$LaCoO_3$ PEROVSKITE, A NEW COBALT REFERENCE FOR EXAFS INVESTIGATIONS

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$LaCoO_3$ perovskite was investigated via EXAFS and XRD measurements. The Fourier transform of the extended X-ray absorption spectrum was simulated using the FEFF8 ab initio XAFS code, which simulates the contributions of the different scattering paths to the EXAFS spectrum. $LaCoO_3$ is a well characterized perovskite and therefore constitutes an interesting reference for data interpretation of related compounds such as $La_{1-x}Ca_xCoO_3$ and $La_{1-x}Sr_xCoO_3$, which are important compounds used in energy technology.

1 INTRODUCTION

Cobalt oxides, and particularly cobaltates with perovskite structure, are endowed with interesting catalytic, ion-conduction, magnetic, and semiconducting properties. $LaCoO_3$ for instance exhibits catalytic activity above 700 °C, where CO can be oxidized and NO_x decomposed[1]. $La_{1-x}Ca_xCoO_3$ can be used in bifunctional porous oxygen diffusion electrodes as a catalyst to reduce and to evolve oxygen[2], while $La_{1-x}Sr_xCoO_3$ is widely used as an oxygen-ion-conducting and electron-conducting electrode material in high temperature fuel cells[3].

Synchrotron x-ray absorption spectroscopy is a very useful tool to investigate the electronic properties and structure of these compounds. In many cases it even offers the possibility for in-situ investigations during ongoing processes. Information about the valence state and electron configuration of cobalt can be obtained from the XANES region, while the EXAFS region offers structural information about nearest-neighbour atoms and geometrical arrangement around the absorbing atom.

2 EXPERIMENTAL

X-ray absorption was measured on beam line X-11A of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL) with the storage ring operating at 2.52 GeV beam energy and with beam currents between 340 mA and 140 mA. A Si(111) double-crystal monochromator was used for energy selection. The intensities of the incident and transmitted X-rays were monitored by nitrogen-filled ionization chambers.

X-ray diffraction data were obtained using a Philips X-Pert Diffractometer with Cu Kα radiation.

The *perovskite catalyst* was prepared by calcination of citric La, Ca, and Co precursor salts at 700 °C, as previously described [2].

Samples for the X-ray absorption measurements were prepared by mixing the pure perovskite powder with BN (1 : 5) and compressing this diluted sample to a pill. The samples were fixed to an adequate sample holder and brought into the X-ray beam.

3 RESULTS AND DISCUSSION

XRD Results and Structure of $LaCoO_3$ The XRD results of the $LaCoO_3$ powder are shown in Figure 1.

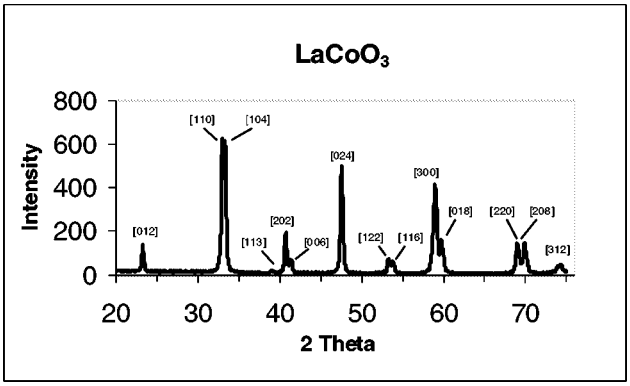

Fig. 1: Powder X-ray diffraction pattern of $LaCoO_3$ prepared by the citrate-precursor method.

They are in good agreement with published X-ray diffraction data of this compound [4]. In a more recent neutron diffraction study [5] the crystal structure has been classified with the space group R-3C (with index #167 in the International Tables of Crystallography). The coordinates of the La, Co, and O atoms having Co in the origin are listed in Table 1.

Atom / M (Wy) *	X	Y	Z
La / 2 (a)	0.25	0.25	0.25
Co / 2 (b)	0.00	0.00	0.00
O / 6 (e)	0.1982	0.3018	0.75

(* M=Multiplicity; Wy=Wyckoff letter)

Table 1: Coordinates of the elements in $LaCoO_3$.

Figure 2 shows the raw Co K-edge EXAFS Spectrum of $LaCoO_3$. The normalized, background-subtracted and k^3-weighted Co EXAFS spectrum is shown in Figure 3, while its Fourier Transform (Bessel function weighted) provides the radial structure function plotted in Figure 4. Figures 3 and 4 also show FEFF simulation fit results for the first and second scattering shells (see below).

