ESRF	**Experiment title:** **High-resolution X-ray diffraction study of atomic structure distortions in non-twinned LaGaO₃ and LaCoO₃ single crystals across metal-insulator and Jahn-Teller transitions**	**Experiment number**: **HC-1882**
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A perovskite-like lanthanum cobalt oxide $LaCoO_3$ is a fascinating material studied since 1950's due to its peculiar structural, transport and magnetic properties, explanation of which still remain controversial. The magnetic susceptibility and thermal expansion coefficient peaks at ~120 K followed by a plateau at ~550 K, which is associated with the metal-insulator transition. Goodenough et al. proposed that these magnetic transitions are spin-state transitions of Co^{3+} ions from the nonmagnetic low-spin state (LS; $t^6_{2g}e^0_g$, $S = 0$) to a high-spin state (HS; $t^4_{2g} e^2_g$, $S = 2$) caused by the close values of the intra-atomic exchange energy (J_H) and crystal field splitting ($10Dq$) at the Co^{3+} sites. Thus, depending on the relative values of the J_H and $10Dq$, either the LS, or the HS could be more stable.
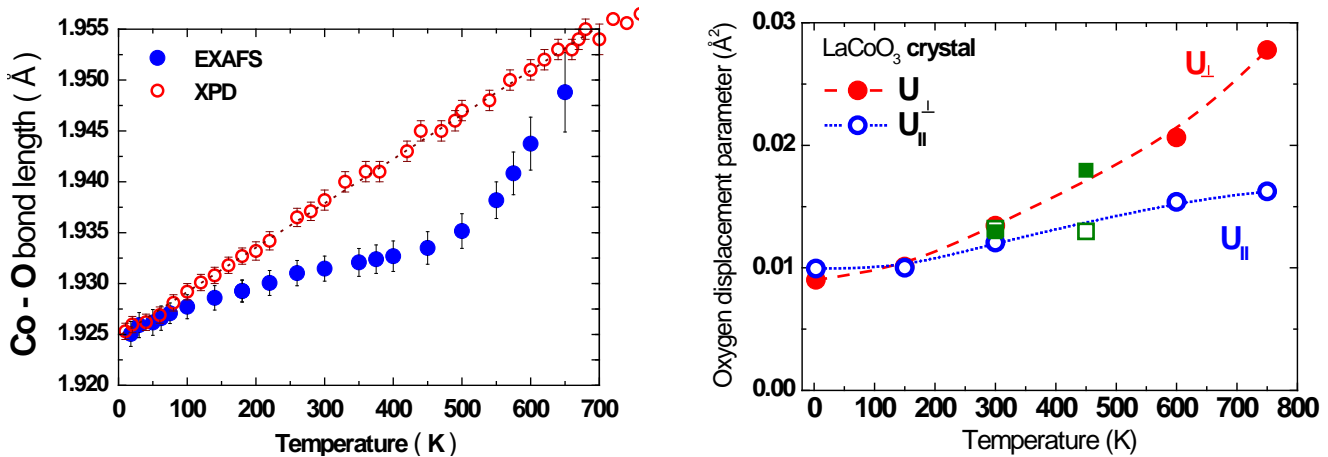

Fig. 1: The temperature dependence of the Co–O bond lengths (a) for $LaCoO_3$ obtained by EXAFS and XPD; (b) temperature dependance of $U_\parallel$ and $U_\perp$ of O for $LaCoO_3$ sample.

The X-ray powder diffraction measurements were performed on the high resolution on BM01A diffractometer at ESRF on the wavelength of ~0.65 Å in the temperature range from 80 K up to 800 K. The Rietveld refinements was performed by software program FULLPROF.

Figure 1 shows the temperature dependence of Co–O bond lengths obtained from the EXAFS and XPD data on $LaCoO_3$ powder as well as oxygen displacement parameters $U_\parallel$ and $U_\perp$ in Co-O-Co bond extracted from single crystal neutron diffraction. We note that the local interatomic distance $<r_{Co-O}> = <|r_O – r_{Co}|>$ probed by EXAFS is usually larger than the equilibrium crystallographic distance between average positions $R_{Co-O}= |<r_O> – <r_{Co}>|$ measured by diffraction. The difference between $<r_{Co-O}>$ and R_{Co-O} is associated with the

influence of the *perpendicular* MSRD$_\perp$ $\langle\Delta\sigma^2_\perp(\text{Co–O})\rangle$, i.e. the thermal atomic displacement in the direction perpendicular to the Co-O bond: $\langle r_{\text{Co-O}}\rangle = R_{\text{Co-O}} + \langle\Delta\sigma^2_\perp(\text{Co–O})\rangle/2R_{\text{Co-O}}$ \hfill (1)

