

DATA VIZUALIZATION: FROM X-RAY MEASUREMENTS TO THE ATOMIC STRUCTURE VIA WAVELET

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ABSTRACT

In this paper an algorithm of the atomic structure visualization is discussed. The atomic structure is presented by a wavelet map. The EXAFS (X-ray absorption fine structure) signal is analyzed by means of the wavelet transform to determine the number of the coordination spheres, the radii of the coordination spheres and to identify the back-scattering centers on each coordination sphere.

Short introduction to the wavelet theory and to the EXAFS theory are given. Analysis of the LDH (layered double hydroxide) EXAFS spectrum illustrates all steps of the algorithm.

INTRODUCTION

Extended X-ray Absorption Fine Structure spectroscopy (Sayers et.al. 1971, Stern 1974, Lytle et.al. 1975 and Stern et.al.1975) is a powerful technique for probing the local structure around almost any specific elements. This technique gives information on the average interatomic distances and chemical identities of near neighbours. The EXAFS technique is used for atoms in various aggregation state (solid or liquid) in all kinds environment: crystalline solids, glasses, amorphous phases, liquids and solutions.

The physical background of the technique is the following. A monochromatic X-ray beam is directed at the sample. The photon energy of the X-rays is gradually increased such that it traverses one of the absorption edges of the elements contained within the sample. Below the absorption edge, the photons cannot ionize the electrons of the relevant atomic level and thus absorption is low. However, when the photon energy is just sufficient to excite the electrons, then a large increase in absorption occurs known as the absorption edge. The emitted photoelectrons have a low kinetic energy and can be backscattered by the atoms surrounding the emitting atom. The probability of backscattering is dependent on the energy of the photoelectrons. Hence, the probability of X-ray absorption will depend on the photon energy (as the photoelectron energy will depend on the photon

energy). The result is the oscillations on the high photon energy side of the absorption edge:

$$\chi(k) = S_0^2 \sum_{i=1}^n \frac{N_i}{R_i^2} \frac{F_i(k, R)}{k} e^{-\frac{2R_i}{\lambda}} e^{-2\sigma_i^2 k^2} \sin(2kR_i + \Psi)$$

(1), where $\chi(k)$ is the measured EXAFS spectrum, and k is the electron wave vector. The fitted parameters are the values for the number of atoms in the i -th coordination sphere N_i , the average radial distance to the i -th coordination sphere R_i , and the Debye Waller factor σ_i^2 (Teo 1986). General EXAFS data analysis is based on the Fourier transform (FT) of the (k^3 -weighted) EXAFS spectra. The modulus of the FT enables a first qualitative estimation of how many co-ordination spheres and at what distances are surrounding the absorbing atom. While the absorbing atom is unequivocally identified by the energy of the absorption edge, the backscattering atoms are identified with limited precision (typically $Z \pm 2$) by a fit to the EXAFS equation (1).

The identity of the backscattering atom is not a fitting parameter. It has to be pre-selected and tested. This pre-selection is based on the energy-dependence of the backscattering amplitude $F_i(k, R)$, which can be derived from the experimental spectra by a Fourier back-transform in the region of interest. The backscattering amplitude is then compared with tabulated values for each element (Teo 1986) or with theoretical ones $F_i(k, R)$, what can be derived together with the sum of the phases of the central- and backscattering atoms $\Psi(k, R)$, the mean free path $\lambda(k)$, and the amplitude reduction factor $S_0^2(k)$ by some simulation code like FEFF8 (Ankudinov et.al. 1998).

The disadvantage of the Fourier transform of a function $f(t)$:

$$\hat{f}(\omega) = \int_{-\infty}^{+\infty} f(t) e^{i\omega t} dt \quad (2)$$

is that if the signal changes at any time moment, the Fourier transform changes everywhere. While the identification of the backscattering atom works fine as long as the shells represent only one type of atoms at one distance, the presence of different types of atoms at one distance, or the presence of single and multiple

scattering paths with identical path length, complicates the analysis substantially.

