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# Improvement in the structural characterization of nanometer-scale metallic oxide. The Xas–Awxas combined approach

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We propose a general schematic view associated to a Exafs-Awxas combined approach in order to study nanometer scale supported metallic oxide. To illustrate our purpose, we focus here on ZnAl<sub>2</sub>O<sub>4</sub> spinel compounds.

Keywords : Exafs, Awxas, Spinel.

## 1. Introduction

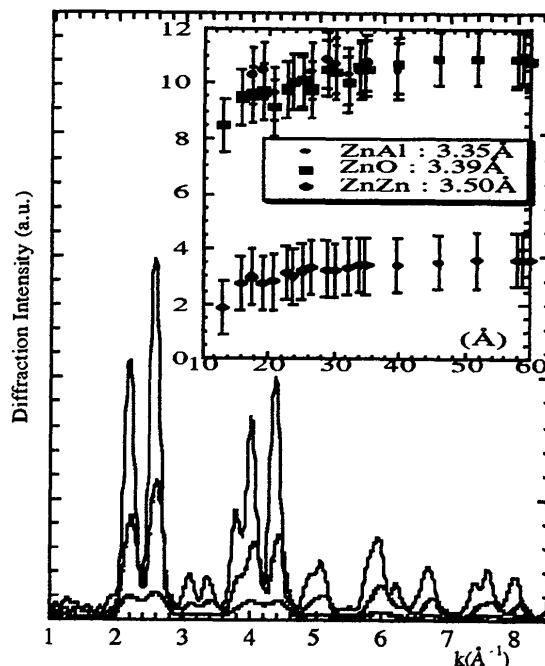
The goal of this paper is to show that major information can be obtained even on poorly ordered supported oxide metallic through a Exafs-Awxas combined approach. To illustrate our purpose we choose spinel compounds and thus we first consider the reference compound ZnAl<sub>2</sub>O<sub>4</sub>. Structural information coming from the second coordination sphere, particular attention has to be paid to photoelectron multiple scattering processes and we have already shown that multiple scattering contributions (table 1) cannot be neglected (BAZIN et al.; 1998). For diffraction, the starting point is given by a simulation of the experimental diagram using the Rietveld method (FULLPROF) in order to test the value of *f*' and *f*'.

**Table I :** Structural parameters associated to the spinel ZnAl<sub>2</sub>O<sub>4</sub> and to the sample "Zn"/Al<sub>2</sub>O<sub>3</sub>

		Reference compound ZnAl <sub>2</sub> O <sub>4</sub>			The sample "Zn"/Al <sub>2</sub> O <sub>3</sub>		
Nature Zn-X-Zn with X=	N	R, Å XRD	R, Å Exafs	σ <sup>2</sup> , Å <sup>2</sup> * 10 <sup>3</sup>	N	R, Å	σ <sup>2</sup> , Å <sup>2</sup> * 10 <sup>3</sup>
O	4	1.95	1.95	3.6	4	1.95	3.6
Al	12	3.35	3.36	4.9	10.9	3.34	4.9
O	12	3.39	3.40	11.1	10.9	3.38	11.1
Zn	4	3.50	3.50	9.3	0.9	3.49	9.3
Al-O	24	3.60	3.62	2.5	23.9	3.62	2.5
O	12	4.27	4.27	2.1	6.6	4.27	2.1
Al-O	24	4.37	4.36	2.8	14.3	4.36	2.8

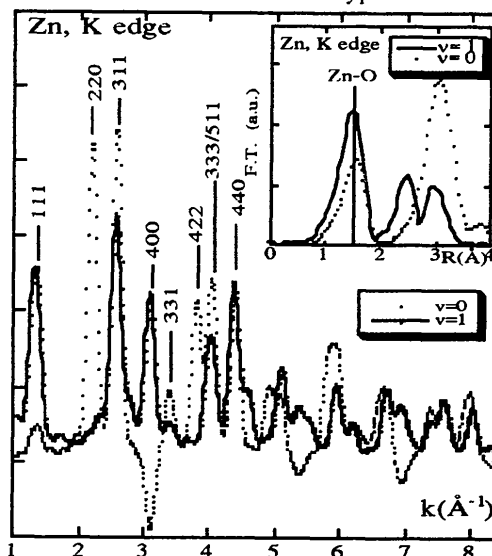
## 2. Ab initio calculations of the Exafs-Awxas data for different structural hypothesis

*The size of the particle* (Fig1). In Exafs, the determination of the size can be done through the coordination numbers only for very small clusters. Due to the mixing of the diffraction features, the Scherrer law cannot be used and thus numerical simulations has to be considered.



