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- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Probing nanoscale structural inhomogeneities in $GdBaCo_2O_{5+\delta}$ by means of the real space analysis of high resolution X-ray powder diffraction	**Experiment number**: HE-3241
Beamline: ID31	**Date of experiment**: from: 28/10/2009 to: 02/11/2009	**Date of report**: 24.02.2010
Shifts: 15	**Local contact(s)**: Dr. Adrian Hill	*Received at ESRF:*

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Report:

The magneto-resistance (MR) property in oxides containing perovskite building blocks is one of the central issues in condensed matter physics both for scientific and technological interest. Recently in order to clarify the MR mechanisms the layered cobalt oxides $GdBaCo_2O_{5+\delta}$ (hereafter GBCO) has been considered as a model system **[1]**.

GBCO displays a large variety of magnetic and transport properties as a function of T and excess oxygen concentration δ **[1]**. In order to account for the co-presence of several magnetic phases as a function of *T*, Taskin et *al.* inferred monophasic domains only for δ=0, 0.5 compositions, while intermediate compositions always tend to phase separate at the nanoscopic scale **[1]**.

The purpose of experiment HE-3241 was to map the local, medium and long structure of $GdBaCo_2O_{5+\delta}$ as a function of δ and T using Pair Distribution Function technique.

Polycrystalline $GdBaCo_2O_{5+\delta}$ samples was prepared by conventional solid state reaction in air. According to TGA measurements five aliquots of the *as prepared* sample were annealed in order to obtain δ=0.0, 0.10, 0.25, 0.37, 0.5, 0.60 respectively.

X-ray powder diffraction (XRPD) patterns were collected covering a Q_{max}~28Å^{-1} (λ=0.35422(1) Å) at the diffraction range $0<2\theta<110°$. XRPD data quality for experimental G(*r*) have been obtained summing 16 scans (~7 hours total measuring time) collected at fixed *T* for δ=0.0, 0.25, 0.5, 0.6. In addition, XRPD patterns for Rietveld refinements have been collected as a function of *T* ($80 \leq T \leq 400$) K for all the samples. To obtain the PDFs, the data were reduced using PDFGetX **[2]**. The *G*(*r*) data have been fitted using a so called *Real Space Rietveld analysis* applying symmetry constrains and varying cell parameters, atomic positions, thermal parameters **[3]**.

The reciprocal-space analysis of the GBCO system has shown a very rich phase diagram as a function of δ and *T* never reported before. In particular, the $GdBaCo_2O_5$ composition shows two structural phase transitions at T>300K (*Pmmm* to *P*4/*mmm*) and at T<250K (*Pmmm* to *Pmmb*). For compositions in the $0.25 \leq \delta \leq 0.5$ range the diffraction patterns were interpreted using *Pmmm* space group. Crossing the MI transition (~340K) a phase transition appears and a biphasic region has been found for all the investigated samples. Two orthorhombic phases coexist in a narrow *T* range (few tens of degrees). Conversely, for compound with δ>0.5

no phase transitions were found above room temperature. However, by lowering *T* down to 150K the orthorhombic distortion (*s*=2(b-a)/(a+b)) seems to progressively decrease. At *T*=80K the value of *s* increases again suggesting that structural changes could be detected at lower temperatures.
Real Space analysis have been carried out on the experimental PDF functions obtained at *T*=295K, 180K, 80K for δ=0.0, 0.5 and at T=295K, 80K for δ=0.25 and 0.60 respectively. Mismatchs between the long range structure described by *Rietveld* models and short range order have been found for all the samples at fixed *T*.
In particular, for δ=0.0 sample at T=295K and *r* > 8-9 Å the long range structural model *Pmmm* obtained by the Rietveld analysis fit very well the experimental *G*(*r*) pattern (see Figure 1). The same agreement with *Pmmb* space group is obtained at T=180K and 80K even at very low interatomic distances range (1.5< *r* <10Å). Conversely, at T=295K and *r*<5 Å the *Pmmm* structural model seems to be inadequate for the description of Ba-O, Gd-O and Co-O first coordination shells (see inset in Figure 1). An improvement of the description of the Ba-O, Gd-O and Co-O first coordination shells was obtained using the charge ordered model *Pmmb* even at T=295K. Incomplete or short range charge ordering have been widely invoked in order to explain the resistivity measurements of $LnBaCo_2O_5$ (Ln=Tb, Dy, Ho) parent compound **[4]**. However, a direct observation of this effect is still lacking. Thus our local analysis for δ=0.0 composition at T=295K, suggest the existence of charge ordered sub-nanodomains at temperature quite above the charge order transition (**T_{CO}<250K**).

