Improving Resolution in k and r Space: A FEFF-based Wavelet for EXAFS Data Analysis

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Abstract. Applying a wavelet analysis based on the Morlet mother function, we previously demonstrated the presence of both Al and Zn atoms in the first metal shell (r ≈ 3 Å from the central Zn atom) of Zn-Al layered double hydroxide (LDH). However, this approach was not suited to resolve the second and third metal shells (r ≈ 5 - 6 Å) in r and k space independently. Therefore, we developed a new FEFF-Morlet wavelet, where the EXAFS function itself, extracted from the FEFF model, is combined with the complex Morlet wavelet. With this method, we were able to distinguish the second metal shell (Zn atoms only) from the third metal shell (Zn and Al atoms), thereby proving a regular, dioctahedral distribution of Zn atoms in the hydroxide layers.

Keywords: EXAFS, wavelet analysis, layered double hydroxides
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INTRODUCTION

Wavelet transformation has been proven as a valuable tool for EXAFS data analysis for structures, where two types of backscattering atoms are at the same distance from the central atom [1,2,3]. The method is therefore well suited to investigate the short-range structure of layered double hydroxides (LDH) [4,5,6]. For Zn-Al LDH we could demonstrate the presence of Zn Al at a distance of 3.06-3.08 Å from the Zn absorber atom [1]. Assuming an even charge distribution [7], the second metal shell at 5.3 Å would contain only Zn atoms and the third metal shell at 6.1 Å would contain both Zn and Al atoms. Our previous approach employing the Morlet wavelet was not suited to resolve both shells in distance and in atom type.

An important advantage of wavelet transformations is that an infinitively large manifold of mother wavelets exists, corresponding to the class of functions l^2. Therefore, we tested a new mother wavelet, where the EXAFS function itself is used to construct the probing wavelet. The envelope and the median wavelength (in the k-space) of the wavelet function are extracted from the appropriate feffxxxx.dat file produced by the FEFF8.2 program. We describe the mathematical steps for the construction of this FEFF-Morlet wavelet, and apply it to a set of LDH phases [5]. The wavelets individually adapted to resolve the second and third metal shell of Zn-Al LDH were now able to resolve Zn in the second metal shell, and both Zn and Al in the third metal shell, in line with the even charge distribution postulated by Brindlay and Kikkawa [7].

LAYERED DOUBLE HYDROXIDES

LDH are a class of minerals hosting a wide range of divalent metal cations like Cr^{2+}, Ni^{2+}, Zn^{2+} (M^{2+}). Due to their relatively low solubility at circumneutral pH values, formation of such phases plays an important role in reducing the toxicity of metals in soils, sediments and nuclear waste repositories [8].

LDH phases consist of layers of edge-sharing metal hydroxide octahedra, where up to 1/3 of the divalent cations are replaced by trivalent Al^{3+}. The resulting net positive layer charge is compensated for by hydrated anions in the interlayer space [9]. Due to their low crystallinity and turbostratic layer structure, LDH are difficult to identify by XRD in environmental media. While EXAFS is much better suited for this purpose, the discrimination from more soluble, simple hydroxide phases is hindered, since the backscattering wave from Al^{3+} is masked by destructive interference with backscattering waves from the heavier M^{2+} [1].

The spectrum of a Zn-Al-LDH were measured at the Rossendorf beamline at ESRF at T=20K in a cryostat.

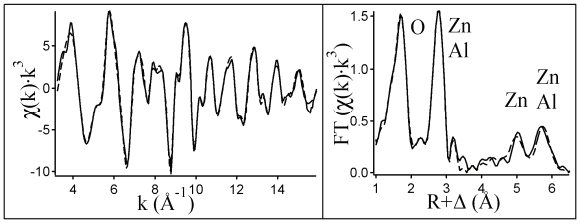

FIGURE 1. Zn K-edge EXAFS spectrum and its FT magnitude of Zn-Al LDH. The fit is shown in dotted lines.

WAVELET ANALYSIS OF THE EXAFS SPECTRUM OF A Zn-AL LDH

The Wavelet transformation of the k^n weighted EXAFS spectrum is given as [1]:

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

Thereby the "Mother" wavelet function may be choosen from the wide class of functions l^2 with the only restriction: $\int \psi(k)dk = 0.$

Wavelet Analysis using Morlet Wavelets

The Morlet wavelet function is defined as a complex sine wave (like in the FT), localized with a Gaussian (bell-shaped) envelope:

$$\psi(k) = \frac{1}{\sqrt{2\pi}\sigma}\exp(i\eta k)\cdot\exp\left(\frac{-k^2}{2\sigma^2}\right).$$

The meaning of the parameters is: η is the number of oscillations in the Morlet wavelet, and σ is the half-with of the gaussian envelope of the Morlet wavelet. The choice of the optimal Morlet parameters η and σ allows to vary the resolution:

Overview wavelet: $\eta\cdot\sigma \geq 15$

Detail wavelet: $\eta\cdot\sigma \approx 2\, r_{opt}$

The detail wavelet optimizes the resolution of k for the distance of interest r_{opt} (see examples). Limitations of the resolution of a WA with Morlet wavelets are given by their uncertainty (Heisenberg) boxes:

$$\left[k-\frac{\eta\sigma}{\sqrt{2}r}, k+\frac{\eta\sigma}{\sqrt{2}r}\right]\times\left[r-\frac{r}{\sqrt{2}\eta\sigma}, r+\frac{r}{\sqrt{2}\eta\sigma}\right].$$

The wavelet approach using Morlet wavelets is applied to resolve the Zn and Al atoms in the structure of Zn-Al LDH. This problem was in detail treated in [1]. The results are:

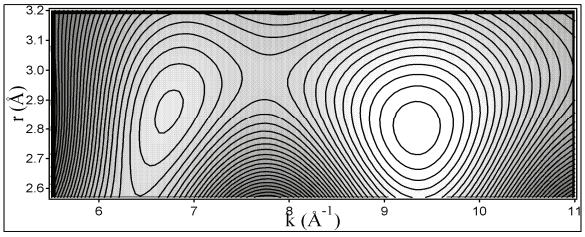

FIGURE 2. Detail wavelet with Morlet parameters: η = 30, σ = 0.184

The wavelet ridge at r ≈ 2.8 Å is clearly resolved and shows two peaks at different k.