**Figure 1**  
Evolution of the differential intensity and the coordination numbers versus the size of the ZnAl<sub>2</sub>O<sub>4</sub> cluster (20, 30 and 40 Å for diffraction, N<sub>ZnAl</sub>, N<sub>ZnO</sub> and N<sub>ZnZn</sub> coordinations in function of the diameter for the Exafs).

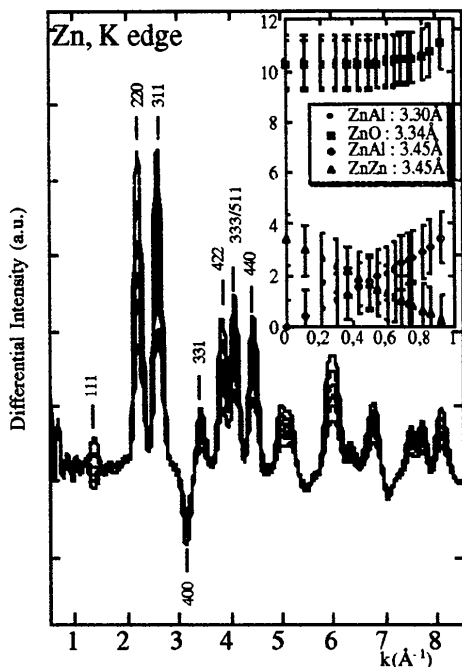
*The inversion of the spinel.* [Zn<sub>1-v</sub>Al<sub>v</sub>]T<sub>d</sub>[Al<sub>2-v</sub>Zn<sub>v</sub>]O<sub>4</sub>. Regarding the second coordination sphere, the inversion of the spinel gives rise to several coordination sphere (table II), a situation which complicates the data analysis. *Ab initio* calculations of differential intensity (Fig.2) show clearly the significant modifications of the 111, 220, 400 and 311 features and thus underline the advantages of the Awxas versus the Exafs for this structural hypothesis.



**Figure 2**  
Modifications on the differential intensity when the inversion factor *v* defined as [Zn<sub>1-v</sub>Al<sub>v</sub>]T<sub>d</sub>[Al<sub>2-v</sub>Zn<sub>v</sub>]O<sub>4</sub> is equal to 0 and 1.

**Table II** : Zn-Zn Coordination numbers versus the inversion factor  $n$  :  $[Zn_{1-n}Al_n]T_d[Al_{2-n}Zn_n]O_hO_4$  (R is also indicated).

$v$	$O_h-O_h$ 3.45Å	$O_h-T_d$ 3.31Å	$T_d-T_d$ 2.83Å	$v$	$O_h-O_h$ 3.45Å	$O_h-T_d$ 3.31Å	$T_d-T_d$ 2.83 Å
0.	3.4	0.0	0.0	0.7	0.3	N=2.1	1.2
0.3	1.5	2.4	0.3	0.8	0.0	N=1.2	1.9
0.6	0.6	2.6	0.7	1	0.0	N=0.0	3.4



