ESRF	**Experiment title:** Crystrallographic structure of layered perovskite-based $NdBaCo_2O_{5+\delta}$ ($0 < \delta < 1$)	**Experiment number**: He1164
Beamline: Bm16	**Date of experiment**: from: 10/02/2002 to: 14/02/2002	**Date of report**: 04/03/2003
Shifts: 12	**Local contact(s)**: F. Fauth	*Received at ESRF:*

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Report:

The aim of the experiment was to precisely determine, using synchrotron powder diffraction (SPD) techniques, the crystallographic structure of the layered perovskite-based series $NdBaCo_2O_{5+\delta}$ ($0< \delta < 1$) and relate it to the fascinating magnetic and transport properties displayed by this material (e.g, magnetoresistivity for δ~0.5 [1], charge ordering for δ=0 [2]). The interest of these compounds resides first of all in the possibility to tune the Co valency (and thus the electronic configuration) with the oxygen content according to the formula : Co^{2+}:Co^{3+}=(1/2-δ):(1/2+δ) for $0.5 \leq \delta$, Co^{3+}:Co^{4+}=(δ-1/2):(3/2-δ) for $\delta \leq 0.5$.

The actual experiment was conducted together with neutron powder diffraction (NPD) measurements performed at the ILL on the same compounds. The measured compounds, as well as some of their properties, are given in Table I. Data were collected on powders enclosed in Ø=0.5mm glass capillaries at λ=0.354483 Å (slightly below the Ba K-edge) to minimize absorption. The nitrogen gas cryostream and L_{He} cryostat were used to collect data in temperature domains 100K-375K and 10-100K, respectively.

The NPD data were of course mainly intended to determine the magnetic structure of the Co ions, but also to accurately determine the oxygen content and localisation. On the other hand, SPD data were particularly used in the study of the $0.3 < \delta < 0.7$ compounds which exhibit a doubled unit cell compared to the oxygen deficient and oxygen rich ones (Fig. 1).

Moreover, the *Ln*$BaCo_2O_{5+\delta}$ with δ~0.5 are known to exhibit metal-insulator transition at a T_{MI} ranging from 290 to 360 K depending on the rare earth ion (e.g. T_{MI}(Nd)~360K, T_{MI}(Y)~290K). From SPD measurements, we observed a cell parameter anomaly at T_{MI} (shrinking of *b* and *c*, expansion of *a* upon cooling) (Fig. 2). In agreement with magnetic susceptibility measurements, this structural anomaly at T_{MI}, implying Co-O bond lengths anomaly as well, is perfectly interpreted as an associated spin-state transition of selected Co^{3+} ions (only those in octahedral environment). However, the exact character of the spin-state transition still remains unclear. Based on similar experiments performed on BM16 on $GdBaCo_2O_{5.5}$, Frontera *et al.* [3] concluded to a spin-state transition from high-spin (HS: $t^4_{2g}e^2_g$) to low-spin (LS: $t^6_{2g}e^0_g$). Whereas we observed qualitatively the same crystallographic behavior at T_{MI} in our $NdBaCo_2O_{5.47}$ compound, we had however to challenge the Frontera's scenario since it appears incompatible with the Co ions magnetic structure derived from our NPD experiments. Based on combined NPD and SPD data, we concluded to a first order spin-state transition of all Co^{3+} from HS to intermediate-spin state (IS: $t^6_{2g}e^0_g$) at T_{MI}, followed by a gradual crossover of Co ions in octahedral environment from IS to LS state when further cooling down. Details on the crystallographic and magnetic structure of the $NdBaCo_2O_{5.47}$.compound have been published in Phys. Rev B (see Ref. 4). Actually, we are achieving the manuscript preparation describing the crystallographic and magnetic structure of the other measured $NdBaCo_2O_{5+\delta}$ ($0< \delta < 1$) compounds.

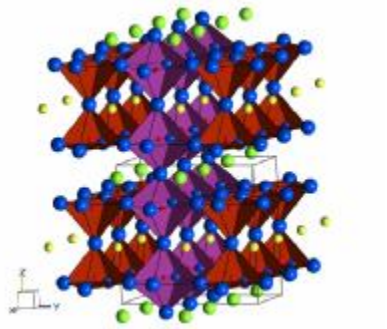

Fig. 1 Crystal structure of nominal *Ln*$BaCo_2O_{5.5}$

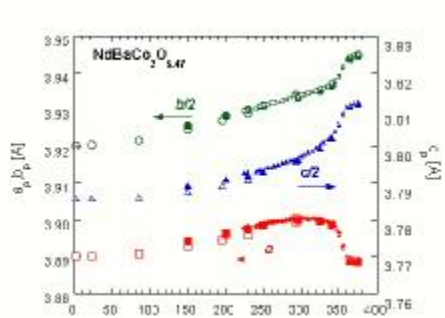

Fig 2 Thermal dependence of cell parameters in *Nd*$BaCo_2O_{5.47}$

Table I : Selected parameters of the measured samples

	Cell parameters at RT	**Transport properties and MI transition as obtained from cell parameter anomaly**
$NdBaCo_2O_{5.15}$	3.9352 * 3.9410 * 7.5766	Insulating over full measured T
$NdBaCo_2O_{5.38}$	3.9009 * 7.8699 * 7.5836	MI at 365 K
$NdBaCo_2O_{5.47}$	3.9011 * 7.8677 * 7.5945	MI at 350 K
$NdBaCo_2O_{5.57}$	3.8982 * 7.8570 * 7.5965	MI at 320 K
$NdBaCo_2O_{5.70}$	3.9041 * 7.7979 * 7.6090	MI at 270 K
$NdBaCo_2O_{5.85}$	3.8859 * 3.8884 * 7.6330	Metallic

[1] C. Martin *et al.*, Appl. Phys. Lett. 71 (1997) 1421
[2] F. Fauth *et al.*, Eur. Phys. J. B 21 (2001) 163 + reference therein
[3] C. Frontera *et al.*, Phys. Rev. B 65 (2002) 180405 (R)
[4] F. Fauth *et al.*, Phys. Rev B 66 (2002) 184421