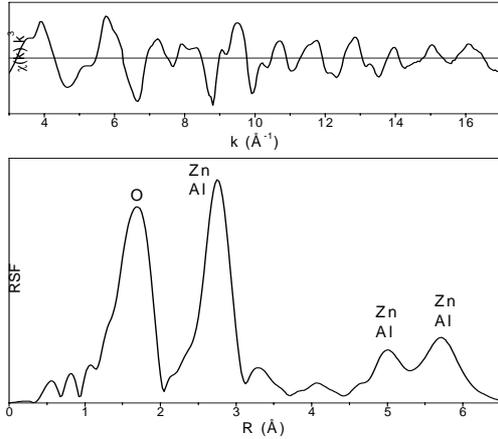


Fig.1. Zn k-edge EXAFS spectrum of LDH (top) and its Fourier transform (bottom).

If one uses localized wave trains (wavelets) as kernels for the integral transform, then one may analyze the frequencies in each place by dilatation and translation of the wavelets. The corresponding transform is the wavelet transform (WT) (Grossmann & Morlet 1984). Thus, the WT is able to extract more information from the k -dependence of the absorption signals, and is therefore better suited to distinguish between heavier and lighter backscattering atoms, even if they are at the same distance from the central atom, according to the backscattering amplitude:

$$W_{\chi}^{\psi}(k', r) = \sqrt{2r} \int_{-\infty}^{\infty} \chi(k) k^3 \psi^*(2r(k - k')) dk. \quad (3)$$

A wavelet ψ is a function of zero average:

$$\int_{-\infty}^{\infty} \psi(k) dk = 0, \quad (4)$$

which is dilated with a scale parameter r , and translated by k' :

$$\psi_{k',r}(k) = \sqrt{2r} \psi(2r(k - k')). \quad (5)$$

Wavelet transform correlates χ with $\psi_{k',r}$ (Mallat 1998).

Dependency of the backscattering amplitude F_i on an atomic number Z , allows us to illuminate the different types of the backscattering atoms in one coordination sphere with the wavelet transform (Funke *et al* 2001, Munoz *et al* 2001).

The WT algorithm for the EXAFS spectra analysis is presented in the work. The WT allows moving from the X-ray spectra (Fig.1) to the k - r images (Fig. 2-3) for visualization of the atomic structure. Zn-Al LDH (layered double hydroxide) spectrum (Scheinost *et al.* 2002) is analysed.

MORLET WAVELET FOR EXAFS SPECTRA ANALYSIS

It was shown (Funke *et al* 2001) that the complex wavelet developed by Morlet

$$\psi(k) = \frac{1}{\sqrt{2\pi\sigma}} \left(e^{i\eta k} - e^{-\eta^2\sigma^2/2} \right) e^{-k^2/2\sigma^2} \quad (6)$$

can be used for EXAFS data analysis. This selection has two reasons. First, the structure of the Morlet wavelet is similar to an EXAFS signal, since the wavelet consists of a slowly varying amplitude term $e^{-k^2/2\sigma^2}$ and a fast oscillating phase term $e^{i\eta k}$. Second, the formal mathematical description of the wavelet analysis can be treated in analogy to the Fourier analysis.

The WL transform was used to resolve Zn and Al atoms in the structure of Zn-Al LDH. The EXAFS spectrum of the structure and its Fourier transform are presented in Fig.1. The overview Morlet wavelet transform is given in Fig.2.

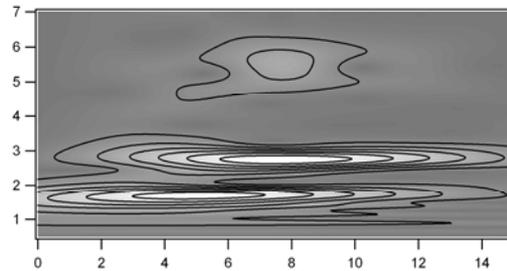


Fig.2. Overview Morlet wavelet transform.

The Fourier transform shows four dominant shells, which can be assigned to the oxygen coordination sphere (O), and to the first, second and third sphere of metal (Zn, Al) neighbors.

