

**Experiment title:****The detailed X-ray diffraction study of atomic structure distortions in LaCoO<sub>3</sub> single crystal****Experiment number:****HE-2643****Beamline:****BM01A****Date of experiment:**from: **21.04.2011** to: **27.04.2011****Date of report:**

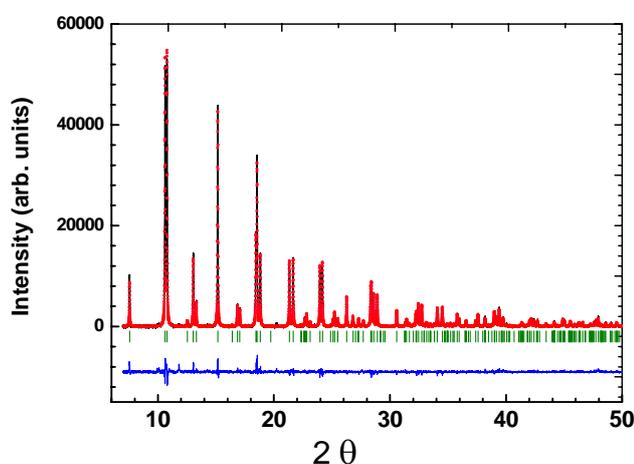
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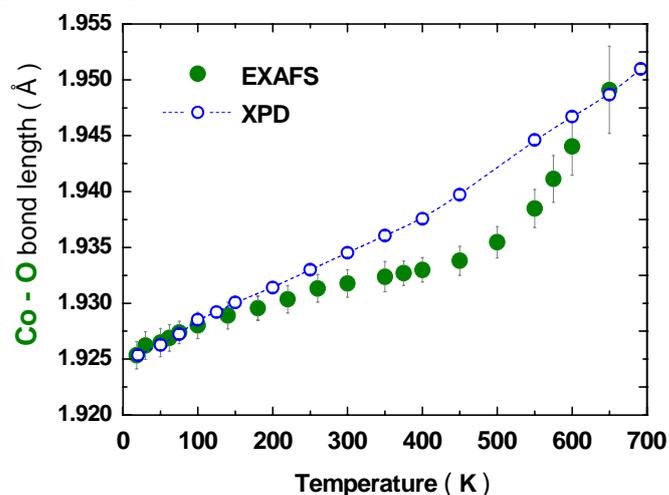
A perovskite-like lanthanum cobalt oxide LaCoO<sub>3</sub> belongs to a family of perovskites that attracts a lot of interest because of their rich variety of physical properties. In the ground state the Co<sup>3+</sup> ions are found to be in the low-spin state (LS;  $t_{2g}^6 e_g^0$ ,  $S = 0$ ). The transition  $\sim 120$  K was ascribed to the thermal activation of the intermediate-spin state (IS;  $t_{2g}^5 e_g^1$ ,  $S = 1$ ) or high-spin state (HS;  $t_{2g}^4 e_g^2$ ,  $S = 2$ ) of Co<sup>3+</sup> [1-3, 5]. The second anomaly in the susceptibility data at  $\sim 500$  K is associated with the metal-insulator transition. In order to explain the nature these two transitions consistently, a lot of spin-state transition models have been proposed [1-4, 5]. However, the problem of the true spin state transitions of the Co<sup>3+</sup> ions  $\sim 120$  K and  $\sim 500$  K for LaCoO<sub>3</sub> is still a matter of debate to date [1-4, 5]. Moreover, there is no agreement concerning the type of the crystal structure of LaCoO<sub>3</sub>. Earlier, a rhombohedral ( $R\bar{3}c$  space group) type of distortions in LaCoO<sub>3</sub> up to 1000 K [2] was suggested. However, recent X-ray [3] single crystal diffraction experiments assume symmetry lowering ( $I2/a$  space group) around 120 K, which is caused, probably, by the orbital ordering induced by the cooperative Jahn-Teller distortions of the Co<sup>3+</sup> ions in the IS state.

The X-ray powder and single crystal diffraction measurements on the LaCoO<sub>3</sub> were performed in temperature range from 80 K to 700 K on a high resolution X-ray diffractometer BM01A at the wavelength  $\lambda = 0.65$  Å.

The obtained X-ray single-crystal and powder diffraction data were analyzed by a Rietveld method with help of the FullProf (**Fig. 1 and 2**) and SHELXLe (**Fig. 3**) programs, respectively.



**Fig. 1.** (Color online) X-ray powder diffraction pattern of LaCoO<sub>3</sub> at the 80 K: experimental curve (open circles), refined curve (solid line) and residual curve (solid line at the bottom). The tick marks indicate the calculated positions of the Bragg peaks.

