

Experiment title: The detailed X-ray diffraction study of atomic structure distortions in LaCoO₃ single crystal		Experiment number: HE-2643
Beamline: BM01A	Date of experiment: from: 21.04.2011 to: 27.04.2011	Date of report: 01.03.2012
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A perovskite-like lanthanum cobalt oxide LaCoO₃ 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 Co³⁺ ions are found to be in the low-spin state (LS; t_{2g}⁶e_g⁰, S = 0). The transition ~120 K was ascribed to the thermal activation of the intermediate-spin state (IS; t_{2g}⁵e_g¹, S = 1) or high-spin state (HS; t_{2g}⁴e_g², S = 2) of Co³⁺ [1-3, 5]. The second anomaly in the susceptibility data at ~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 Co³⁺ ions ~120 K and ~500 K for LaCoO₃ is still a matter of debate to date [1-4, 5]. Moreover, there is no agreement concerning the type of the crystal structure of LaCoO₃. Earlier, a rhombohedral (*R*-3c space group) type of distortions in LaCoO₃ up to 1000 K [2] was suggested. However, recent X-ray [3] single crystal diffraction experiments assume symmetry lowering (*I*2/a space group) around 120 K, which is caused, probably, by the orbital ordering induced by the cooperative Jahn-Teller distortions of the Co³⁺ ions in the IS state.

The X-ray powder and single crystal diffraction measurements on the LaCoO₃ were performed in temperature range from 80 K to 700 K on a high resolution X-ray diffractometer BM01A at the wavelength $\lambda = 0.65 \text{ \AA}$. 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.

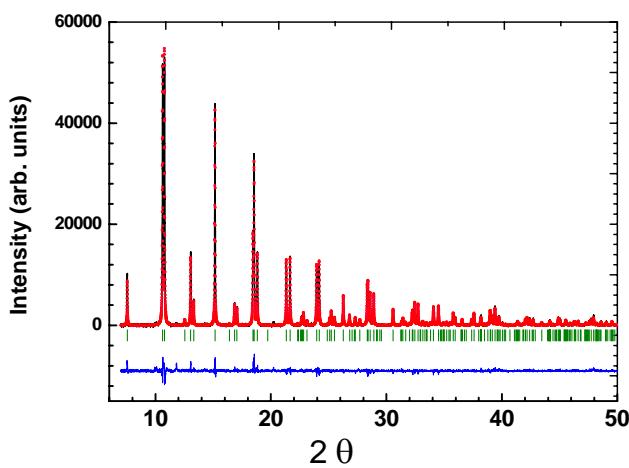


Fig. 1. (Color online) X-ray powder diffraction pattern of LaCoO₃ at the 80 K: experimental curve (open circles), refined curve (solid line) and residual curve (solid line at the bottom). The tick marks indicate the calculated positions of the Bragg peaks.

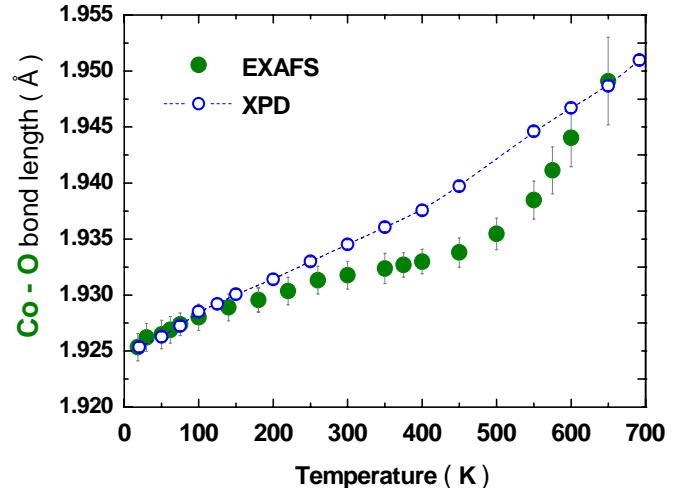


Fig. 2: The temperature dependence of the MSRD_{II} and Co-O distance for LaCoO₃ obtained by EXAFS and XPD.