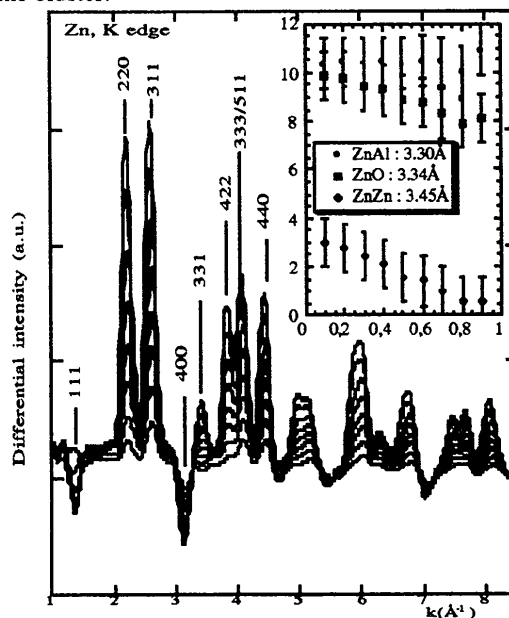
**Figure 3**  
Evolution of the differential intensity in the case of the substitution  $[Zn_{1-x}Al_x]T_d[Al]O_hO_4$ .

*The Zn/Al substitution* :  $[Zn_{1-x}Al_x]T_d[Al]O_hO_4$ . An obvious relationship exists between the substitution factor  $n$  and the number of  $Zn(T_d)-Al(T_d)$  bonds (3.45 Å). Compare to the precedent situation, we can note that  $Zn(T_d)-Zn(T_d)$  doesn't exist here. Also the maximum value of this parameter is controlled by the cluster size. If the amplitude of the different diffraction features 220,... seems to decrease linearly with the number of Zn atoms, (fig. 3) it is not the case of the amplitude of the 111 diffraction peak which goes from positive to negative.

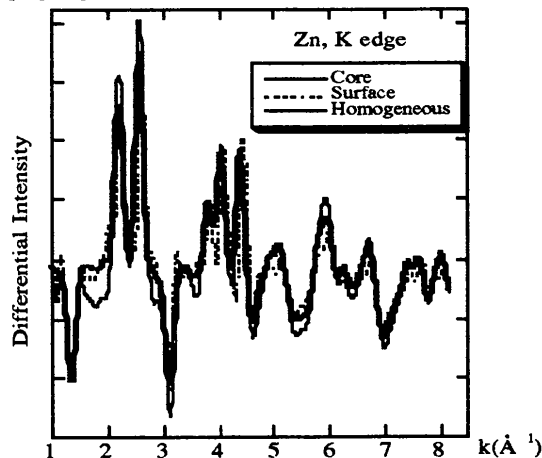
If we compare the differential intensity associated to the inversion and to the substitution, these two structural hypotheses can be distinguish if the ratio of the amplitude of the feature 220 and 311 is considered. The 220 features almost disappears in the first case while the ratio is quite constant in the second one.

*The case of Zn vacancies* :  $[Zn_{1-v}]T_d[Al]O_hO_4$ . We finish by this structural possibility which is a general property associated to spinel materials. The decrease of  $N_{ZnZn}$  (3.45Å) is a fingerprint of the appearance of Zn vacancy, a trends we have already observed for the precedent case but now without the appearance of Zn-Al bonds (3.45Å). Regarding the diffraction (fig. 4), the difference with the precedent case is given by the amplitude of the 111 feature.

*Distribution of the vacancies inside the cluster.* We discuss now a point which is not given by Rietveld method, the spatial distribution of the vacancy inside the  $ZnAl_2O_4$  cluster : Are the vacancies located at the surface of the clusters or at the core? In order to discuss this point we consider three possibilities for  $ZnAl_2O_4$  clusters : a homogeneous distribution of the vacancies, Zn atoms positioned at the core (vacancies at the surface) and the opposite configuration Zn atoms are at the surface (vacancies at the core). Even if we consider the error attributed to the coordination numbers (table V), we can in principle distinguish between these configurations through the coordination numbers  $N_{ZnZn}$ ,  $N_{ZnAl}$ ,  $N_{ZnO}$ . Regarding the anomalous diffraction technique (fig. 5), these different distributions are associated to differential intensities and it seems that a additional feature appears (arrow) which allows the knowledge of the distribution of the vacancies inside the cluster.



**Figure 4**  
Evolution of the differential intensity versus the number of Zn vacancies i.e. for the formulae  $[Zn_{1-x}]T_d[Al_2]O_hO_4$ .



