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► **To cite this version:**

M. Lenglet, R. Guillaumet, A. d'Huysser, J. Durr, C. Jørgensen. Fe, Ni COORDINATION AND OXIDATION STATES IN CHROMITES AND COBALTITES BY XPS AND XANES. Journal de Physique Colloques, 1986, 47 (C8), pp.C8-765-C8-769. 10.1051/jphyscol:19868146 . jpa-00226048

**HAL Id: jpa-00226048**

**<https://hal.science/jpa-00226048v1>**

Submitted on 4 Feb 2008

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**Fe, Ni COORDINATION AND OXIDATION STATES IN CHROMITES AND COBALTITES BY XPS AND XANES**

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**Résumé** - La structure fine du préseuil de spectres d'absorption K du fer dans les spinelles peut être interprétée au moyen de l'analogie  $Z + 1$ . Des applications de la spectrométrie d'absorption X en vue de la caractérisation de la liaison chimique dans différents oxydes mixtes de nickel sont présentées.

**Abstract** - The pre-edge fine structure of iron K-edge in spinels may be interpreted by a final  $Z + 1$ ,  $(3d)^{n+1}$  configuration. The application of XANES for determining the local structure and chemical bonding in nickelcobaltite and ferrichromites are discussed.

The X-ray absorption high resolution Fe and Ni k-edges in  $\text{NiFe}_{2-x}\text{Cr}_x\text{O}_4$ ,  $\text{Ni}_x\text{FeCr}_{2-x}\text{O}_4$  and  $\text{Ni}_{1-x}\text{CO}_{2+x}\text{O}_4$  systems are recorded using synchrotron radiation at LURE, Orsay.

**Fe K-edges in**  $\text{Fe}_{1-x}^{2+}\text{Fe}_x^{3+} [\text{Cr}_{2-x}^{3+}\text{Ni}_x^{2+}] \text{O}_4^{2-}$  **compounds** ( $0 < x < 1$ )

The Fe pre-edge fine structure in Fe (II) and Fe (III) reference compounds is analysed as a function of coordination number (Table 1). The experimental results are associated with optical spectroscopic data and may be interpreted by a final  $Z + 1$   $(3d)^{n+1}$  configuration in agreement with previous study (1). Since there is no inversion center in tetrahedral coordination the mixing of Fe 3d with oxygen-2p orbital is more important than in octahedral symmetry: the pre-edge in  $\text{NiFeCrO}_4$  is ten times stronger than in  $\text{ZnFe}_2\text{O}_4$ .

The fine structure of the pre-edge in Fe K-edge absorption spectra of mixed valence compounds like  $\text{Fe}_{1-x}^{2+}\text{Fe}_x^{3+} [\text{Cr}_{2-x}^{3+}\text{Ni}_x^{2+}] \text{O}_4^{2-}$  may be interpreted with these data (Fig. 1).

In such compounds with a mixed valence tetrahedral sublattice, the experimental intensity of the two components located at 7095.5 and 7097 eV may be correlated with the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio (2).

**TABLE 1 - Fine structure of the Fe pre-edge in spinels**

Compounds	NiFeCrO <sub>4</sub>	ZnFe <sub>2</sub> O <sub>4</sub>	FeCr <sub>2</sub> O <sub>4</sub>	Ni <sub>x</sub> FeCr <sub>2-x</sub> O <sub>4</sub>		
				x=0.75	0.5	0.25
Fe coordination	Td	Oh	Td	Td	Td	Td
Energy in eV and intensity <sup>#</sup> of the pre-edge components	7097.3(127%)	7096.8	7095.6(65%)	7097.2(10%)	7095.7(49%)	7095.7(54%)
$\Delta E_K^*$ (eV)	9.3	10	7		7.6	7.4
Spectroscopic data (from Z+1 analogy)	10dq 0.5eV	1.5eV	$\Delta(4F-4P) : 1.4eV$			
# The absorbance is normalized by reference to the maximum absorption						
* $\Delta E_K$ : chemical shift oxide minus metal.						

**XANES and X-ray photoelectron spectra in Ni compounds**

The effect of coordination geometry and effective atomic charge on the absorbing atom is shown in figures 2, 3 and 4 where X-ray absorption spectra near the K-edge in various nickel compounds are plotted. The Racah parameter and K-edge chemical shift may be correlated with the bond ionicity for Ni (II) compounds, and the energy position of the first maximum  $E_A$  after the rising edge follow the rule :  $\Delta_{AC} \cdot d^2 = \text{Const.}(5)$ , ( $E_A$  : energy position of the transition to an antibonding state of 3d character on the metal ion) :

