



Experiment title:

A detailed high-resolution X-ray diffraction study of atomic structure distortions in untwinned LaCoO₃ single crystal across spin-state and metal-insulator transitions

Experiment number:

01-02-992

Beamline:

BM-01

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Perovskite-like lanthanum cobalt oxide LaCoO₃ is a fascinating material studied since the 1950's with many controversial explanations of its peculiar structural [1], transport [2] and magnetic [3] properties. With temperature increase a maximum of the magnetic susceptibility [4] and thermal expansion coefficient was observed near 120 K whereas a second anomaly [1-3] followed by a plateau at 500 K ÷ 520 K is associated with the metal-insulator transition. Goodenough et al. [5] originally interpreted these magnetic transitions as spin-state transitions of Co³⁺ ions from the nonmagnetic ground low-spin state (LS; $t^6_{2g}e^0_g$, $S = 0$) to a high-spin state (HS; $t^4_{2g}e^2_g$, $S = 2$) due to the close values of the intra-atomic exchange energy (J_H) and the crystal field splitting ($10Dq$) at the Co³⁺ sites. These spin-state transitions are further manifested by observable changes in the crystal structure with increasing spin state and produce anomalies in thermal expansion since the HS Co³⁺ has a much larger radius (0.61 Å) than the LS state (0.54 Å) [6].

XRD experiments of LaCoO₃ were carried out at the BM01A beamline in the temperature range 80 – 800 K on the single crystal diffractometer KUMA.

The obtained X-ray powder diffraction data were analyzed by a Rietveld method using FullProf program. All observed Bragg peaks for LaCoO₃ in the temperature range from 10 K to 800 K were indexed in the frame of the rhombohedral $R\bar{3}c$ space group.

The temperature dependence of the MSD_{||} and diffraction Debye-Waller factor or uncorrelated mean squared displacement (MSD) for Co and O atoms in LaCoO₃ is shown in Fig. 1. The DCF (difference between MSD_{||} and MSD), reflecting the correlation in atomic motion of distant atoms (cobalt and oxygen), grows with temperature (Figure 1). Such growth of the strength interactions between atoms in the Co-O pairs can be associated obviously with gradual transition from HS Co³⁺ ions to IS spin state.

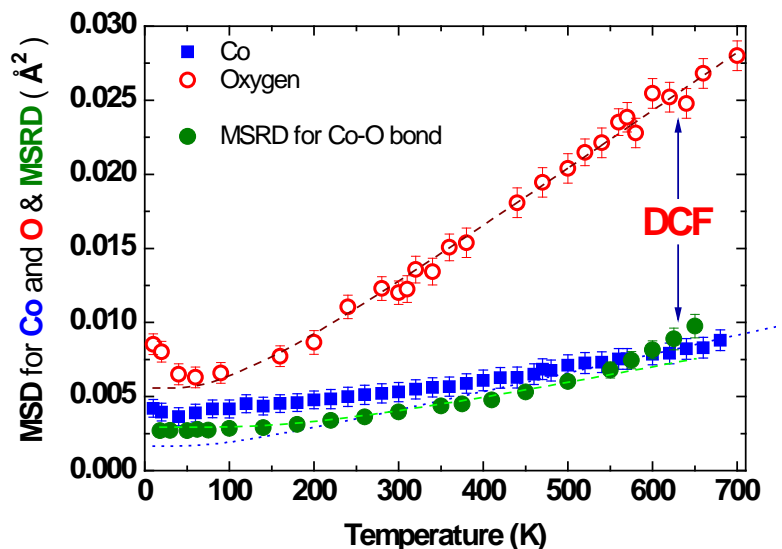


Fig. 1. Temperature dependence of MSD calculated from XRD) for cobalt (squares) and oxygen (empty circles) and correlated MSD_{||} (full circles) for Co-O bond in LaCoO₃.