The goal of the WT is to give an answer about the placement of Zn and Al atoms in the structure. In Fig.2. the overview Morlet wavelet ($\eta = 15, \sigma = 1$) map is presented. The oxygen sphere ($R \approx 1.7 \text{ \AA}, k \approx 5 \text{ \AA}^{-1}$) and the first metallic sphere ($R \approx 2.8 \text{ \AA}, k \approx 8 \text{ \AA}^{-1}$) are presented very brightly but the second and third metallic spheres ($R \approx 5.5 \text{ \AA}, k \approx 8 \text{ \AA}^{-1}$) have an overlapping.

The k - r resolution is determined by the “time-frequency” window (Chui 1992). For Morlet wavelet the window size depends on the position of the window center (k, r) and on the Morlet parameters (η, σ):

$$\left[k \pm \frac{\sqrt{2}\eta\sigma}{r}; r \pm \frac{\sqrt{2}r}{\eta\sigma} \right]. \quad (7)$$

To increase the k -resolution, η parameter was decreased up to 5.5. Result of the WT calculation for the region of interest is presented in Fig.3. Two maxima ($r \approx 2.6 \text{ \AA}, k \approx 5.2 \text{ \AA}^{-1}$) and ($r \approx 2.6 \text{ \AA}, k \approx 7.5 \text{ \AA}^{-1}$) correspond to Al and Zn backscatterers at the same distance.

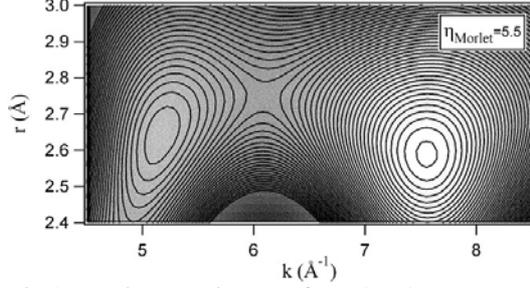


Fig.3. Morlet wavelet transform (part).

It was found that there are no (η, σ) values to follow the resolution condition for the second $r = 5.2 \text{ \AA}$ and third $r = 6 \text{ \AA}$ coordination spheres:

$$\begin{cases} \frac{\eta\sigma}{\sqrt{2}r} < \frac{k^2 - k^1}{2} \\ \frac{r}{\sqrt{2}\eta\sigma} < \frac{r^2 - r^1}{2} \end{cases} \quad (8)$$

Here (k^1, r^1) and (k^2, r^2) are the maxima positions of the backscattering amplitude functions for Al and Zn.

FEFF-MORLET WAVELET

To increase the k -resolution a new wavelet was constructed. The base of the new wavelet is a simulated (for example, by FEFF8) EXAFS spectrum. Simulation parameters are taken in agreement with the task: the atomic number of the central atom, the position and the atomic number of the tested backscatterer. For the second and third metallic spheres, Al and then Zn atom were tested. Zn is taken as the central atom.

The simulated spectrum is used to construct a new FEFF-Morlet wavelet.

The steps of the construction algorithm: sophisticated cutting out of the model spectrum; modeling the envelope with a spline function; adapting the EXAFS oscillations within the envelope to the cos function \Rightarrow real part of the FEFF-Morlet wavelet; adding the same function with a phase shift of $\pi/2 \Rightarrow$ imaginary part of the FEFF-Morlet wavelet; setting the “center of gravity” of the curve to zero.

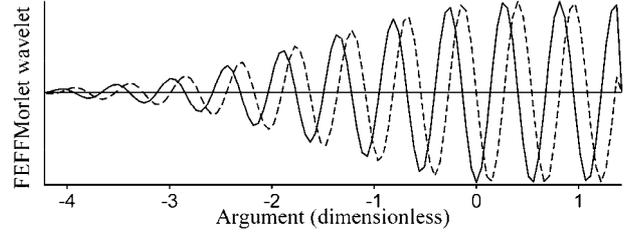


Fig. 4: Real (full line) and imaginary (dashed line) part of the FEFFMorlet wavelet constructed from the model spectrum Zn-Zn @ 6 Å.

