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Influence of cations vacancies on the K and L_{III} Zn edges of spinel-related compounds

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To describe the different structural and electronic information which can be obtained on metallic oxide compounds having anion or cation vacancies, XANES experiments are performed at K and L edge of the cations. Data collected on ZnAl₂O₄ spinel compounds as well as numerical simulations are discussed.

Keywords : Zinc, spinel, L edges, XANES

1. Introduction

Compounds having oxygen vacancies exhibit particular physico-chemical properties. For example, in the case of the perovskite type cubic system, disordered oxygen vacancies are intimately linked to ionic conductivity (Mori *et al.*, 1994). Here we conduct a fundamental research study dedicated to spinel related compounds in order to discuss the information which can be extracted from the XANES part of the absorption spectra. In order to achieve this goal, we first recall the structural characteristics of the ZnAl₂O₄ reference compound and the structural parameters derived from the numerical simulations of the EXAFS modulations collected at the Zn K edge on a set of original materials coming from soft chemistry (Bazin *et al.*, 1998). Then, we will discuss the XANES data obtained at the Zn K and L_{III} edges as well as the numerical simulations performed using the FeFF program and corresponding to several structural hypothesis (essentially influence of Zn or O vacancies).

2. Experimental conditions

Absorption spectra were collected at the LURE synchrotron facility from the SACO storage ring (positron beam) running at 800 MeV with an average current of 200 mA for the Zn L_{III} edge and from the DCI storage ring (positron beam) running at 1.85 GeV with an average current of 300 mA for the Zn K edge.

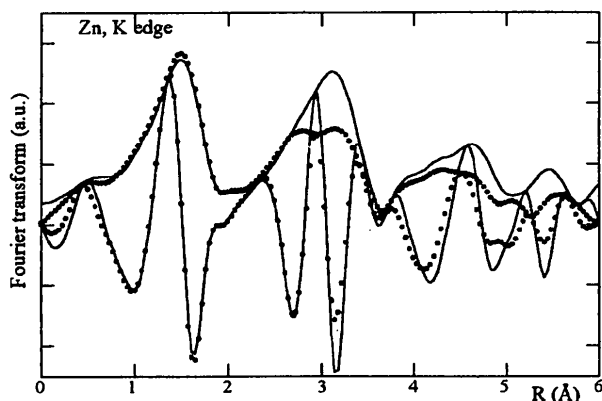


Figure 1
F. T. obtained for the reference compound ZnAl₂O₄ and for sample 1 at the Zn K edge.

For the experiments at SACO (Zn L edge), the experimental set-up is equipped with a double crystal (beryl) monochromator (fixed exit) and with a single grazing mirror for harmonic rejection. Data were collected in total electron yield, the counting time per point being equal to one second. The energy resolution was equal to 0.5 eV. For the second set of experiments (Zn K edge), a double crystal (Si 311) monochromator (fixed-exit, no harmonic rejection) with ion chambers as detectors in transmission geometry was used. The counting time per point was equal to one second.

3. The structural characteristics of the different samples

The quantitative analysis of the EXAFS oscillations (Fig. 1) beyond the Zn K edge shows that the loss of the second peak amplitude of the Fourier transform is mainly due to the fact that the number of Zn-Zn bonds is significantly reduced (fig. 1). The absorption spectroscopy here provides a key result, the high vacancy concentration in the two samples.

Table I

Structural parameters associated to the spinel ZnAl₂O₄ and to the two samples.

