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Abstract. A combined high-resolution Co K-edge extended x-ray absorption fine structure (EXAFS) and high-resolution X-ray powder diffraction (XRD) study has been performed to clarify the detail of anomalous behavior of temperature-dependent magnetic susceptibility curve on the LaCoO$_3$ across the spin-state (~120 K) transition. According to XRD analysis, the Debye-Waller factor of Co-O bond exhibit rapid growth below 20 K whereas the temperature dependence of the average Co-O bond length shows linear behavior from 10 K to 400 K. The EXAFS data show an anomalous decrease of the Co–O bond lengths with respect to those obtained by XRD. No local distortion of CoO$_6$ octahedral as temperature increases up to 400 K has been detected.

1. Introduction

Perovskite-like lanthanum cobalt oxide LaCoO$_3$ is a fascinating material studied since the 1950’s with many controversial explanations of its peculiar structural [1,2], transport [3] and magnetic [4,5] properties. With temperature increase a maximum of the magnetic susceptibility [4] and thermal expansion coefficient [3] was observed near 120 K whereas a second anomaly [3] followed by a plateau at 500 K ÷ 520 K is associated with the metal-insulator transition. Goodenough et al. [6] originally interpreted these magnetic transitions as spin-state transitions of Co$^{3+}$ ions from the nonmagnetic ground state low-spin state (LS; $t^{5}_{2g}e^{0}_{g}$, $S = 0$) 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 (10$Dq$) at the Co$^{3+}$ sites. These spin-state transitions are further manifested by observable changes in the crystal structure since the HS Co$^{3+}$ has a much larger radius (0.61 Å) than the LS state (0.54 Å) and intermediate IS (0.55 Å) [7].
Potze et al introduced the concept of intermediate-spin state (IS; \( t^1_e \), \( S = 1 \) [8]) and showed that the spin-state transition near 120 K is associated with the thermal excitation of \( \text{Co}^{3+} \) ions from the LS ground state to an IS [8]. Moreover, this point of view was supported by Korotin and coworkers [9] who performed the LDA+U band structure calculations assuming that temperature effects and spin state transition can be simulated by expanding the lattice parameter. According to the Korotin and coworkers [9] the stabilization of the IS state due to the large hybridization between the Co-e\(_g\) and O-2p levels. Due to the partially filled e\(_g\) level, the IS state is Jahn–Teller (JT) active. The LS-IS scenario became widely used in interpretation of numerous experimental data [1-6, 8, 9]. However, in recent works, including EXAFS [10], magnetic circular dichroism (XMCD) [11], inelastic neutron scattering [12] as well as recent theoretical work on GGA+U (GGA-generalized gradient approximation) calculations [13] and theoretical study by Pandey et al. [13] has attempted to revive the LS-HS scenario.

Here we present the analysis result of EXAFS and XRD experiments on LaCoO\(_3\) powder.

2. Experimental

The powder sample LaCoO\(_3\) was synthesized using the method described in [1]. XRD experiments were carried out at the synchrotron facility HASYLAB/DESY (Hamburg, Germany) using the powder diffractometer at the B2 beamline with the temperature range 10 – 290 K and the single crystal diffractometer at the BM01A beamline at ESRF in the temperature range 80 – 400 K. The obtained X-ray powder diffraction data were analyzed by a Rietveld method using FullProf program. EXAFS experiments have been performed at the beam line BM29 of ESRF (Grenoble, France). The EXAFS spectra were measured at the Co K-edge in the energy range 7400 eV – 9500 eV in standard transmission mode simultaneously with reference sample (cobalt thickness 9 \( \mu \)m metallic foil – in order to fix \( E_0 \) not bigger 0.005 Å) in the temperature range 20 – 400 K. Each temperature point was measured 3 times with a count rate of 2.5 seconds per point. To reduce the harmonic content in the x-ray beam, we detuned the monochromator crystals 40\% at 7900 eV. The LaCoO\(_3\) powder sample were deposited on the millipore cellulose membranes with thicknesses specially selected to obtain an X-ray absorption edge jump \( \Delta \mu \cdot x \sim 1 \) at the Co K-edge.

A curve fitting procedure by the EDA software package [14] was used to determine the average \( R(\text{Co–O}) \) distance and the parallel mean square relative displacement (MSRD\(_p\)) \( \Delta \sigma^2_{\text{Co–O}} \) (or EXAFS Debye-Waller factor). The energy position \( E_0 \), used in the definition of the photoelectron wave number \( k = [(2m/\hbar^2)(E - E_0)]^{1/2}, \) was set at the threshold energy \( E_0 = 7714 \) eV. The energy position \( E_0 \) was fixed 7714 eV. The Fourier transforms (FTs) of the EXAFS \( \chi(k)k^2 \) spectra were calculated in the wave number interval up to \( k = 1.0 \div 20 \) Å\(^{-1}\); however, it deteriorates at high \( k \) as the temperature increases and is poor beyond about 18.0 Å\(^{-1}\) at 300 K. Consequently, in all the fits the upper end of the FT \( k \) range is restricted to 17.5 Å\(^{-1}\).