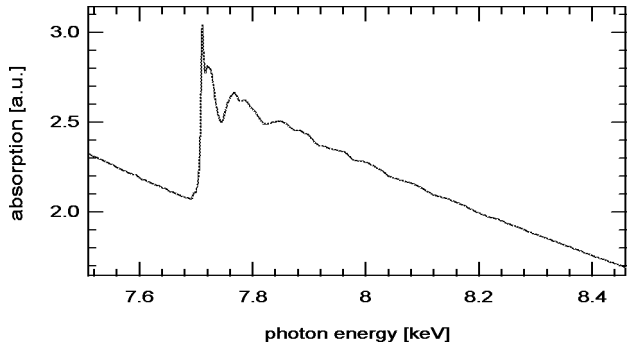

Fig. 2: Raw Co K-edge EXAFS spectrum of $LaCoO_3$.

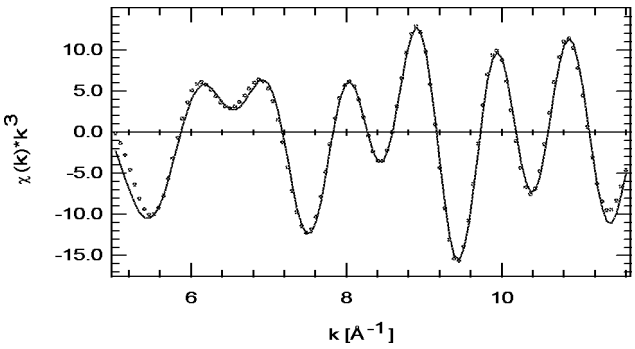

Fig. 3: Normalized, background-subtracted and k^3-weighted Co EXAFS spectrum of $LaCoO_3$. Drawn curve represents fitted results through the experimentally derived data points (o).

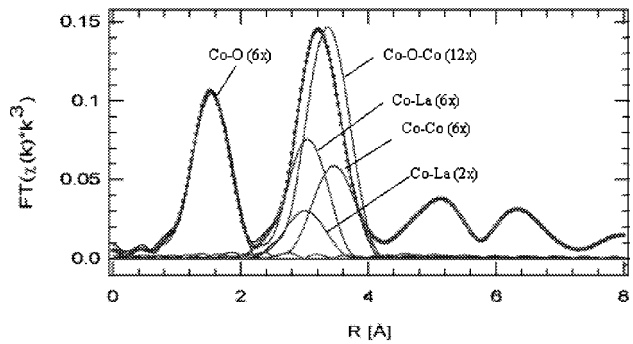

Fig. 4: Radial structure function from Fourier Transformation of $k^3\chi(k)$ shown in Figure 3. Also shown are fitted shell contributions as discussed in the text.

The Fourier transform was performed using the k-space range between 5.0 and 11.6 $Å^{-1}$. It shows two strong and well-defined peaks and two weaker, more structured peaks at higher interatomic distances. The peak positions are close to the radius of the back-scattering shells. However, to obtain the correct radius of the shells, the data have to be amplitude and phase corrected. This can be done using the FEFF8 simulation mentioned. Taken together with the crystal data, we obtained an almost perfect fit of the EXAFS spectrum and its Fourier transform by using the most important scattering paths indicated in Table 2. The FEFF parameters used to fit the EXAFS $k^3\chi(k)$ Fourier transform shown in Figure 4 are listed for the most important scattering paths in Table 2.

FIT RESULTS	S.G.= R –3 C (#167)			
Path	**CN ***	**R**	**σ^2**	**ΔE_o**
Co-O	6	1.925	4.67	1.66
Co-La	2	3.273	7.19	-6.25
Co-La	6	3.316	8.20	-5.75
Co-Co	6	3.826	7.21	2.61
Co-O-Co (MS)	12	3.826	6.78	-5.12

(*= Fixed in fit; MS=Multi-scattering)

Table 2: Structural parameters of $LaCoO_3$ sample derived from Co-EXAFS analysis: Phase shifts (ΔE_o, eV), Interatomic distances (R, Å), Coordination numbers (CN), and Debye-Waller factors (σ^2, $Å^2 \bullet 10^{-3}$).

The fitted interatomic distances differed by less than 0.01 Å from the crystallographic data. The Debye-Waller factors, σ^2, all below 0.01, indicate low thermal disorder in the sample.

4 CONCLUSION

The X-ray diffraction data of $LaCoO_3$ perovskite are helpful for an accurate simulation of EXAFS spectra of this compound and their Fourier transforms. The FEFF fitting parameters obtained will be good starting values for the simulation of spectra of technically important related perovskites such as $La_{1-x}Ca_xCoO_3$ and $La_{1-x}Sr_xCoO_3$.

5 REFERENCES

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