) Å at 300 K (Fig. 1). In the Fm3m space group, the Y and half of the Mn atoms (Mn1) occupy randomly the 8c site whereas the remaining Mn atoms (Mn₂ in 4a site) are surrounded by 6 H atoms (24e site). This structure is not derived from that of the C15 YMn₂ and the H atoms form covalent bonding with Mn atoms. RMn2D6 phases, isostructural to YMn2D6, were also obtained starting either from C15 (R =Dy, Ho) or C14 (R=Er) Laves phases. YMn2D6 displays a modified Curie Weiss behaviour and the NPD study shows the absence of long range magnetic order. The M(H) curves of the RMn₂D₆ compounds (R=Ho, Dy and Er) at 4.2 K show a ferromagnetic behaviour but the saturation magnetization is only half that of the parent compound. NPD studies on ErMn₂D₆ [2] revealed only local magnetic order of Er moment below 5 K, with ferro and antiferromagnetic correlations (Fig. 2). This has been related to the chemical disorder of R and Mn atoms on the 8c site. [1] V. Paul-Boncour, S. M. Filipek, M. Dorogova, et al. J. Sol. State Chem., 178 (2005) 356

[2] V. Paul-Boncour, S. M. Filipek, G. André, F. Bourée et al., J. Phys. : Cond. Mat., 18 (2006) 6409

[Collaboration: V. Paul-Boncour, LCMTR Thiais; S.M. Filipek (Poland), G. André, LLB ; F. Bourée LLB]

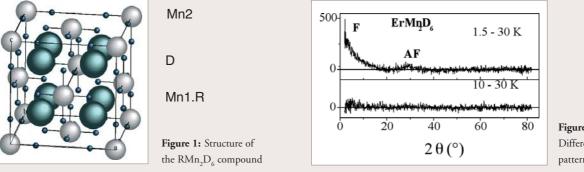


Figure 2: Difference NPD patterns of ErMn₂D₆