Experimental scattering amplitudes and phase shift functions for the Co-O atom pair were used in the EXAFS analysis. They were obtained from the EXAFS spectra of a reference Co-foil sample at \( T = 20 \) K. We assumed that in these conditions, anharmonicity effects in the dynamics of the CoO\(_6\) octahedron can be neglected, and the sample is composed of regular CoO\(_6\) octahedra. The cobalt coordination number and the Co-O distance were set respectively equal to \( N_{\text{ref}} = 6 \) and \( R_{\text{ref}} = 1.925 \) Å, according to the results of the Rietveld refinement of our X-ray powder diffraction data on the same LaCoO\(_3\) sample.

3. Results and discussion

All observed Bragg peaks for LaCoO\(_3\) in the temperature range from 10 K to 400 K were indexed in the frame of the rhombohedral \( R-3c \) space group. The temperature dependence of MSRD\(_p\) is the set of the contributions of all normal modes and can be well approximated by the correlated Einstein model [15].

The temperature dependence of the MSRD\(_p\) and diffraction Debye-Waller factor or uncorrelated mean squared displacement (MSD) for Co and O atoms in LaCoO\(_3\) is shown in Fig. 1. Our experimental
MSRD$_\parallel$ $\Delta \sigma^2$(Co–O) values for LaCoO$_3$ are in agreement with the previous EXAFS data [10] which are limited 300 K. The MSRD$_\parallel$ values in the range from 20 K to 400 K are reasonably well fitted by the Einstein model [15] with a characteristic temperature of 550 K. The DCF (i.e. difference between MSRD$_\parallel$ and MSD), reflecting the correlation in atomic motion of distant atoms (cobalt and oxygen), grows gradually with temperature (Fig. 1). Such growth of the interaction strength between atoms in the Co–O pairs can be associated to a gradual transition from HS Co$^{3+}$ ions to an high-hybridized IS spin state [9].

The absence of growth MSRD$_\parallel$ in temperature range from 5 K to 20 K is probably associated to a high correlation of both LS and of HS Co$^{3+}$ ions motion with the motion of oxygen.

Figure 1. Temperature dependence of MSD (calculated from XRD) for cobalt (squares) and oxygen (empty circles) and correlated MSRD$_\parallel$ (full circles) for Co-O bond in LaCoO$_3$. The dot line is Einstein model best-fitting the MSRD$_\parallel$ ($\Theta_\text{E} = 550$ K).

Figure 2. The temperature dependence of the Co–O bond lengths for LaCoO$_3$ obtained by EXAFS and XRD.

Fig. 2 shows the result of the temperature-dependant Co–O bond lengths obtained by the EXAFS fitting procedure and the Rietveld refinement of diffraction data. Note that the local interatomic distance $<r_{\text{Co-O}}>$ = $\langle |r_O - r_{\text{Co}}| \rangle$ probed by EXAFS is usually larger than the equilibrium crystallographic distance $R_{\text{Co-O}} = \langle |r_O - r_{\text{Co}}| \rangle$ measured by diffraction. The difference between $<r_{\text{Co-O}}>$ and $R_{\text{Co-O}}$ is associated with the influence of the perpendicular MSRD$_\perp$ $\Delta \sigma^2_{\perp}$(Co–O), i.e. the thermal atomic displacement in the direction perpendicular to the Co-O bond. However, the Co–O bond lengths determined from the EXAFS analysis in our experiment are always shorter with respect to those obtained from the diffraction, and this deviation increases with temperature. We interpret this deviation to the Co$^{3+}$ spin-state transition from HS to IS at ~80 K, leading to important difference Co–O bond lengths measured by EXAFS and XRD. The observed anomalous decrease of EXAFS Co–O bond lengths with respect to diffraction Co–O bond lengths above ~80 K could be explained in the frame of a model based on the gradual growth of IS/HS ratio Co$^{3+}$ fraction in a LS basic matrix. Such result can be explained by similar values of small ion radiiues of LS and IS with respect to the HS ion radius [7], i.e. the HS Co–O distance essentially bigger LS and IS Co-O distance. The existing of significant fraction of HS states in LS basic matrix at low temperature can be also confirmed by an increase of Debye-Waller factor at low temperatures (Fig. 1).

4. Conclusions

We have observed an anomalous temperature behaviour of the Co–O bond length in LaCoO$_3$ by a combined analysis of EXAFS and diffraction results which is well described by a thermally induced spin-state transition from HS to the IS in LS matrix in both cases [4, 10-13, 17-19]. An increase of
Debye-Waller factor obtained from XRD at 10-20 K can be explained by the contribution of HS Co$^{3+}$ stabilized by influence of structural defects due to oxygen vacancies and scraps of chemical bonds at the boundary of powder grains [16].

The main results our study are supported by the existing magnetic susceptibility [3], the MCD measurements [11], inelastic neutron data [12] as well as by structural properties under high pressure [17-19].

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References