	NiCr <sub>2</sub> O <sub>4</sub>	Ni <sub>0.5</sub> Zn <sub>0.5</sub> Cr <sub>2</sub> O <sub>4</sub>	NiO	NiGa <sub>2</sub> O <sub>4</sub>	NiF <sub>2</sub>	Ref
Ni <sup>2+</sup> coordination	Td	Td	Oh	Oh	Oh	
$D_q$ (cm <sup>-1</sup> )	400	390	880	940	760	3
B (cm <sup>-1</sup> )	750	780	800	930	950	3
$\Delta E_K$ (eV)	8.4	8.6	~ 9	10.7	10.5	
$\Delta_{AC} \cdot d^2$		77.5	74.8	71.8	73	

The Ni 2p photoelectron spectra have been analysed for tetrahedral and octahedral Ni<sup>2+</sup> environments in reference compounds : Ni<sub>0.5</sub>Zn<sub>0.5</sub>Cr<sub>2</sub>O<sub>4</sub> and NiFe<sub>2</sub>O<sub>4</sub> (4).

From this study, one can conclude that the changes of XPS parameters (energy separation  $E$  and relative intensity ratio  $I_s/I_m$  of the satellite to the main peak for Ni 2p 1/2 and Ni 2p 3/2 in each coordination) allow the identification of different nickel species in the spinel structure.

**Analytical applications**

- NiFe<sub>2-x</sub>Cr<sub>x</sub>O<sub>4</sub> system

In nickel ferrichromites the crystallographic transition (Q + C, I 4<sub>1</sub>/amd + (Fd 3m) and the migration of Ni<sup>2+</sup> ions from A<sub>1</sub> to B sites in the range  $1 \leq x \leq 2$  due to the high octahedral site preference of Cr<sup>3+</sup> ion (8) may be correlated with the evolution of the XPS parameters (9). The main line of Ni 2p 3/2 spectra in ferrimagnetic compounds ( $x < 1$  Ni<sup>2+</sup> in Oh symmetry) is characterized by a variable peak asymmetry decreasing with the attenuation of the magnetic interaction as in Ni<sub>x</sub>Mg<sub>1-x</sub>O (6).

From XAS measurements (chemical shift and fine structure of the main peak) it is possible to get information upon the Ni<sup>2+</sup> coordination. The intensity of the pre-edge allows to estimate the 4-fold to 6-fold ratio of nickel sites in the range  $1 \leq x \leq 2$  (fig. 5). A good correlation is obtained with the ionic configuration issued from neutron diffraction (7), Mössbauer and optical data (Table 2).

- NiCO<sub>2</sub>O<sub>4</sub>

From XPS and XAS studies, it may be concluded that NiCO<sub>2</sub>O<sub>4</sub> is a mixed valence compound with a mixture Ni<sup>2+</sup> + Ni<sup>3+</sup> on octahedral sites (neutron diffraction data disclose 90 per cent of nickel in Oh symmetry for NiCO<sub>2</sub>O<sub>4</sub> and Ni<sub>0.5</sub>CO<sub>2.5</sub>O<sub>4</sub>).

In Ni<sub>x</sub>CO<sub>3-x</sub>O<sub>4</sub> system (0.5 < x < 1) the redox equilibrium

Ni<sub>Oh</sub><sup>3+</sup> + CO<sup>2+</sup> ⇌ Ni<sub>Oh</sub><sup>2+</sup> + CO<sup>3+</sup> is more shifted towards the left hand side with x decreasing values.

**TABLE 2**

	x	0	0.8	1	1.2	1.4	1.6	1.7	1.8	2	Réf.
% Ni <sup>2+</sup> in tetrahedral coordination	(a)	0	2	15	30	52	70		80	100	9
	(b)			~ 10		~ 50		80			9
	(c)	0	0	10	25		65		85		this work
ΔE <sub>K</sub> (eV)		10.2	10.2	9.7	9.4		9		8.5	8.4	
Δ <sub>AC</sub> = E <sub>C</sub> - E <sub>A</sub> (eV)		18.5	18.6	18.9	19	19.1	19.6		20	20.7	
ionic configuration issued from optical absorption at 2100 nm (a), from Mössbauer (b) and X-ray absorption (c) measurements.											

