INFLUENCE OF OXIDATION DEGREE AND SYMMETRY OF THE SITE ON K-ABSORPTION SPECTRA OF SIX COORDINATED IRON AND COBALT IN OXIDES

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RESUME : L'étude du fer et du cobalt dans des états d'oxydation élevés (Fe : +3, +4, +5 ; Co : +3, +4), en coordination métal-oxygène régulière (O_h) et distordue

(D_{4h}) a été réalisée par spectrométrie d'absorption X aux seuils K de Fe et Co. Nous avons montré comment l'analyse de l'EXAFS permet de préciser l'information qualitative obtenue sur la distorsion du site de l'atome absorbant à partir de la forme de la région spectrale du seuil K du métal.

ABSTRACT : EXAFS and near K-edge absorption spectra of iron and cobalt in high oxidation states (Fe : +3, +4, +5 ; Co : +3, +4), with regular (O_h) and distorted (D_{4h}) octahedral metal-oxygen coordination, have been studied. It is shown how EXAFS allows to specify the qualitative information obtained on the distortion of the absorbing atom site from the shape of the near edge absorption spectra.

I - INTRODUCTION

A comparative study of various valencies of iron in six-fold oxygen coordination has been recently reported, showing the influence of both oxidation state and distortion of the iron site on the shape of the Fe K-absorption spectrum (1). New results are presented here on some cobalt oxides. Near-edge absorption spectra and EXAFS are used together to investigate the distortion of the transition metal sites.

II - EXPERIMENTS, MATERIALS AND DATA ANALYSIS

The X-ray absorption spectra of iron and cobalt in high oxidation states (Fe : +3, +4, +5, Co : +3, +4) have been recorded using synchrotron radiation of DCI (LURE), in transmission mode. More details are given in Ref. 1.

The studied compounds, whose structure are described elsewhere (1,2), can be classified in two series :

- $LaFe^{3+}O_3$, $SrFe^{4+}O_3$, $La_2LiFe^{5+}O_6$, $LaCo^{3+}O_3$ crystallize in perovskite-like structures. In each of the four, the transition metal site presents a regular octahedral symmetry.

- $Sr_{0.5}La_{1.5}Li_{0.5}Fe^{4+}O_4$, $La_2Li_{0.5}Co^{3+}O_4$, $La_2Li_{0.5}Cu_{0.4}Co_{0.1}^{3+}O_4$, $Sr_{0.5}La_{1.5}Li_{0.5}Fe^{4+}O_4$ have the K_2NiF_4 type structure. In their case the symmetry of the transition metal site is lowered from O_h to D_{4h} .

The near K-edge spectra of the Fe and Co oxides are presented on the figures 1-a and 2-a respectively, together with the $X(E)$ data (fig. 1-b and 2-b). The window used for the FT of the $k^3X(k)$ data (fig. 1-c and 2-c) extends from 38 to 315 eV for

Figure 1: Fe K-edge absorption spectra of the investigated iron oxides (a) Near edge region; (b) $X(E)$ data; (c) R.D.F. (without phase corrections; (d) Back FT of the first shell (dots) and results of the calculations (full lines).

iron data and 45 to 315 eV for cobalt data. The amplitudes and phase-shifts used for the calculation of the back FT of the first oxygen neighbours shell are extracted from the same analysis of LaFeO_3 and LaCoO_3 , whose coordination polyhedra are regular (3,4). On the figures 1d and 2d are drawn the back FT of the experimental data (dotted lines), and the calculated curves (full lines), using the parameters reported in table 1.

Figure 2: Co K-edge absorption spectra of the investigated cobalt oxides (a) Near edge region; (b) $X(E)$ data; (c) R.D.F. (without phase corrections; (d) Back FT of the first shell (dots) and results of the calculations (full lines).

III - RESULTS AND DISCUSSION

III-a) O_h transition metal symmetry

The regular octahedral symmetry of the metallic site (O_h) is characterized by a symmetrical and rather narrow line in oxides of perovskite like structure : $\text{LaFe}^{3+}\text{O}_3$, $\text{La}_2\text{LiFe}^{5+}\text{O}_6$, $\text{LaCo}^{3+}\text{O}_3$, $\text{SrFe}^{4+}\text{O}_3$. The expected shift towards the high

energies (2.4 eV) is observed when the oxidation state of iron increases from + 3 to +5. The peculiar case of SrFeO_3 has been discussed in Ref. 1.

For $\text{La}_2\text{LiFe}^{5+}_6\text{O}_6$ and $\text{SrFe}^{4+}_3\text{O}_3$, fitting of the back FT of the first oxygen shell yields 6 and 5.7 atoms at 1.93 and 1.86 Å respectively, which is a good confirmation of the regular six-fold coordination of Fe^{4+} and Fe^{5+} in those oxides, as evidenced previously by X-ray diffraction (fig. 1-d and Table 1).

