



	Experiment title: Determination of Co electronic states by using exact structural determinations	Experiment number: 01-02 870
Beamline: BM01A	Date of experiment: from: 12 Feb 2010 to: 14 Feb 2010	Date of report: 24/02/2010
Shifts: 9	Local contact(s): P. Pattison	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

V. Scagnoli*

Paul Scherrer Institut, 5232 Villigen PSI, Switzerland

M. Allieta*, M. Coduri*

Dip. di Chimica Fisica e Electrochimica Universita di Milano, Via Venezian 21 I-20133 Milano Italy.

Introduction

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 $\text{GdBaCo}_2\text{O}_{5+\delta}$ (hereafter GBCO) has been considered as a model system [1],[2].

GBCO displays a large variety of magnetic and transport properties, which depend on the tunable oxygen concentration [2]. It is believed that the magnetic and transport behaviors are driven by the mixed valence state of the cobalt ions and possible orbital ordering and therefore by the $\text{Co}^{2+}/\text{Co}^{3+}$ ($\text{Co}^{4+}/\text{Co}^{3+}$) ratio determined by the oxygen content of the material.

In particular for $\delta=0.0$ composition, for which a $\text{Co}^{2+}/\text{Co}^{3+}=1$ is expected, heat capacity and internal friction measurements carried out as a function of temperature suggest the occurrence of charge ordering (CO) at $T_{\text{CO}}=248\text{K}$ [3] and Néel transition at $T_{\text{N}}=350\text{K}$ [4].

Since in layered perovskite based materials the charge, magnetic and lattice degrees of freedom are intimately intertwined [5], a structural characterization of $\text{GdBaCo}_2\text{O}_5$ as a function of T would provide fundamental informations to understand its rich phase diagram.

Experimental

$\text{GdBaCo}_2\text{O}_{5+\delta}$ single crystals have been grown using an infrared image furnace. A polycrystalline feed rod for the crystal growth sample was prepared by conventional solid state reaction in air [2]. The crystal growth was performed in a flow of dried air at a constant rate of 0.5 mm/h. In order to reach the oxygen deficient composition $\delta=0.0$ the crystals were annealed at $T=850^\circ\text{C}$ during 72h in a flow of pure nitrogen.

Single crystal diffraction experiments as a function of temperature were performed at the six circle KUMA6 diffractometer using an charge coupled device (CCD) detector with $\lambda=0.70826 \text{ \AA}$. The temperature was controlled with Oxford Cryostream. The data has been reduced using CRYNALIS software [6]. Selected layers of reciprocal space have been reconstructed with the same software.

Diffraction data from a crystal of $\sim 50 \mu\text{m}$ size were collected in the temperature range 380K to 100K selecting two different strategies as a function of temperature. In particular we have collected at $T=380, 298\text{K}, 250\text{K}, 240\text{K}, 220\text{K}, 200\text{K}, 180\text{K}, 160\text{K}, 130\text{K}$ with a 2.5 hours scan in order to map the structural modification at varying T . Conversely at $T=100\text{K}$ we have performed the diffraction scan with a 8 hours program in order to collect data of satisfactory quality for the electron density determination. Moreover the temperature dependence of selected reflection was monitored during a heating process in the $80 \leq T \leq 250\text{K}$ range.

Results

According to our preliminary reductions, at room temperature the structure belongs to a orthorhombic system with cell parameters $a \sim b \sim a_p$ and $c \sim 2a_p$ (hereafter a_p =cell parameter of the cubic perovskite lattice). It should be noted that this result is in contrast with previous investigation where a tetragonal symmetry was reported for that composition [2]. At $T=380\text{K}$ (above the T_N [4]) we have mapped an orthorhombic to tetragonal (unit cell metric $a_p \times a_p \times 2a_p$) transition never reported before for GBCO single crystal. Below $T=240\text{K}$ a new orthorhombic structure have been indexed using a unit cell doubled along the b axis ($a_p \times 2a_p \times 2a_p$). This new structural phase is associated with the charge ordering occurring at $T_{CO}=248\text{K}$ [3],[7].

The temperature dependence of one of the superstructure reflection (116) related with the charge ordering is reported in Figure 1. Critical exponent for the order parameter is found to be $\beta=0.483(5)$ indicating a second order transition.

