EXAFS study of $LaMn_{1-x}Co_xO_3$ compounds

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Abstract

A systematic study of cobalt environment in the $LaMn_{1-x}Co_xO_3$ perovskite series by means of X-ray absorption spectroscopy in the EXAFS range is reported. The spectra were measured at the K edge of Co on powder samples at room temperature and analysed using multiple scattering paths calculated with the FEFF8 computer program. The next neighbor oxygen shell of cobalt shows a decrease of the distance from the central ion with increasing Co doping. This corresponds to an increased oxidation level of 3d ions. An information on the distortion of the oxygen octahedra and the Debye–Waller factor is discussed.
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1. Introduction

The compounds $LaMn_{1-x}Co_xO_3$ belong to the family of manganites and cobaltites which exhibit exciting structural, electronic and magnetic properties. These properties depend strongly on spin, lattice, orbital and charge degrees of freedom which are interrelated. The two main interactions responsible for magnetic ordering in manganites/cobaltites are the double exchange and the superexchange interaction. The double exchange occurs e.g. between $Mn^{3+}-O-Mn^{4+}$ and leads to ferromagnetic ordering and metallicity. The superexchange interaction dominates for the neighboring ions of the same nominal valence, e.g. $Mn^{3+}-O-Mn^{3+}$. It usually leads to antiferromagnetic ordering and corresponds to insulating properties.

The $LaMn_{1-x}Co_xO_3$ series exhibits a change of structure from orthorhombic, space group Pbnm, to rhombohedral, space group R-3c [1]. This change occurs around $x = 0.6$ and is accompanied with a jump in the unit cell volume. The transition metal ion is located inside of ideal or distorted oxygen octahedron in the rhombohedral and the orthorhombic structure, respectively. For the orthorhom-

bic structure three different distances between the transition metal and the nearest oxygen ions can be found. The lanthanum and the transition metal ions form a NaCl-like lattice. In order to study details of the evolution of local environment of transition metal ions with doping, the X-ray absorption spectroscopy in the EXAFS (Extended X-ray Absorption Fine Structure) range was used.

2. Experimental

The EXAFS measurements were carried out at the K edge of Co in transmission mode at room temperature on the A1 station in HASYLAB/DESY, Hamburg. Double Si(1 1 1) crystal monochromator with energy resolution of order of 2 eV was used and absorption spectra μ were measured in the energy range from 7500 to 8700 eV. Polycrystalline samples of $LaMn_{1-x}Co_xO_3$ with (x = 0.2, 0.4, 0.5, 0.6, 0.8, 1.0), the same as in Ref. [2], were used.

3. Data analysis

The experimental data were analysed with software packages FEFF [3]. First, in the IFEFFIT program the edge energy E_0 was determined as a maximum of the first

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derivative of the experimentally determined absorption μ function. The pre-edge and the post-edge regions were fitted by linear and quadratic functions, respectively. The difference between linear and quadratic function at the edge energy was taken as the edge step value, $\Delta\mu(E_0)$ and the absorption was normalised to this value. The EXAFS function $\chi(k)$ and its Fourier transformation $\chi(R)$ were determined by removing the free atom background (by applying the AUTOBK function) from $\mu(k)$. The free atom background was found by minimising $\chi(R)$ in the R-range $0-1.2$ Å. For the Fourier transformation the Hanning window with the shape parameter $dk = 3$ in the IFEFFIT program was used.

All the possible scattering paths of the photoelectron for the nearest neighbors and their contributions to the total $\chi(k)$ were considered. The effective backscattering amplitude F_{eff}, the phase correction $\gamma(k)$ and the total central atom phase shift ξ were calculated for each scattering path with the FEFF8 program. The structural data obtained from X-ray diffraction measurements [1] served as the input parameters for calculations and the starting values for fitting. Total χ function was constructed according to the equation:

$$\chi(k) = S_0^2 \, \mathscr{R} \left[\sum_{\text{shell}} \frac{N F_{\text{eff}}}{kR^2} e^{\frac{-2R}{\lambda} - 2k^2\sigma^2} \sin\left(2kR + \gamma(k) + \xi\right) \right],$$

where N is a number of atoms in each shell and S_0^2 is the amplitude of $\chi(k)$ function, σ^2 is Debye–Waller factor, λ is the mean free path and $\mathscr{R}$ is the total central atom loss factor. This function was fitted to the experimental data. The fitting was carried out in the R space in the k-range $2.5-12$ Å^{-1} and R-range $0.7-1.9$ Å. The number of independent points for this range is slightly higher than 6.

