



	Experiment title: Crystal structure and magnetic state in $\text{La}_{0.75}\text{Ba}_{0.25}\text{CoO}_{3-d}$ under high pressure	Experiment number: HC-1888
Beamline: ID-09A	Date of experiment: from: 23.07.2015 to: 26.07.2015	Date of report: 17.12.2016
Shifts: 8	Local contact(s): Michael Hanfland	<i>Received at ESRF:</i>
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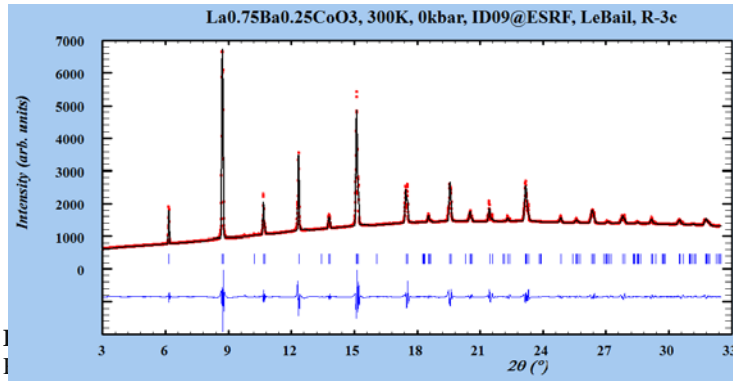
Rare earth cobaltites with perovskite structure of general formula LnCoO_3 and hole-doped $\text{Ln}_{1-x}\text{A}_x\text{CoO}_3$ (Ln = lanthanide, A = Ca, Sr or Ba) attract a great interest as they exhibit many unusual magnetic and transport phenomena [1,2]. Co ions in an octahedral symmetry are found either in high (HS), intermediate (IS) or low spin state (LS) as the energy of the crystal-field splitting of the Co 3d states (E_{cf}) and the Hund's rule exchange energy (E_{ex}) are comparable. Among the doped cobaltites, the system $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ is the most extensively investigated. A spin glass behavior has been reported for the region $0.01 < x < 0.18$ where short-range ordered ferromagnetic clusters develop. With further increasing x ferromagnetic long-range order sets in exactly at a concentration $x = 0.18$ where the insulator – metal transition (IMT) is situated [3]. A similar metallic ferromagnetic state appears in barium doped cobaltites at a critical barium content of $x = 0.22$, where a structural transition is concomitant to the IMT [4]. In this system, $\text{La}_{1-x}\text{Ba}_x\text{CoO}_3$, long-range antiferromagnetic order is present at a composition $x = 0.17$ [4]. The nature of the ferromagnetic interactions in hole-doped cobaltites has been under intense debate for a long time [1] without a complete consensus being reached. Structural studies performed on the nearly oxygen-stoichiometric perovskite $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$ have revealed a change of the structure from cubic to tetragonal below the paramagnet-ferromagnet transition occurring at $T_c = 190$ K [5,6].

A relatively small decrease of the oxygen content leads in $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-\delta}$ ($\delta = 0.13$) to a macroscopic structural separation at low temperature into cubic antiferromagnetic and ferromagnetic phases [9]. The antiferromagnetic phase has a larger unit cell volume than the ferromagnetic one [9]. The cubic $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-\delta}$ compositions with a large oxygen deficit ($\delta > 0.25$) are pure antiferromagnets with Neel points well above room temperature [10].

The oxygen deficit stabilizes an antiferromagnetic phase in $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-d}$. However, external pressure induces antiferromagnet-ferromagnet transition in $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_{2.8}$, which mostly contains Co^{3+} species. [11]. The small doping by Ba and Sr ions has different effect on ground magnetic state. The low doped Ba cobaltites are characterized by antiferromagnetic insulating state [12] whereas the low-doped Sr cobaltites are predominantly ferromagnetic. The data specific to Ba-doped cobaltites can be understood in frame of stabilization of HS spin state of Co ions. In fact the ionic radius of Ba^{2+} is much larger than the Sr^{2+} one. It was found that relatively small external pressure enhances the ferromagnetism in Ba and Sr lightly doped cobaltites resulting in an increase of both spontaneous magnetization and T_c , while in Ca-doped cobaltites the T_c and magnetization decrease under a pressure [13-14]. These facts could be understood in terms of pressure-induced transition from HS/LS states into ferromagnetic IS one (Ba, Sr-doping) and from IS into LS state (Ca-doping). However, in predominately ferromagnetic $\text{La}_{1-x}\text{Ba}_x\text{CoO}_3$ ($x > 0.2$) external pressure leads to a decrease of magnetization at low temperature. Surprisingly the Curie point of these compositions increases under pressure [14]. This means that there is a reversal pressure effect with variation of temperature. Beside it was observed that the compositions close to $x=0.25$ undergo structural transition near the Curie point from rhombohedral symmetry $R-3c$ (high temperature) into orthorhombic $Pnma$ (low temperature) [12]. The origin of the magnetostructural phase transition is unknown. Note that the structural phase transition does not change metallic character of resistivity. The ferromagnetic compositions $x=0.2$ and