With new wavelet (Fig.4) a new scale parameter s is used instead of the distance $2r$ (Eq. 3). If $s = l$ then the wavelet is not dilated. Hence, the WT should have a maximum for $s = l$, if the selected model function for a given distance is correct. Thus the peak at $s = l$ corresponds to the backscatterer distance 6.0 Å in the spectrum, evaluated with a wavelet which is built from a FEFF backscatterer model at 6.0 Å.

With the Morlet wavelet, it was possible to distinguish Zn and Al in the first shell ($\sim 3 \text{ \AA}$) (Funke et.al. 2005b). However, it was not possible to resolve the two more distant shells at 5.2 Å and 6 Å simultaneously with respect to wave number k (element identity) and the distance r . FEFFMorlet wavelet has “solved” the problem for the second and third coordination spheres.

In order to make easy the presentation of the WT analysis results to specific distances and specific k ranges, the power density functions (PDF) $\Phi(k)$ and $\Phi(s)$ is calculated depending on either k or s (Funke et al 2005a):

$$\Phi(k) = \int [W_z^\psi(k, s)]^2 ds, \quad \Phi(s) = \int [W_z^\psi(k, s)]^2 dk. \quad (9)$$

Now, it is investigated the WT of the LDH spectrum using the following 4 wavelet functions which are constructed from the FEFF spectra: Zn-Zn @ 6 Å (Fig 4), Zn-Al @ 6 Å, Zn-Zn @ 5.2 Å, and Zn-Al @ 5.2 Å.

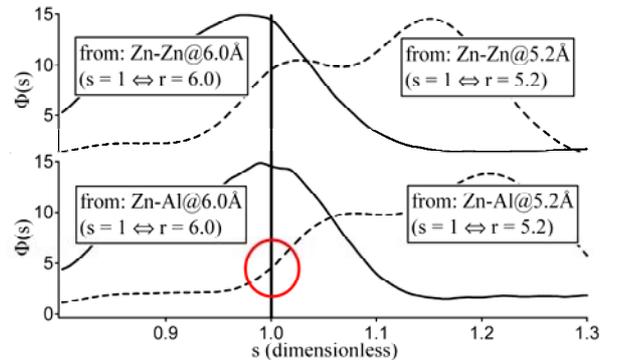


Fig.5. Four PDF's in the region $\approx 4.8, \dots, 6.6 \text{ \AA}$.

The PDF analysis shows clearly peaks at $\approx 6 \text{ \AA}$ for the wavelets built from FEFF spectra at 6 Å. For the wavelets from spectra at 5.2 Å it is different. Zn-Zn

shows a peak at $s=1$ (5.2 Å), but Zn-Al does not show a peak at $s=1$ (5.2 Å), see the circle in Fig.5.

That means that the second metal shell does not contain Al, which is in agreement with a regular metal distribution in the LDH.

CONCLUSION

The mathematical processing of the measured signals is an important step for data visualization. The problem of identifying the scattering centers placed in one coordination sphere has been solved only with the use of the wavelet transform, which has the property of locality in both k -space and reciprocal space. The composition of metallic spheres for the structure of Zn-Al LDH has been found:

1st shell contains Al and Zn atoms,

2nd shell contains only Zn atoms,

3rd shell contains Al and Zn atoms.

In Fig.6 the atomic structure of the Zn-Al LDH is presented.

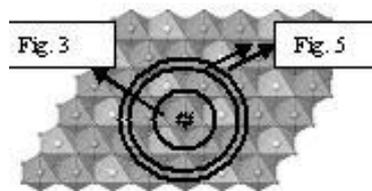


Fig. 6. Model of octahedral structure of LDH.

The calculations were done using a software package developed by the author and Dr. H. Funke and which is

available on the Internet

<http://www.esrf.fr/UsersAndScience/Experiments/CRG/BM20/Software/Wavelets/Wavelets>.

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