4. Fitting

In order to find the best model for fitting the experimental data, different models were tested for individual compounds taking their symmetry into account. The best model for the rhombohedral structure was obtained with four fitted parameters: E_0 (edge energy), S_0^2 (amplitude of χ function), a single Co–O distance and the Debye–Waller factor σ^2 (rhombohedral model). For the orthorhombic

structure the best model included five fitted parameters: E_0, S_0^2 and three Co–O distances (orthorhombic model). The Debye–Waller factor was left out from the fit to keep the number of fitted parameters smaller than the number of independent points. For the compound with $x = 0.6$, where the structural change occurs, both models were applied and the results are consistent for this sample (see Fig. 1).

The fitting proceeded in several steps. At first the E_0 and S_0^2 were fitted, then σ^2 was added (when used) and finally all the parameters were fitted together. The values of the fitted parameters are presented in Table 1.

5. Results and discussion

Our main finding is a decrease of the Co–O distances with increasing Co content in the compound, which can be seen in Fig. 1. The decrease of Co–O distance is around 5% for $0.2 \leqslant x \leqslant 0.6$ and 2.5% for $0.6 \leqslant x \leqslant 1$ contrary to composition dependence of the lattice parameters [1] where the decrease of lattice parameter is up to 2% in the whole region $0.2 \leqslant x \leqslant 1$.

The effect of Co-O distance decreasing can be attributed to a change of the mean Co valence with doping, when we consider a decrease of the ionic radius with increasing Co
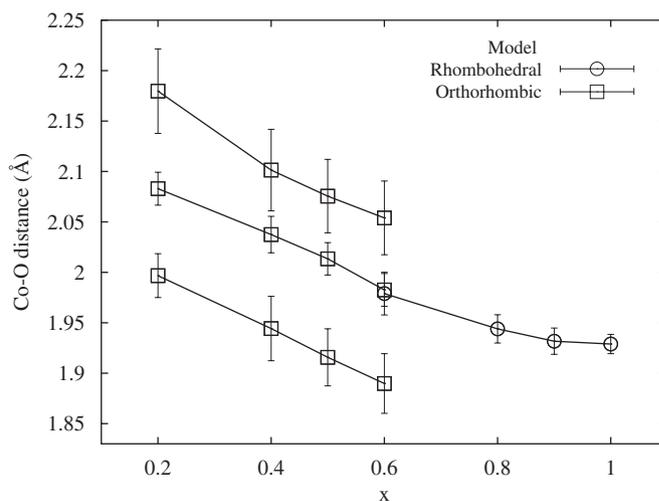

Fig. 1. The fitted values of cobalt–oxygen distances in the series of samples LaMn$_{1-x}$Co$_x$O$_3$.

Table 1
The values of fitted parameters E_0, S_0^2, σ^2 and used model

x	(E_0 eV)	S_0^2 (a.u.)	σ^2 (10^{-3} Å^2)	Model
1.0	−8 (2)	0.53(4)	2 (1)	Rhomb.
0.9	−9 (2)	0.44(5)	3 (1)	Rhomb.
0.8	−8 (2)	0.47(5)	4 (1)	Rhomb.
0.6	−8 (4)	0.41(7)	6 (2)	Rhomb.
0.6	−10 (2)	0.62(7)	–	Orth.
0.5	−8 (2)	0.64(6)	–	Orth.
0.4	−9 (2)	0.67(8)	–	Orth.
0.2	−7 (2)	0.75(8)	–	Orth.

oxidation. The result is consistent with that found in the edge energy shifts on doping in the XANES study of this series [2]. Debye–Waller factor shows (Table 1) a systematic increase with decreasing Co content, which can possibly be attributed to the increasing distortion of the oxygen octahedra around cobalt with manganese doping.

Acknowledgement

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