Samples	ZnAl ₂ O ₄ †			Sample 1 †			Sample 2 †		
	N	R(Å)	σ ² (Å ²)	N	R(Å)	σ ² (Å ²)	N	R(Å)	σ ² (Å ²)
Zn-O-Zn	4	1.95	3.6	4	1.95	3.6	4	1.95	3.5
Zn-Al-Zn	12	3.36	4.9	10.9	3.34	4.9	10.9	3.35	6.1
Zn-O-Zn	12	3.40	11.1	10.9	3.38	11.1	10.3	3.39	14.5
Zn-Zn-Zn	4	3.50	9.3	0.9	3.49	9.3	2.0	3.50	16.1
Zn-Al-O-Zr	24	3.62	2.5	23.9	3.62	2.5	23.4	3.60	3.7
Zn-O-Zn	12	4.27	2.1	6.6	4.27	2.1	10.9	4.27	2.1
Zn-Al-O-Zr	24	4.36	2.8	14.3	4.36	2.8	22.7	4.37	2.8

†For the debye-waller factor, we report σ²(Å²).10³

4. Results obtained at the Zn K and L_{III} edges.

Fig. 2. and 3 show the K and L_{III} edge of the two samples compared to that of the reference compound ZnAl₂O₄. At the Zn K edge, the shape and the position are quite similar. A significant difference in the XANES part of the absorption spectrum occurs for the amplitude of the first feature.

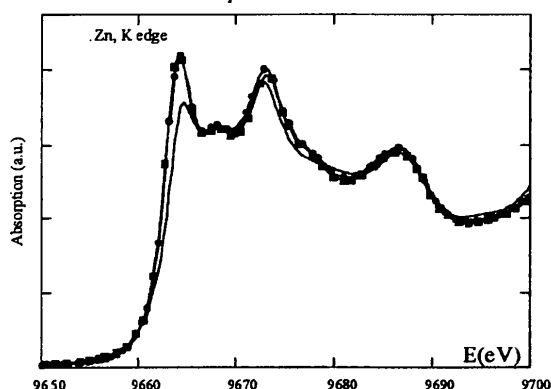


Figure 2
Zn K edge measured for the two samples (Sample 1 circles, sample 2 square) and for the reference compound ZnAl₂O₄ (line)

Regarding the Zn L_{III} edge, again, a great similarity exists between the two samples. Nevertheless, the absorption spectra corresponding to the reference compound ZnAl₂O₄ is more structured.

5. Numerical simulation and discussion

Among the structural hypothesis which have been made, we consider here :

Influence of Zn vacancies. In the case of the ZnAl₂O₄ compound, if the different features positioned at the Zn K edge

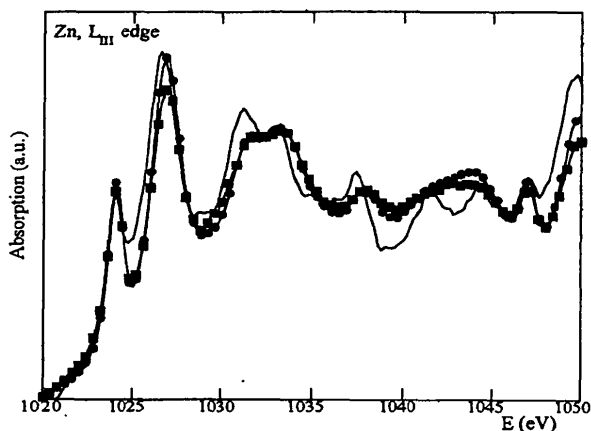


Figure 3

Zn L_{III} edge measured for the two samples (sample 1 circles, sample 2 square) and for the reference compound $ZnAl_2O_4$ (line).

are simulated, their amplitudes are not correct. In the case of Zn vacancies, we can easily see that the different numerical simulations are similar (fig 4).

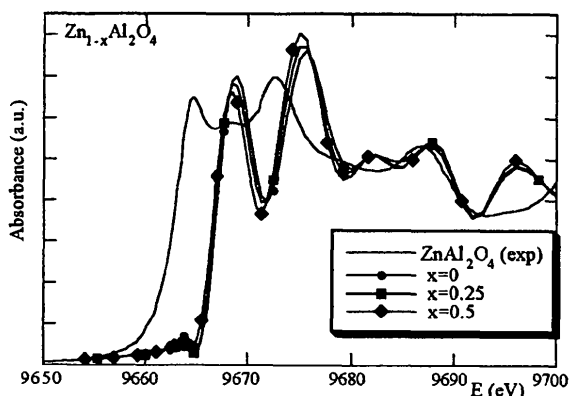


Figure 4

Influence of the Zn vacancy on the Zn K edge as calculated by the FeFF code compare to the reference compound $ZnAl_2O_4$.

