

Anomalous behavior of displacement correlation function and strain in lanthanum cobalt oxide analyzed both from X-ray powder diffraction and EXAFS data

V. Efimov,^{1,a)} V. Sikolenko,^{1,2} I. O. Troyanchuk,³ D. Karpinsky,³ E. Efimova,¹ S. I. Tiutiunnikov,¹ B. N. Savenko,¹ D. Novoselov,^{4,5} and D. Prabhakaran⁶

¹Joint Institute for Nuclear Research, Joliot-Curie 6, 141980 Dubna, Russia

²REC “Functional nanomaterials” Immanuel Kant Baltic Federal University, 236041 Kaliningrad, Russia

³Scientific-Practical Material Research Center NAS Belarus, 220072 Minsk, Belarus

⁴M.N. Miheev Institute of Metal Physics, S.Kovalevskoy 18, 620990 Ekaterinburg, Russia

⁵Department of Physics, Ural Federal University, Mira Street 19, 620002 Ekaterinburg, Russia

⁶Department of Physics, University of Oxford, OX1 3PU Oxford, United Kingdom

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A combined X-ray powder diffraction (XPD) and high-resolution extended X-ray absorption fine structure (EXAFS) at the Co and Ga *K*-edges study has been performed for LaCoO₃ and LaGaO₃ ceramics, the latter sample was used as a reference without spin transitions. Based on the X-ray diffraction data, we have found that isotropic atomic displacement parameters (ADP) or mean-squared displacement of the Co–O bond exhibit gradual growth below ~50 K, wherein the strain dependencies testify rapid increase below 150 K for the LaCoO₃ having rhombohedral structure. No similar features could be observed for LaGaO₃ sample. Above ~100 K the isotropic ADP of the Co–O bond indicate a gradual growth, whereas strain curves show distinct bend near the spin-state transition temperature at about 150 K. According to the EXAFS data, the correlated parallel mean squared relative displacement (MSRD_{||}) of Co–O and Ga–O bonds exhibit a gradual growth above 150 K; however, in the LaCoO₃ this parameter is notably bigger. It is supposed that at low temperature the cobalt ions are dominantly in low-spin (LS) state, while certain amount of Co³⁺ ions located within the surface layer of the crystallines have high-spin state (HS). Temperature growth leads to a gradual transformation of the HS state of the cobalt ions into the highly-hybridized intermediate-spin (IS) state, while the cobalt ions located in the inner part of the crystallines remain LS configuration up to 150 K. Further temperature increase leads to a spin transition of the Co³⁺ ions located within the crystallines from the LS state into the IS one. © 2017 International Centre for Diffraction Data.

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I. INTRODUCTION

A perovskite-like lanthanum cobalt oxide LaCoO₃ is a fascinating material studied since the 1950s with controversial explanations of its peculiar structural (Radaelli and Cheong, 2002; Maris *et al.* 2003), transport (Schmidt *et al.* 2009), and magnetic (Zobel *et al.* 2002; Kyomen *et al.* 2003) properties. With temperature increase a maximum of the magnetic susceptibility was observed near 120 K, whereas the second anomaly followed by a plateau at 500–520 K is associated with the metal–insulator transition. Goodenough (Senaris-Rodriguez and Goodenough, 1995) originally interpreted these magnetic transitions as spin-state transitions of Co³⁺ ions from the nonmagnetic ground state low-spin state (LS; $t_{2g}^6 e_g^0$, $S = 0$) to a high-spin state (HS; $t_{2g}^4 e_g^2$, $S = 2$) due to the close values of the intra-atomic exchange energy (J_H) and the crystal field splitting ($10Dq$) at the Co³⁺ sites. Thus, depending on the relative values of the J_H and $10Dq$, either

the LS, or the HS were suggested to be more stable. These spin-state transitions are further manifested by observable changes in the crystal structure since the HS Co³⁺ has a much larger radius (0.61 Å) than the LS state (0.54 Å) (Shannon, 1976).

Later, Potze *et al.*, introduced the concept of intermediate-spin state (IS; $t_{2g}^5 e_g^1$, $S = 1$) (Potze *et al.*, 1995) and showed that the spin-state transition near 120 K is associated with the thermal excitation of Co³⁺ ions from the LS ground state to an IS, whereas the second transition around 500 K corresponds to a crossover from the IS state to a mixed state of IS and the HS state. Moreover, this point of view was supported by Korotin (Korotin *et al.*, 1996) who performed the LDA+U band structure calculations assuming that temperature effects and spin state transition can be simulated by the lattice parameter expansion. According to (Korotin *et al.*, 1996) the stabilization of the IS state can be explained by large hybridization between the Co- e_g and O- $2p$ levels.