However, the Co–O bond lengths determined from the EXAFS analysis are gradually shorten 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$_{MI}$ ~ 550 K (**Fig. 1a**). 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$_{||}$ (Fig. **1b**), we conclude that such effect on Fig. 1a 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 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 matrix and possible appearance of the small concentration of HS domains. This effect is also confirmed by gradual increase of parallel displacement correlation function DCF$_{\text{Co-O}}$ (i.e. difference between uncorrelated mean square displacement MSD or isotropic ADP obtained by diffraction and correlated MSRD$_{||}$) for Co-O bond with temperature for LaCoO$_3$ (**Fig. 2**), reflecting the correlation in atomic motion of cobalt/gallium and oxygen, whereas for LaGaO$_3$ the DCF$_{\text{Ga-O}}$ is approximately constant up to 650 K (**Fig. 2**). Moreover, we observed unusual increase of MSD$_{\text{Co-O}}$ below ~50 K only in LaCoO$_3$ while in LaGaO$_3$ there are no other abnormal features of MSD$_{\text{Co-O}}$ and MSRD$_{||}$ (**Fig. 2**). Such small increase of the 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 LaCoO$_3$ granules with basic LS matrix in the bulk and highly-hybridized IS between them. A gradual growth of the DCF$_{\text{Co-O}}$ as the sample is heated from 50 K to ~550 K is associated with gradual growth of the highly-hybridized metallic IS state fraction (up to saturation) with a small increase concentration of HS domains above T$_{MI}$ ~ 550 K. Latter assumption is confirmed a bend of MSRD$_{||}$ above T$_{MI}$ ~ 550 K (**Fig. 2**) as an additional local
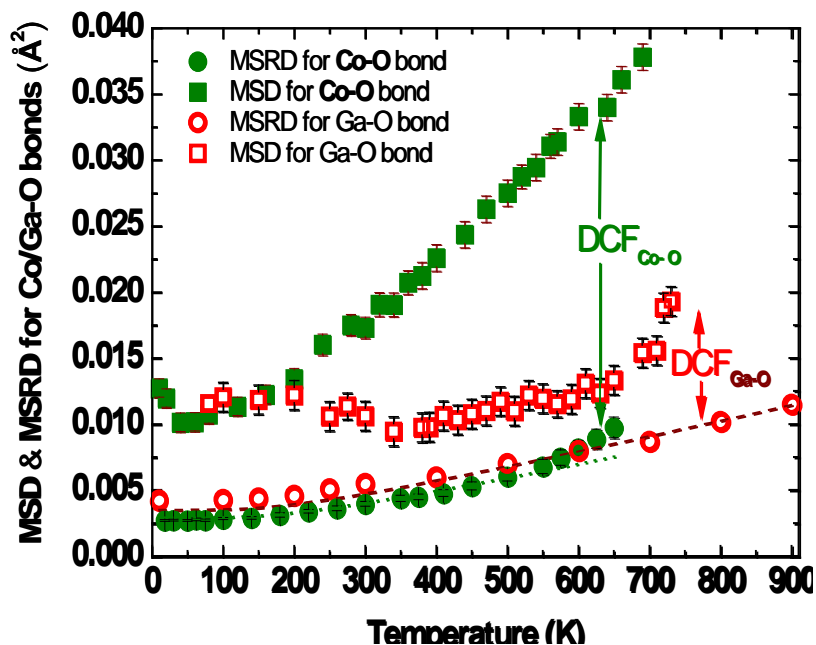

Fig. 2. Temperature dependence of MSD (calculated from XRD) for Co-O bond (green full squares) and Ga-O bond (red empty squares) as well as the MSRD$_{||}$ for Co-O bond in LaCoO$_3$ (full green circles) and Ga-O bond in LaGaO$_3$ (empty red circles).

Co-O bond distortions due to a mixture of substantial different ion radiuses.

In conclusion we have used the combination of high-resolution extended x-ray absorption fine structure (EXAFS), X-ray powder diffraction (XPD) and neutron crystal diffraction to study spin-state and metal-insulator transitions of Co^{3+} in LaCoO$_3$, using the LaGaO$_3$ powder a reference, with no spin-state and metal-insulator transitions. Our results suggested that the Co^{3+} ions are mainly in low spin (LS) state at temperatures below ~120 K, with minority of ions in the high-spin (HS) state. We also shown that intermediate spin (IS) state playes a critical role at high temperatures.