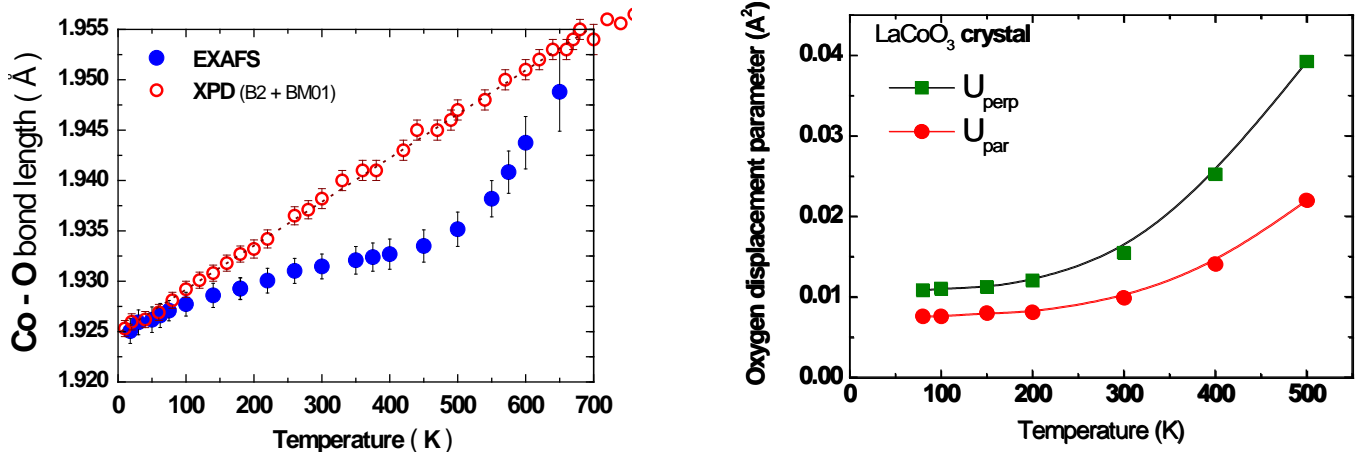


Fig. 2: The temperature dependence of the Co–O bond lengths (a) for LaCoO₃ obtained by EXAFS and XPD; (b) temperature dependence of U_{\parallel} and U_{\perp} of O for LaCoO₃ sample.

Figure 2 shows the temperature dependence of Co–O bond lengths obtained from the EXAFS and XPD data on LaCoO₃ powder as well as oxygen displacement parameters U_{\parallel} and U_{\perp} in Co–O–Co bond extracted from single crystal X-ray diffraction. We note that the local interatomic distance $\langle r_{\text{Co-O}} \rangle = \langle |r_{\text{O}} - r_{\text{Co}}| \rangle$ probed by EXAFS is usually larger than the equilibrium crystallographic distance between average positions $R_{\text{Co-O}} = | \langle r_{\text{O}} \rangle - \langle r_{\text{Co}} \rangle |$ measured by diffraction. The difference between $\langle r_{\text{Co-O}} \rangle$ and $R_{\text{Co-O}}$ is associated with the influence of the *perpendicular* $\text{MSRD}_{\perp} \langle \Delta \sigma_{\perp}^2(\text{Co-O}) \rangle$, i.e. the thermal atomic displacement in the direction perpendicular to the Co–O bond [41, 42]: $\langle r_{\text{Co-O}} \rangle = R_{\text{Co-O}} + \langle \Delta \sigma_{\perp}^2(\text{Co-O}) \rangle / 2R_{\text{Co-O}}$. However, the Co–O bond lengths determined from the EXAFS analysis are gradually shortened with respect to the ones obtained from the diffraction experiments with temperature increasing up to a maximum difference around the metal-insulator transition temperature $T_{\text{MI}} \sim 550$ K (**Fig. 2a**). It indicates an anomalous behavior because one would normally expect the EXAFS-measured distances to be essentially longer than the ones obtained from diffraction (see to Eq. 1). Taking into account that oxygen U_{\perp} is essential increasing with temperature in contrast to U_{\parallel} (**Fig. 2b**), we conclude that such effect on **Fig. 2a** could only be associated with the cobalt spin-state transition. Considering the difference in ions radius of Co^{3+} for HS (0.61 Å), LS (0.54 Å) and IS (0.56 Å) and futures between EXAFS and XRD a gradual increase of the deviation of Co–O bond lengths obtained by EXAFS and diffraction measurements would likely correspond to the Co^{3+} spin-state transition from HS fraction (located on the surface of ~ 0.5 mkm powders/granules) to high-hybridized metallic IS one in basic LS matrix, whereas a minimal difference of the Co–O bond lengths around ~ 700 K could be associated with a gradual growth of the long-range IS domains (up to saturation) from basic LS fraction and possible appearance of the small concentration of HS domains.

Moreover, we observed unusual increase of $\text{MSD}_{\text{Co-O}}$ below ~ 50 K. Such effect was impossible to resolve in the neutron powder diffraction [1] due to lower resolution (in determination of cobalt ADP compared to X-ray) as well as due to the difference in contrast for Co and O atoms for neutrons and X-rays. Such small increase of the $\text{MSD}_{\text{Co-O}}$ could be explained by coexistence of several Co^{3+} spin states with substantially different ion radiuses (i.e. incommensurability effect of Co^{3+} ions radii within granules) such as HS in the distorted surface layers of the LaCoO₃ granules with basic LS phase in the bulk and highly-hybridized IS between them.

References:

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