In most recent alternative LS–HS state transition model, the LaCoO₃ is assumed to be in an inhomogeneous mixed state of LS and HS areas between 120 and 550 K

^{a)}Author to whom correspondence should be addressed. Electronic mail: efimovvv2006@mail.ru

and it transforms to a metallic HS state above 500 K (Knížek *et al.* 2009; Siurakshina *et al.*, 2010). According to this model, the population levels of LS and HS states would be temperature dependent and a coexistence of the cobalt ions being in LS and HS states is supposed to be in the temperature range from about 120 K up to 550 K. Therefore, the problem of the true spin state transitions of the Co^{3+} ions ~ 120 and ~ 500 K for LaCoO_3 is still a matter of debate to date.

In this paper, we present an investigation of the anomalous temperature-dependent ($17 \text{ K} \leq T \leq 420 \text{ K}$) behavior of displacement correlation function (DCF) and strains within the granules of LaCoO_3 powder across the spin-state transition ($\sim 150 \text{ K}$) performed by a comparison of the X-ray powder diffraction (XPD) and high-resolution extended X-ray absorption fine structure (EXAFS) spectroscopy data. To distinguish carefully an influence of different spin states we have used a reference LaGaO_3 , which is characterized by $[\text{Ar}] 3d^{10}$ configuration for Ga^{3+} ions as they remain in a LS configuration regardless the temperature change.

II. EXPERIMENTAL

Polycrystalline LaCoO_3 and LaGaO_3 powders were grown and characterized as described elsewhere (Prabhakaran *et al.*, 2005). The XPD measurements were performed on the high-resolution diffractometer at the B2 beamline (DORIS III, DESY) in temperature range from 17 to 290 K for LaCoO_3 at the wavelength $\lambda = 0.8 \text{ \AA}$ and on BM01 beamline (ESRF) in temperature range from 80 to 420 K for LaCoO_3 and LaGaO_3 at the wavelength $\lambda = 0.65 \text{ \AA}$.

The obtained powder diffraction data were used for refining the corresponding crystal structures with the Rietveld method using FullProf software package (Rodriguez-Carvajal, 1993). Microstrains were refined by a STRAIN-program in the frame of this package using Voigt approximation by variation of Lorentzian contribution in peaks shape, taking into account an anisotropical broadening of the Bragg reflections.

The EXAFS experiments have been performed at the BL01B1 beamline of SPring-8 synchrotron. A fixed-exit Si (111) double-crystal monochromator was used, the estimated energy resolution being $\Delta E/E \sim 0.8 \cdot 10^{-4}$. The EXAFS spectra

above the Co *K*-edge were measured in the energy range 7400–9500 eV in standard transmission mode.

At the Ga *K*-edge extension of the spectra in *k*-space reached 22 \AA^{-1} for the cryogenic measurements and 18 \AA^{-1} for high temperature. At least two spectra were measured for every temperature point in order to achieve better quality. Measurement control routine was set up to increase the accumulation time proportionally to the k^2 law in the EXAFS region. Precision of the energy position was controlled with the encoder installed on the Bragg rotation axis of the monochromator.

Standard least-squares curve fitting procedure for the first coordination sphere was used to determine the average $R(\text{Co-O})$ distance and the parallel mean-squared relative displacement (MSRD_{\parallel}) $\Delta\sigma_{\text{Co-O}}^2$. The experimental scattering amplitude and phase shift functions for the Co–O atom pair were used in the EXAFS analysis. They were obtained from the EXAFS spectra for reference LaGaO_3 sample, measured at $T = 17 \text{ K}$, where it is assumed that there no an essential anharmonicity in dynamics of Co/ GaO_6 octahedron and composed of the regular Co/ GaO_6 octahedra: the cobalt coordination number $N_{\text{ref}} = 6$ and the Co–O distance $R_{\text{ref}} = 1.925 \text{ \AA}$ were set according to the results of the Rietveld refinement using our X-ray diffraction (XRD) data of the same LaCoO_3 powder.

It should be noted that the fitting result is in very good agreement with the experimental spectra for all three temperature points up to 17.5 \AA^{-1} that guarantees the high-resolution in determination of Co–O bond lengths and MSRD_{\parallel} values.

III. RESULTS AND DISCUSSION

The obtained XPD patterns are shown in Figure 1.

Typical fits of the XPD patterns for LaCoO_3 at 17 K and for LaGaO_3 at 80 K are displayed in Figure 1. All observed Bragg peaks for LaCoO_3 in temperature range from 17 to 420 K were indexed in the rhombohedral *R-3c* space group in hexagonal axes setting [Figure 1(a)], while for LaGaO_3 in temperature range 80–420 K were indexed in orthorhombic space group *Pbnm* [Figure 1(b)]. Note that these results (bond lengths for all samples) agree well within approximately $\pm 7 \cdot 10^{-4} \text{ \AA}$ with that obtained before in (Radaelli and Cheong, 2002; Maris *et al.* 2003).