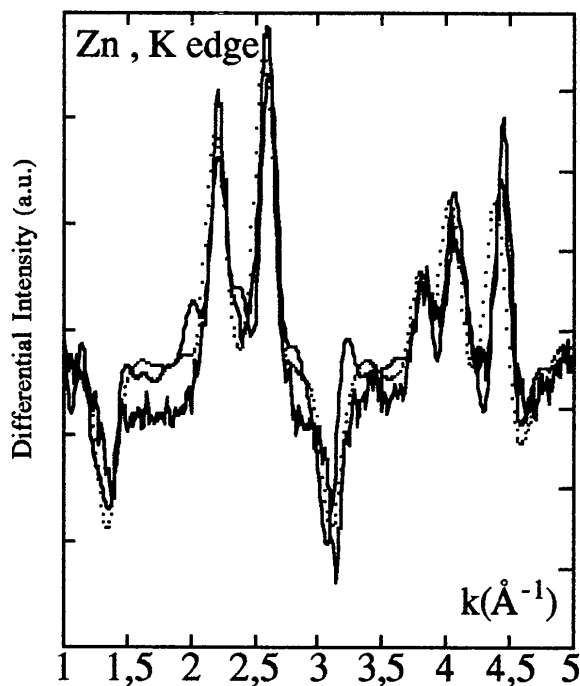
**Figure 5**  
Differential intensities calculated for different distribution of the vacancies inside a  $ZnAl_2O_4$  cluster with a diameter of 40Å.

**Table III :** Coordination numbers calculated for different distribution of the vacancy inside a  $ZnAl_2O_4$  cluster with a diameter of 40Å, the number of Zn atoms is divided by 4.

	$N_{ZnAl}$ R=3.35Å	$N_{ZnO}$ R=3.39Å	$N_{ZnZn}$ R=3.50Å
Homogeneous distribution	10.4	10.7	0.7
Zn at the core, vacancies at the surface	12	12	3.3
Zn at the surface, vacancies at the core	7.4	8.1	1.1

*The Exafs-Awaxs approach.* At this point, we can resume the approach we have followed. At first, an evaluation of the amplitude of multiple scattering process versus single scattering one is done for Exafs. Then, the values of  $f'$  and  $f''$  for the different elements are checked. A list of structural hypothesis is done based on the chemical information. For spinel compounds we can consider : the size and the dimension (2d or 3d) of the cluster, inversion, substitution or the distribution of the vacancy inside the cluster. Finally, in order to build a significant structural model, a comparison is done between the experiments and the simulation.

### 3. The "Zn" /Al<sub>2</sub>O<sub>3</sub> sample



**Figure 6**  
Comparison between the experimental data and the differential intensities calculated for vacancies at the Zinc atoms at the surface (line) and an homogeneous distribution (dots).

The local structure around Zn atoms can be considered similar to that existing for a  $ZnAl_2O_4$  spinel (Fig. 6). The coherence length associated to such  $ZnAl_2O_4$  entities given by the first numerical simulations is around 40 Å.

Moreover, if we want to take into account the amplitude of the 111 feature as well as the intensity ratio between the 220 and the 311 we have to introduce vacancies. This result is in line with Exafs, the number of Zn-Zn bonds at 3.50 Å being equal to 1, no Zn-Al bonds at 3.50 Å being measured.

A last question has to be answer : Can we get some information on the distribution of the vacancies inside the  $ZnAl_2O_4$  cluster. Then, comparing the experimental results with the coordination numbers gathered in table III, we can reject the case where Zn atoms are at the core of the cluster and vacancies are at the surface. If we consider the anomalous diffraction technique, the positions of the diffraction features between 4 and 5 Å<sup>-1</sup> indicate that Zn atoms are at the surface. In conclusion, a structural hypothesis in line with Exafs and Awaxs is to say that a Zn concentration gradient decreasing from the surface is present.

### 4. Conclusion

For spinel compounds, we have shown the necessity to combine Exafs and Awaxs to build a significant structural model. Moreover, *in situ* experiments can be done and thus such experimental approach leads to a significant correlation between structural characteristics of poorly ordered supported metallic oxide and their specific chemical properties.

### References

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