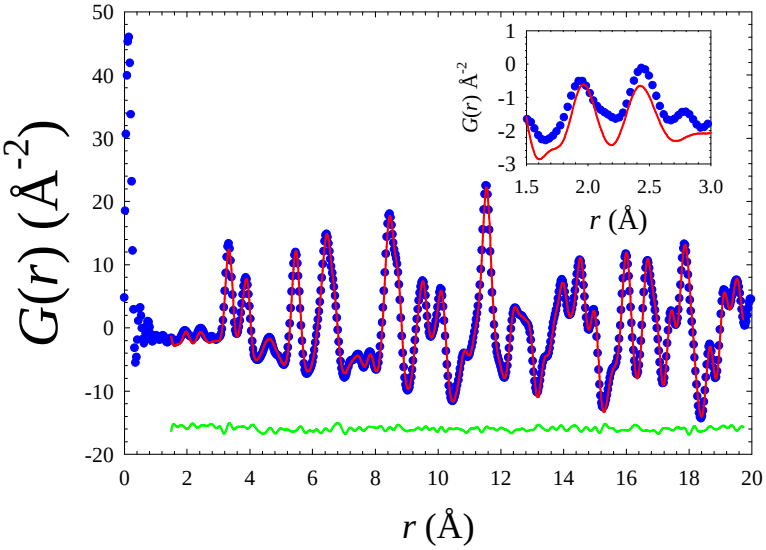

Figure 1. PDFs for δ=0.0 at room temperature. Blue dots: experimental PDF, Red continuous line: calculated model PDF, Green bottom curve: difference plot. The agreement factor is Rw=0.057. The inset highlights the *r* range related to the Ba-O, Gd-O and Co-O interatomic distances.

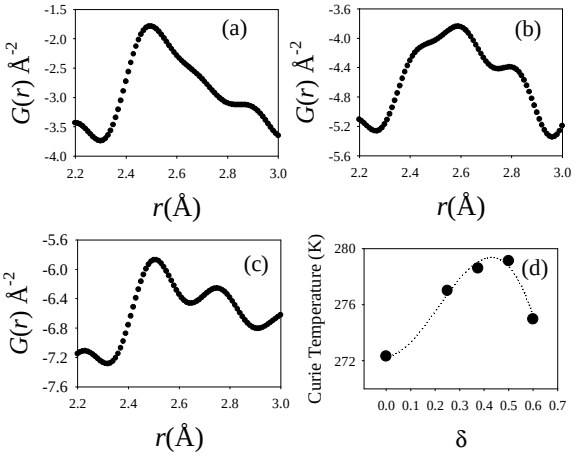

Figure 2. Portions of PDFs for δ=0.25 (a), δ=0.50 (b) and δ=0.60 (c) at T=295K. In the figure the measured Curie temperatures as a function of δ are also shown (d).

In Figure 2, selected portions of short range PDFs for δ=0.25, 0.50, 0.60 samples at T=295K are displayed. Despite the reciprocal space analysis where all these compositions belong to the same structural model (*Pmmm*) at room temperature, some differences in the Gd-O shell (2.3~<*r* <~2.6Å) can be clearly appreciated. It should be noted that in GBCO system the magnetic and transport behaviours are driven by the mixed valence state of the cobalt ions determined by the oxygen content δ in the GdO_δ plane **[1]** (As an example in Figure 2 (d) the Curie tempetures for all the samples are reported). If some local distortions in GdO_δ plane occur as a function of δ, these could be constitute a basis for understanding the transport and magnetic behavior of this material over the entire doping range. The interplay between magnetic ordering and local structure of GBCO system is still under investigation.

References

[1] A. A. Taskin *et al.*, Phys. Rev. B **71,** 134414 (2005).
[2] X. Qiu *et Al., J. Appl. Cryst.* (2004), **37**, 678–678.
[3] C. L. Farrow *et Al., J. Phys.: Condens. Matter* **19** (2007) 335219.
[4] F. Fauth *et al.*, Eur. Phys. J. B **21**, 163 (2001).