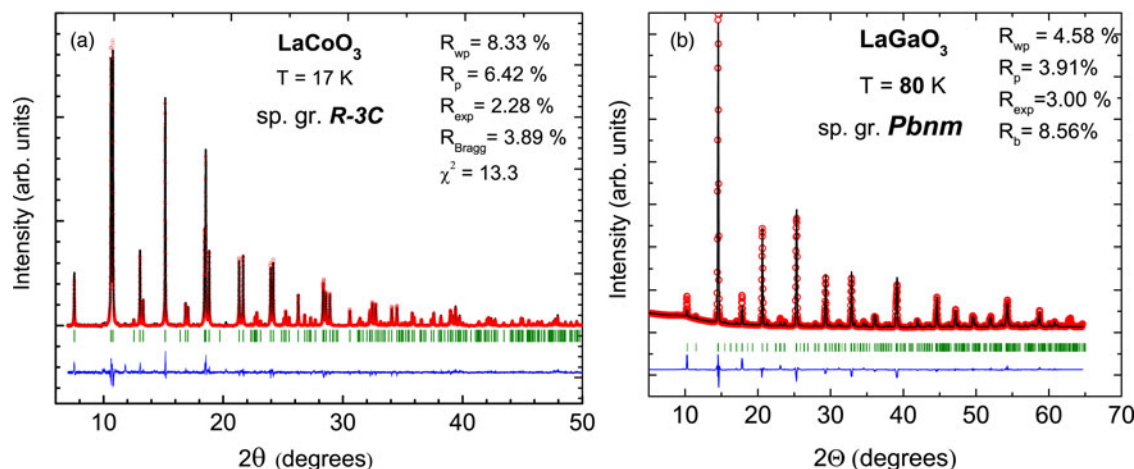


Figure 1. (Colour online) XPD pattern of (a) LaCoO_3 at 10 K and (b) LaGaO_3 at 80 K. Experimental curve (open red circles), calculated curve (solid black line), and residual curve (solid blue line bottom). The green tick marks indicate the calculated positions of the Bragg peaks.

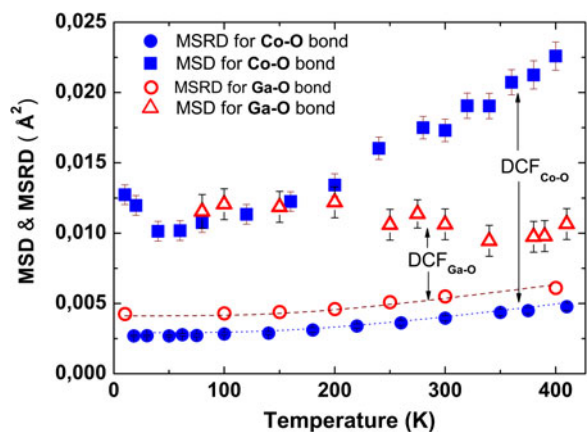


Figure 2. (Colour online) Temperature dependence of uncorrelated MSD (calculated from XRD) for Co–O bond (full squares) in LaCoO₃ and Ga–O bond (empty triangle) LaGaO₃ as well as the correlated MSRD_{||} for Co–O bond (full circles) and Ga–O bond (empty circles).

EXAFS technique allows establishing directly the Debye–Waller factor of selected pairs of atoms. The EXAFS Debye–Waller factor gives the information on the correlated parallel $\text{MSRD}_{||}(\Delta\sigma_{||}^2(\text{Co–O}))$, which is equal to the sum of the uncorrelated mean-squared displacements (MSD or isotropic thermal parameters) amplitudes (measured by diffraction) of the pair of absorber $\langle(R_{\text{Co–O}} \cdot \sigma_{\text{Co}})^2\rangle$ and back-scattered $\langle(R_{\text{Co–O}} \cdot \sigma_{\text{O}})^2\rangle$ atoms along the bonding direction $R_{\text{Co–O}} = |r_{\text{O}} - r_{\text{Co}}|$ minus the parallel $\text{DCF} = 2 \langle(R_{\text{Co–O}} \cdot \sigma_{\text{Co}})(R_{\text{Co–O}} \cdot \sigma_{\text{O}})\rangle$ (Boysen *et al.*, 2002) (σ_{Co} and σ_{O} are instantaneous displacements of the absorber and back-scatter atoms, respectively).