TABLE 1

Compound	CRYSTALLOGRAPHY					X RAY ABSORPTION									
						K-edge			E.X.A.F.S.						
	Struct.	$\frac{c}{a}$	d_{eq} (Å)	d_{ax} (Å)	$\frac{d_{ax}}{d_{eq}}$	Edge energy (eV)	Max energy (eV)	ΔE (eV)	N_{eq}	d_{eq} (Å)	d_{ax} (Å)	N_{ax}	d_{ax} (Å)	Δr_{ax} (Å)	$\frac{d_{ax}}{d_{eq}}$
$\text{LaFe}^{3+}_3\text{O}_3$	perovsk.	-	2.006	2.006	1	7122	7125.6	3.6	4.0 ^a	2.006 ^a	-	2.0 ^a	2.006 ^a	-	1
$\text{SrFe}^{4+}_3\text{O}_3$	perovsk.	-	1.925	1.925	1	7122	7125.7	3.7	4.0	1.93	0	2.0	1.93	0	1
$\text{La}_2\text{LiFe}^{5+}_6\text{O}_6$	perovsk.	-	1.858	1.858	1	7124	7128.0	4.0	4.0	1.86	0.04	1.7	1.86	0.04	1
$\text{Sr}_{0.5}\text{La}_{1.5}\text{Li}_{0.5}\text{Fe}^{4+}_{0.5}\text{O}_4$	K_2NiF_4	3.45	1.79	2.29	1.28	7122	7124.0 7127.0	2.0 5.0	4.0	1.83	0.04	2.0	2.29	0.10	1.25
$\text{LaCo}^{3+}_3\text{O}_3$	perovsk.	-	1.932	1.932	1	7718	7721.2	3.2	4.0 ^a	1.932 ^a	-	2.0 ^a	1.932	-	1
$\text{La}_2\text{Li}_{0.5}\text{Co}^{3+}_{0.5}\text{O}_4$	K_2NiF_4	3.34	-	-	-	7717	7720.5	3.5	4.0	1.86	0	2.0	2.16	0.17	1.16
$\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.4}\text{Co}^{3+}_{0.1}\text{O}_4$	K_2NiF_4	3.50	-	-	-	7717	7720.5	3.5	-	-	-	-	-	-	-
$\text{Sr}_{0.5}\text{La}_{1.5}\text{Li}_{0.5}\text{Co}^{4+}_{0.5}\text{O}_4$	K_2NiF_4	3.36	-	-	-	7718	7722.4	4.4	4.0	1.87	0	2.0	2.20	0.17	1.16

(a) Reference compound

III-b) D_{4h} transition metal symmetry

When the symmetry of the metallic site is lowered from O_h to D_{4h} in $\text{Sr}_{0.5}\text{La}_{1.5}\text{Li}_{0.5}\text{Fe}^{4+}_{0.5}\text{O}_4$, the main absorption line is split. This can be explained by a lifting of the degeneracy of the t_{1u} level in D_{4h} symmetry ($t_{1u} \rightarrow a_{2u} + e_u$) (fig.3) (1). Despite the higher value of $\Delta\sigma$ for the coaxial Fe-O bonds, we are able to evidence their contribution to the back FT of the first shell, and to measure their distances with a rather good accuracy (fig. 1-d and Table 1). Their are very close to those obtained by neutron diffraction (2).

For cobalt oxides of K_2NiF_4 structure, $\text{La}_2\text{Li}_{0.5}\text{Co}^{3+}_{0.5}\text{O}_4$, $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.4}\text{Co}^{3+}_{0.1}\text{O}_4$, $\text{Sr}_{0.5}\text{La}_{1.5}\text{Li}_{0.5}\text{Co}^{4+}_{0.5}\text{O}_4$, only a broadening measured by ΔE , of the absorption line is observed. The K-edge cobalt spectra are less resolved than K-edge iron spectra, partly due to the increase of the natural width of the 1s level, partly due to lower splitting of the t_{1u} M.O. (fig. 3) (2). This suggests that the distortion of the octahedral metallic sites is less marked in the cobalt compounds.

For $\text{La}_2\text{Li}_{0.5}\text{Co}^{3+}_{0.5}\text{O}_4$ and $\text{Sr}_{0.5}\text{La}_{1.5}\text{Li}_{0.5}\text{Co}^{4+}_{0.5}\text{O}_4$, a two subshells fitting procedure leads to the first measurement of the Co-O bond lengths, respectively 1.86 and 1.87 Å for $d_{\text{equatorial}}$ and 2.16 and 2.20 Å for d_{axial} (fig. 2-d and table 1). The distortion of the cobalt site is smaller than that of the iron site in $\text{Sr}_{0.5}\text{La}_{1.5}\text{Li}_{0.5}\text{Fe}^{4+}_{0.5}\text{O}_4$, in agreement with our interpretation of near edge spectra. These results are well correlated with c/a ratios of the K_2NiF_4 crystal cells, which are often considered to be representative of the distortion of the metallic surrounding.

XANES theory is difficult to carry out for the study of the distortion of the absorbing atom site in such crystalline compounds. The shape of the near K-edge spectra of transition metals can bring a qualitative information on the regularity of their coordination polyhedra, which is well correlated with the numerical results deduced from EXAFS analysis.

Figure 3 : Qualitative M.O. scheme for a regular MO_6 octahedron (here $\text{M}=\text{Fe}^{5+}$).

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