In Figure 2 the (0kl) reciprocal lattice plane reconstructed from the experiment performed at $T=100\text{K}$ is shown. The reflections associated with the charge ordering are clearly visible. Unfortunately, the presence of twins precluded a detailed study of the electron density in the crystal. The twin formation takes place at the charge ordering transition temperature and also crystal of few microns size (~ 15) are affected. Nevertheless, precious information about the charge states of Co ions above and below the T_{CO} can be obtained using the bond-valence sums [8]. In particular we collected several data set close to the charge ordering temperature, which enable us to map in details the change in the bond lengths.

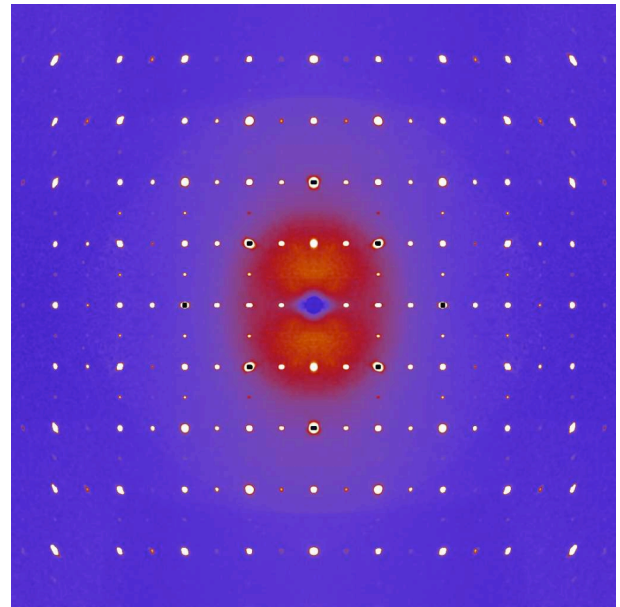
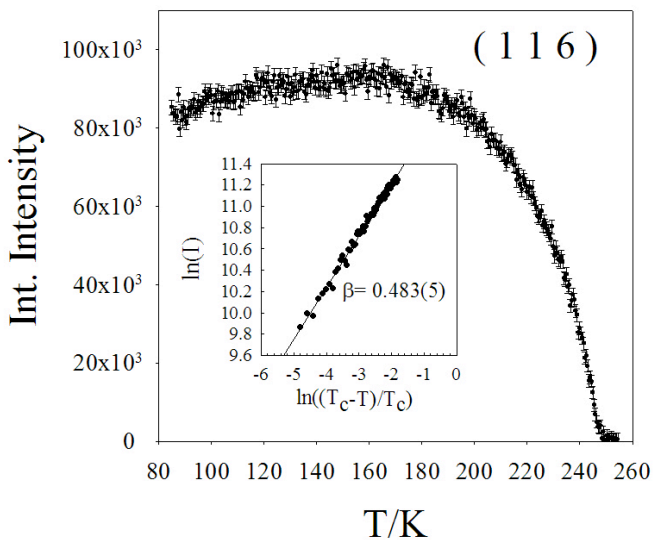


Figure 1. Temperature dependence of the (116) superlattice reflection associated with the charge ordering. . In the insert the log-log plot of the intensity vs. reduced temperature is reported.

Figure 2. Reconstruction of the (0kl) plane in reciprocal space at $T=100\text{K}$. Weaker spots correspond to the doubling of the unit cell along the b-axis.

References

- [1] C. Martin, *et al*, Appl. Phys. Lett. **71**, 1421 (1997).
- [2] A. A. Taskin *et al.*, Phys. Rev. B **71**, 134414 (2005).
- [3] X. F. Sun *et al.*, Phys. Rev. B **77**, 054436 (2008).
- [4] X. S. Wu *et al.*, Phys. Rev. B **76**, 094106 (2007).
- [5] F. Fauth *et al.*, Eur. Phys. J. B **21**, 163 (2001)
- [6] CRYCALIS Software System, Ver. 1.171.31.4, Oxford-diffraction Ltd., Oxford (England), 2006.
- [7] V. Scagnoli *et al.*, paper in preparation.
- [8] I. D. Brown & D. Altermatt, Acta Cryst. B **41**, 244 (1985).