All observed Bragg peaks for LaCoO₃ in temperature range from 5 K to 700 K were indexed in the rhombohedral *R*-3c 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 LaCoO₃ 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 (~ 120 K) and the metal-insulator (~ 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].

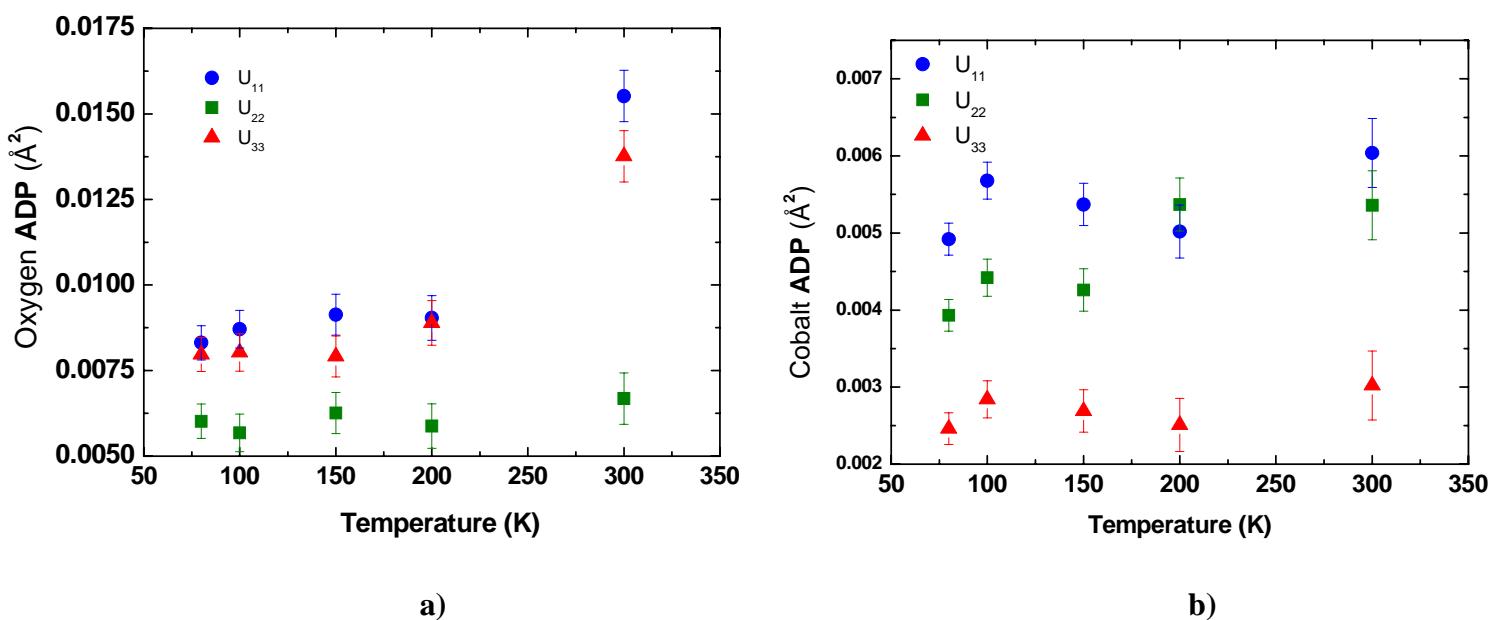


Fig. 3: Oxygen (a) and cobalt (b) ADP in LaCoO₃ single crystal obtained by BM-01A and TRICS diffractometers.

Analysis of the X-ray diffraction at ESRF ($\lambda = 0.65$ Å, BM-01A) across the spin-state transition on LaCoO₃ 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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