ESRF

Experiment title:
Crystal structure of the perovskite based compounds LnBaCo2O5.5 and LaBaCo_2O_6, (Part I)

Experiment number:
1.01.233

Beamline:
Bm1b

Date of experiment:
from: 17/07/2000 to: 18/07/2000

Date of report:
2/03.2002

Shifts:
3

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Report:

This report concerns the “$LaBaCo_2O_6$“ part of the original proposal, which has been divided in two measurement sessions. This compound is one particular case of the more general system $\mathit{Ln}BaCo_2O_{5+d}$ (*Ln*= lanthanide, $0 <= d <= 1$) we are investigating since two years, using different techniques (neutron and synchrotron powder diffraction, electron diffraction, magnetic measurements, …) [1]. The main interest of this series of compounds resides in their rich variety of electronic and magnetic properties depending on the oxygen content *d*, or equivalently, the oxidation state of the Co ions. For example, in $\mathit{Ln}BaCo_2O_5$ (*Ln*=Ho, Tb, Dy), we have evidenced charge ordering of the Co^{2+} and Co^{3+} species below ~210K [1,2]. In $LaBaCo_2O_6$, we could expect a charge ordering of the Co^{4+} and Co^{3+} ions which is not the case as shown below.

The crystal structure of $LaBaCo_2O_6$ (or equivalently $La_{0.5}Ba_{0.5}CoO_3$) at room temperature is very simple since it adopts the ideal perovskite structure of cell parameter a_p=3.8843 A. (space group Pm-3m). This structure means first of all that both La and Ba ions are statistically distributed on the body center site, whereas Co ions are embedded at the center of the regular octahedron formed by its six neighboring oxygen ions.

Below T_C~180K, the Co moments order in a ferromagnetic structure. From previous high resolution neutron powder diffraction measurements performed at 2K on D2B (ILL), we noticed the splitting of the (004/400) reflection indicating a possible phase transition from Pm-3m to P4/mmm.

This result has been confirmed by the actual BM1B measurements (Fig.1) and additional ones done on BM16 more recently (in-house research). Furthermore, synchrotron experiments clearly indicated the crystal transition to coincide with the Curie temperature T_C~180K. (Fig. 2)

This lowering of crystal symmetry is interpreted as a Jahn-Teller (JT) induced long-range ferrodistortive structure of the CoO_6 network resulting from $d_{3z^2-r^2}$ orbital ordering. The JT effect appears to be favored by a simple electronic configuration picture involving intermediate spin-states, $t^5_{2g}e^1_g$ and $t^5_{2g}e^1_g\underline{L}$, for the Co^{3+} (d^6) and Co^{4+} (d^5) species occurring in the structure.

The present results have been recently published and more details can be obtained from Ref. [3].

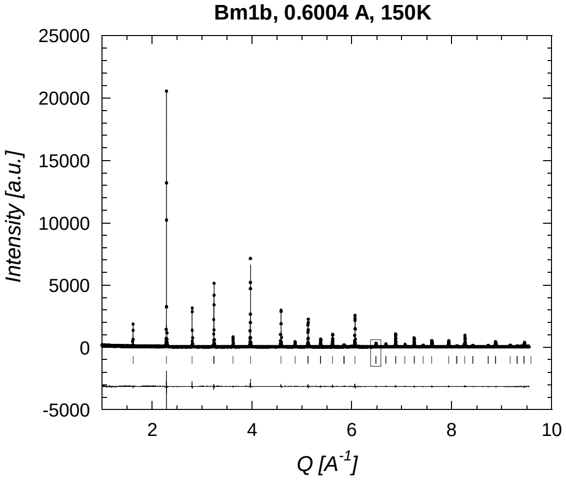

Fig.1: Observed and calculated patterns (P4/mm model) of $La_{0.5}Ba_{0.5}CoO_3$ collected at 150K on Bm1B (l=0.6004 A). The rectangle indicates the 004/400 reflections for which we see the splitting as best (see Fig. 2).

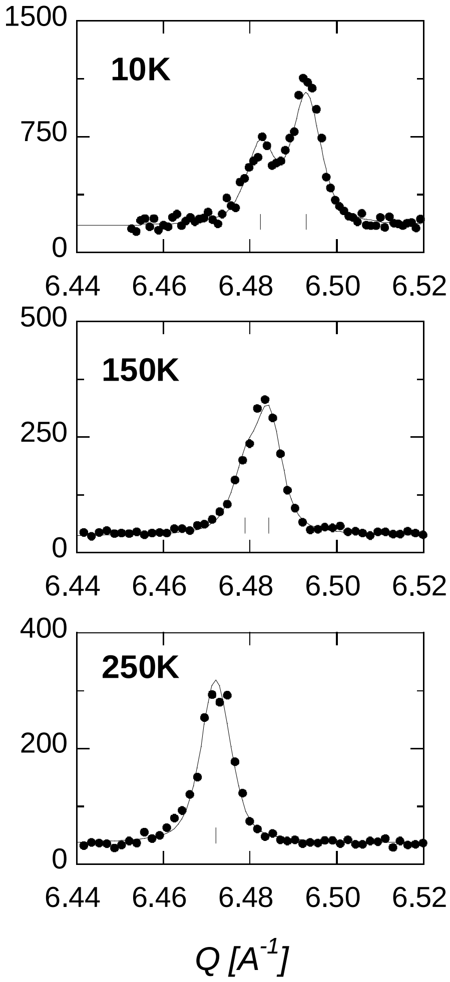

Fig.2: 004/400 reflection measured on BM1B at selected temperatures

[1] Fauth *et al*, Eur. Phys. J. B**21** (2001) 163

[2] Suard *et al*, Phys Rev. B**61** (2000) R11871

[3] Fauth *et al*, Phys Rev. B**65** (2002) 06040(R)