The DCF (i.e. difference between MSD and $\text{MSRD}_{||}$), reflecting the correlation in atomic motion of distant atoms and, as a consequence, the interaction strength between cobalt/gallium and oxygen, grows gradually with temperature for LaCoO₃, whereas for LaGaO₃ the DCF is approximately constant in the whole-measured temperature range (small decreasing till 300 K and then small increasing at the temperature higher than 300 K) as we can see at Figure 2. Moreover, we observe unusual growth of DCF below ~50 K only in LaCoO₃, while in LaGaO₃ there are no any features of MSD (Boysen *et al.*, 2002) and $\text{MSRD}_{||}$ (Figure 2). Such growth of the $\text{DCF}_{\text{Co–O}}$ can be explained by a coexistence of several Co³⁺ spin states during the phase transition: HS in the distorted surface layers of the LaCoO₃ granules, LS in the bulk and highly hybridized IS state is in the intermediate layer. Here we imply that electronic configuration of Co³⁺ changes from HS (ionic radius 0.61 Å) into the IS state (ionic radius 0.56 Å) and finally to the LS state (0.54 Å) (Shannon, 1976; Radaelli and Cheong, 2002; Maris *et al.* 2003). Gradual growth of the $\text{DCF}_{\text{Co–O}}$ as the sample is heated from 50 to 420 K is associated with gradual growth of the IS/HS ratio up to saturation in basic LS volume and then local range IS/LS ratio.

Note that our experimental $\text{MSRD}_{||}$ values for LaCoO₃ are in agreement with the previous EXAFS data (Jiang *et al.*, 2009), which are limited to a temperature of 290 K. Moreover, an increased value of $\text{MSRD}_{||}$ in the extended temperature range and a small rise of MSD below 200 K for LaGaO₃ compared with the LaCoO₃ ones is associated with the static distortions of the GaO₆ octahedra because of the

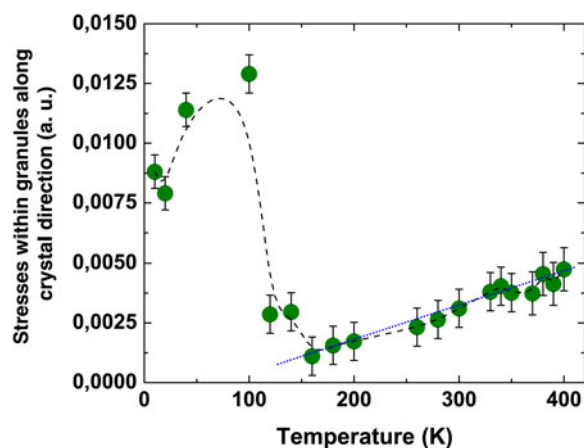


Figure 3. (Colour online) Temperature dependence of strains within granules obtained by Rietveld analysis using high-resolution XPD data for LaCoO₃

existence of three Ga–O distances, so that the average Ga–O distance is bigger than Co–O in LaCoO₃ as given by the *P6mm* symmetry.

The absence of $\text{MSRD}_{||}$ growth in temperature range from 50 to 17 K is probably associated with a high correlation of atomic motion with small amplitude of both LS and HS Co³⁺ with oxygen as well as with maximal distortion of Co–O–Co angle (maximal deviation from 180°).

Most sensitive effect of mixture of surface-distorted HS layer in basic LS volume with intermediate IS phase in micro-grains below 150 K is observed in the temperature dependence of strain within crystallines obtained by Rietveld analysis for LaCoO₃ (Figure 3). Note that LaGaO₃ does not have similar effect. A broad peak in this curve with a maximum around 50 K is associated with the mixture of the HS states on the surface crystallines, the LS in the inner part of the crystallines and the IS states located in between. Such mixing of three different spin-states leads to the growth of distortion strain in CoO₆ octahedra inside the crystallines.

High sensitivity to local lattice distortions caused by the difference in atomic radii of the Co³⁺ atoms in different spin states makes DCF a useful indicator of the spin-state transitions. Comparison of the diffraction data with the EXAFS-derived MSRD for in-plane and apical Co–O bonds allows to distinguish between local and long-range effects.

IV. CONCLUSIONS

We have clarified the origin of anomalous temperature behavior of the DCF and strain curves in a wide temperature range for LaCoO₃ and LaGaO₃ ceramics. Combined analysis of the EXAFS results and XRD data have led us to the conclusion about thermally induced spin-state transition in LaCoO₃ from a mixture of HS and LS configurations of the Co³⁺ ions located respectively in outer layer and inner part of the crystallines into the highly hybridized IS configuration of the cobalt ions, while the majority of Co³⁺ ions remains in the LS state up to the temperature of ~150 K.

Gradual growth of DCF and strain parameters estimated for the LaCoO₃ compound in the temperature range from ~150 to 420 K has been interpreted by assuming an ongoing spin-state transition from basic LS state to the IS specific for

local-range domains. The results derived from this study are in accordance with available experimental data on electron spin resonance (Noguchi *et al.*, 2002), MCD measurements (Haverkort *et al.*, 2006), and inelastic neutron data (Podlesnyak *et al.*, 2006).

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