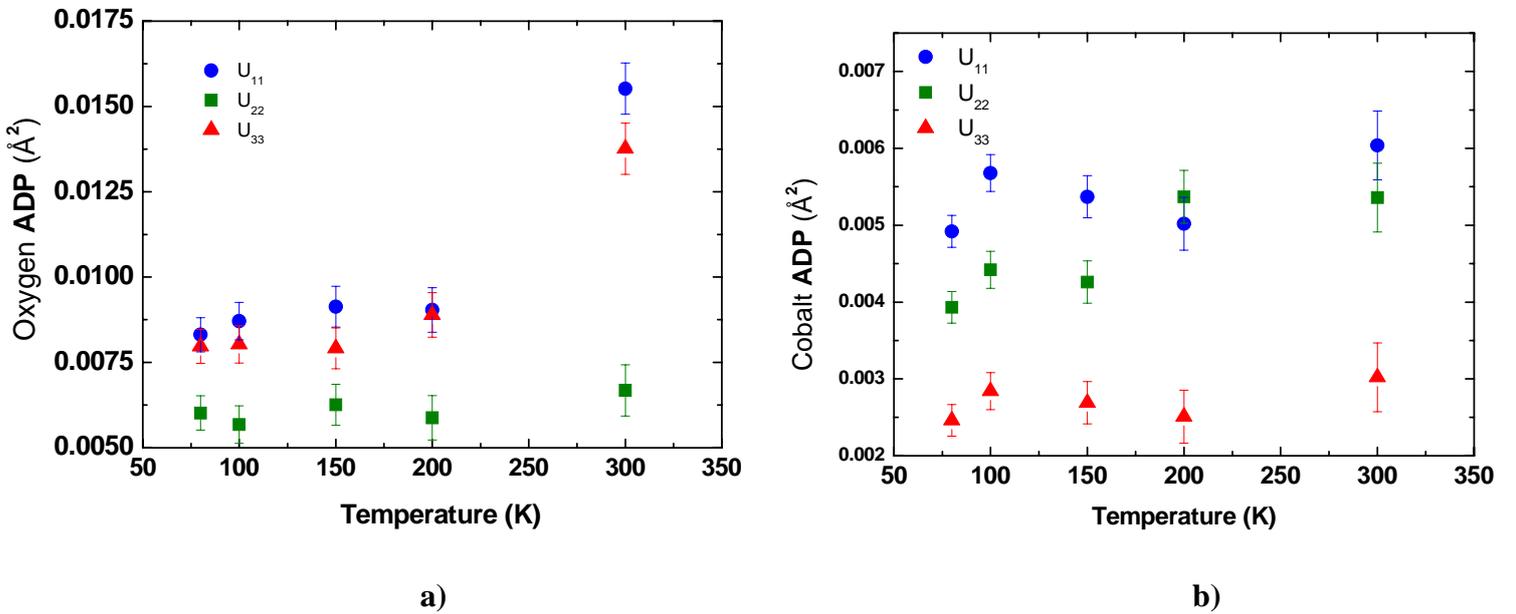


**Fig. 2:** The temperature dependence of the MSR<sub>D11</sub> and Co-O distance for LaCoO<sub>3</sub> obtained by EXAFS and XPD.

All observed Bragg peaks for LaCoO<sub>3</sub> in temperature range from 5 K to 700 K were indexed in the rhombohedral  $R\bar{3}c$  space group in hexagonal axes setting. Note that these results (bond lengths for all samples) agree well within approximately  $\pm 7 \cdot 10^{-4}$  Å with that obtained before in [2, 3, 5].

Our recent extended X-ray absorption fine structure (EXAFS) studies (ESRF, BM29 beamline) of LaCoO<sub>3</sub> at the Co  $K$ -edge indicate the existence of two anomalies in the temperature dependence of the Co-O bond length near the spin-state ( $\sim 120$  K) and the metal-insulator ( $\sim 500$  K) transitions (**Fig. 2**).

The Co-O distances determined from the EXAFS analysis are found to be shorter than that obtained from the X-ray powder diffraction (XPD) studies in a broad temperature range (**Fig. 2**). This already looks like an anomalous behavior because one would normally expect the EXAFS-measured distances be essentially longer [4] than the XPD ones due to the motion of the oxygen atoms in the direction perpendicular to the Co-O bond with the difference progressively increasing with temperature. Moreover the EXAFS data have shown a clear broad anomaly of the Co-O bond (**Fig. 2**) around the metal-insulator transition temperature  $T_{MI} \sim 500$  K and also  $T_{JT} \sim 700$  K. The observed unusual behaviour is not fully understood and possibly can be related to the mixed state of LS and HS between 120 K and 500 K [5] and to a metallic IS state above 500 K which coupling to the Jahn-Teller lattice distortion [5].



**Fig. 3:** Oxygen (a) and cobalt (b) ADP in LaCoO<sub>3</sub> single crystal obtained by BM-01A and TRICS diffractometers.

Analysis of the X-ray diffraction at ESRF ( $\lambda = 0.65$  Å, BM-01A) across the spin-state transition on LaCoO<sub>3</sub> single crystal revealed that x-ray diffraction provide the most reliable and detailed experimental information on oxygen and cobalt anisotropic atomic displacement parameters (ADPs) (**Fig. 2** and **3**) than in neutron powder diffraction data at D2B [2]. Knowledge of oxygen and cobalt ADP is indispensable to explain differences between the Co-O distributions from long-range X-ray diffraction and atomic-range EXAFS spectroscopy (**Fig. 2**).

## References

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