$x=0.3$ do not undergo a structural transition and their symmetry remains rhombohedral both above and below the Curie point [12].

X-ray powder diffraction (XPD) data at have been collected at the 5, 100 and 300 K at the pressure varied from ambient to 16 GPa.



K. Tick marks below the graph indicate the calculated positions of the Bragg peaks for nuclear diffraction.

Rietveld refinement carried out on the XPD patterns (Fig. 2) assumes cubic symmetry of the lattice (space group $Pm-3m$) at ambient pressure. Diffraction data at high pressure demonstrate that the crystal structure under applied pressure gradually changes from initial rhombohedral to pure cubic one at the pressure 16 GPa. These results testify that under high pressure Co^{3+} ions stabilize in low spin state with a lower ion radius in comparison with a cobalt in intermediate or high spin state due to crystal field splitting between t_{2g} and e_g energy levels. Co^{4+} ions are present prior in low spin state and partly in intermediate spin state. Co-O distances and Co-O-Co angle (Fig.2 and Fig.3) are strong dependent on pressure and their pressure behavior correspond to changes in magnetic structure and a value of Curie/Neel point, this fact shows an important role of cobalt spin state, direct connected with a Co-O distance

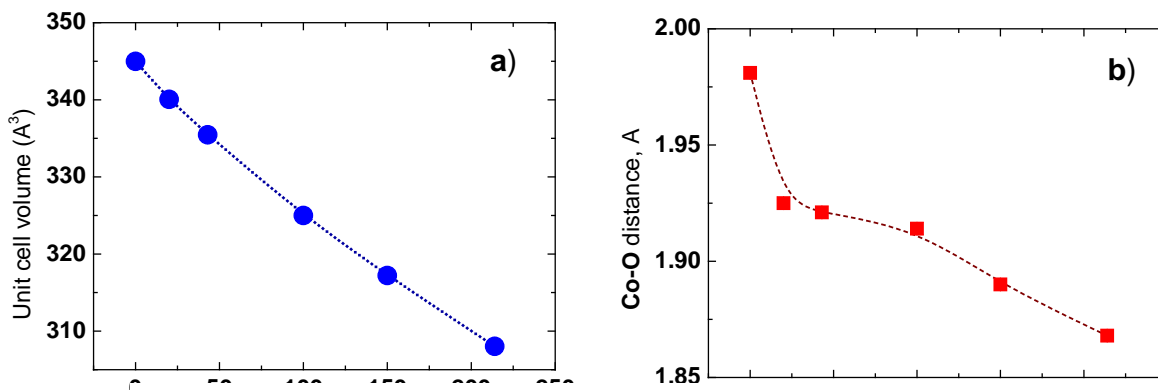
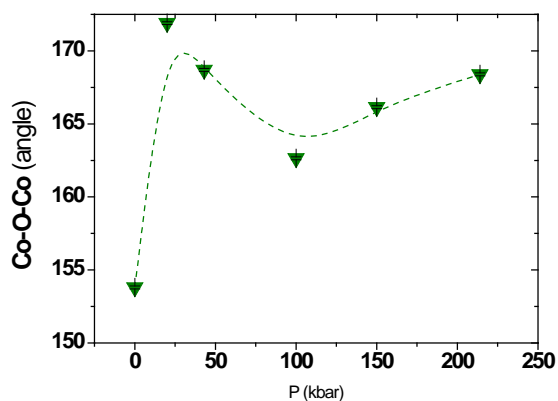


Fig. 2. Pressure dependence of unit cell volume (a) and Co-O distance (b) obtained at 300 K.

Fig.3. Pressure dependence of Co-O-Co angle.



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