Influence of O vacancies. Contrary to the effect of Zn vacancies, this set of numerical simulations indicates that, when the number of O vacancies varies, the Zn K edge exhibits significant variations of the shape and the position of the different features (fig 5).

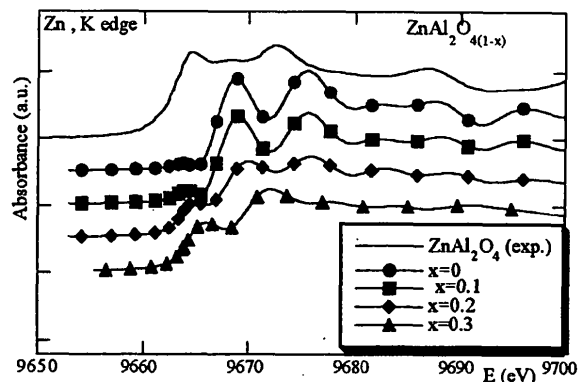


Figure 5

Influence of the Zn vacancy on the Zn K edge as calculated by the FeFF code compare to the reference compound $ZnAl_2O_4$.

Comparison between the Zn K and L_{III} edges. In the case of the reference compound $ZnAl_2O_4$, the electronic state of Zn atoms is $2+$ corresponding to a $3d^{10}$ configuration. The strongest bonding effect in this 3d oxide is the overlap between the oxygen 2p band (filled) and the Zn 4s and 4p-bands (empty). This overlap determines the shape of the oxygen 2p valence band and also the Zn 4s and 4p conduction band. It is the fluctuation of this conduction band which is measured in the K edge of Zn. The similarity between the Zn K and L_{III} edge (fig 6) leads to the conclusion that some overlap exists between the conduction band (zinc 4s and 4p with oxygen 2p) and the 3d band, creating very weak 3d-character with the same shape as the 4p-states.

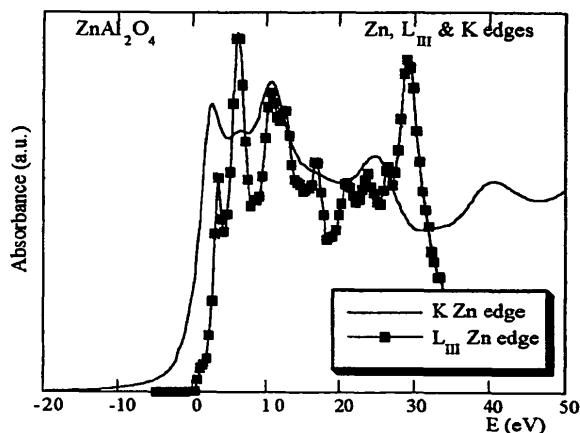


Figure 6

Comparison between the K and L_{III} Zn edge of the reference compound.

6. Conclusion

We have shown through numerical simulations using the FeFF code that, while the effect of cation vacancies is low, fluctuations of the number of oxygen vacancies induce significant modifications in the Zn K edge. We assume here that there is no size effect, the coherence length associated to the two samples being 40 Å. Thus, a clear complementarity is pointed out in this study. The EXAFS analysis underlines a lacunar cation aspect of the solids while the numerical simulation of Zn K edge establishes a significant level of oxygen vacancy. Moreover, the similarity between the Zn K and the Zn L_{III} edges gives evidence of an overlap between the 3d band and the conduction band (Zn 4s and 4p with O 2p). Finally, comments by Dr. F. M. F. De Groot are greatly appreciated.

References

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