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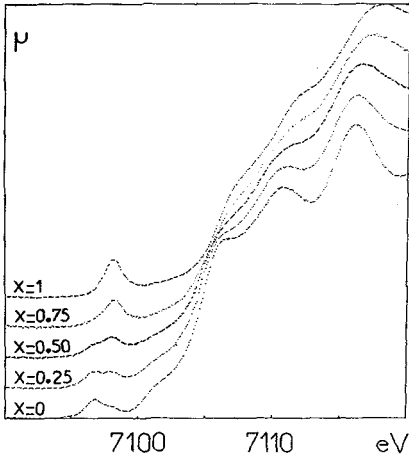


Fig. 1 - Fe K-edge in  $\text{Ni}_x\text{FeCr}_{2-x}\text{O}_4$

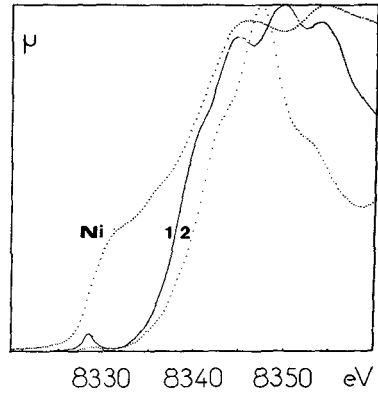


Fig. 2 - Ni K-edge in spinels :  $\text{NiCr}_2\text{O}_4$  (1) and  $\text{NiGa}_2\text{O}_4$  (2)

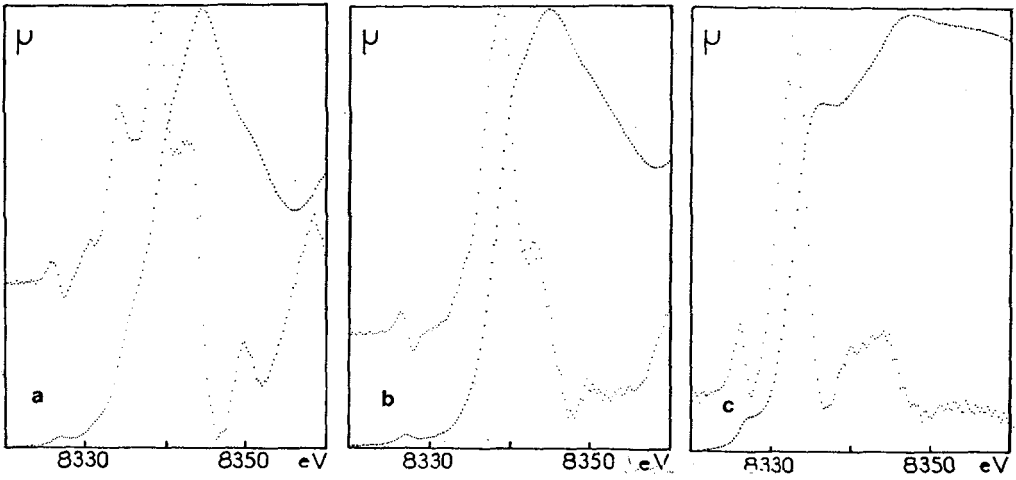


Fig. 3 - Ni K-edge in  $\text{NiO}$  (a) ,  $\text{NiF}_2$  (b) and  $\text{NiS}$  (c)

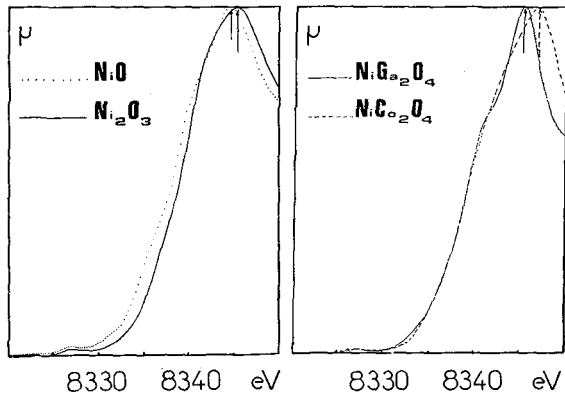


Fig. 4 - Ni K-edge in  $\text{Ni}_2\text{O}_3$  and  $\text{NiCo}_2\text{O}_4$

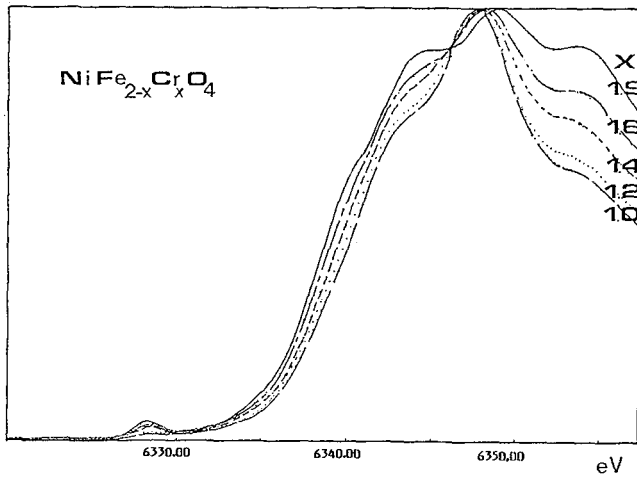


Fig. 5 - Ni-K-edge in cubic compounds of the  $\text{NiFe}_{2-x}\text{Cr}_x\text{O}_4$