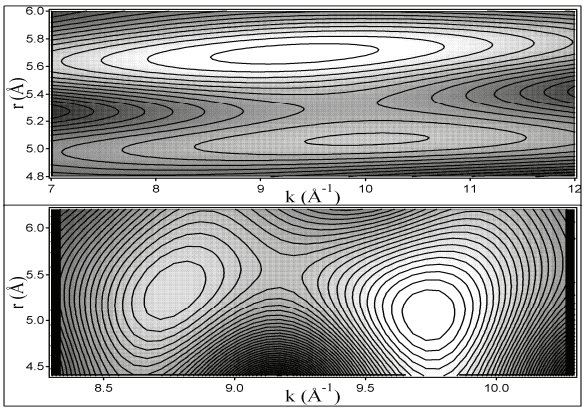

FIGURE 3. Overview wavelet with Morlet parameters: η = 30, σ = 1 and the detail wavelet with η = 30, σ = 0.155

The ridges at r ≈ 5.1 Å and r ≈ 5.8 Å are resolved and show two peaks at different k. But, the simultaneous resolution in r- and k- space of the third and fourth peaks in the FT is impossible using the Morlet wavelet.

Wavelet Analysis using the FEFF-Morlet Wavelet

A maximum of an integral transformation (convolution) of a signal arises, if the information in the signal coincide with the kernel (e.g. wavelet- or sine/cosine function) of the transformation. Therefore, we design a new mother wavelet, the FEFF-Morlet wavelet, which combines a model EXAFS function derived from the FEFF code and the advantages of the complex Morlet wavelet.

We propose to generate FEFF-Morlet mother wavelets in five steps:

1) Cut out the first maximum of the envelopes of the model spectrum,
2) Model the envelopes with a spline function,
3) Adapt the EXAFS oscillations within the envelopes to the cos function ⇒ real part,
4) Add the same function with a phase shift of π/2 ⇒ imaginary part,
5) Set the "center of gravity" of the curve to zero.

An example of the result of the construction is shown in Figure 4.

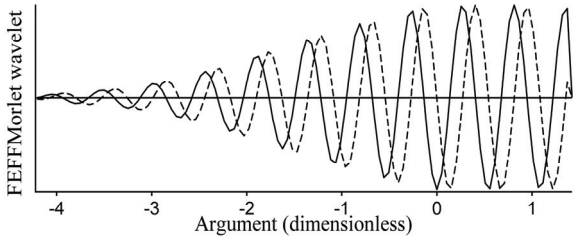

FIGURE 4. Real (full) and imaginary (dashed) part of the FEFF-Morlet wavelet constructed from the model spectrum Zn-Zn @ 6 Å.

The FEFF Morlet technique is applied to verify the model of Brindley & Kikkawa [7]. A top view of the octahedral layer of Zn-Al LDH shows 3 metal shells:

1st metal shell (~3.0 Å): 3 Zn, 3 Al
2nd metal shell (~5.2 Å = $\sqrt{3} \cdot R_{Zn\text{-}Zn}$): 6 Zn
3rd metal shell (~6.0 Å = $2 \cdot R_{Zn\text{-}Zn}$): 3 Zn, 3 Al

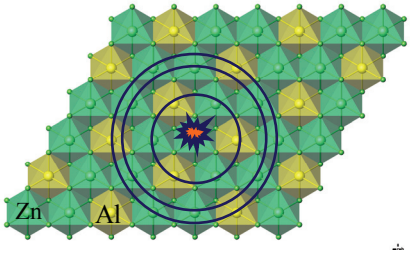

FIGURE 5. Top view of the octahedral layer of Zn-Al LDH.

For convenience we use a scale parameter s instead of the distance r with the property: **s = 1 if the wavelet is not dilated**. Hence, the WT has a maximum for s = 1, if the selected model function and the given distance are correct. The relation between the distances and the scale parameter is: $r = r_{opt} \cdot s$, par ex.: $r_{opt} = 6$ *Å*.

In order to concentrate the WT analysis to specific distances and specific k ranges, we introduced the power density functions (PDF) $\Phi(k)$ and $\Phi(s)$ depending on either k or s:

$$\Phi(k) = \int \left[W_\chi^\psi (k,s) \right]^2 ds, \quad \Phi(s) = \int \left[W_\chi^\psi (k,s) \right]^2 dk.$$

Now, we will investigate the WT of the LDH spectrum using the following 4 wavelet functions calculated with FEFF: Zn-Zn @ 6 Å, Zn-Al @ 6 Å, Zn-Zn @ 5.2 Å, and Zn-Al @ 5.2 Å. The PDF analysis shows the expected maxima at s=1 for both Zn and Al at ≈ 6 Å, confirming that both atoms are present (Fig. 6). At a distance of 5.2 Å, however, only the path involving Zn shows a maximum at s=1, while Al does not (circle). This confirms that the second metal shell does not contain Al, indicating an even metal distribution in LDH, in line with a regular charge distribution.

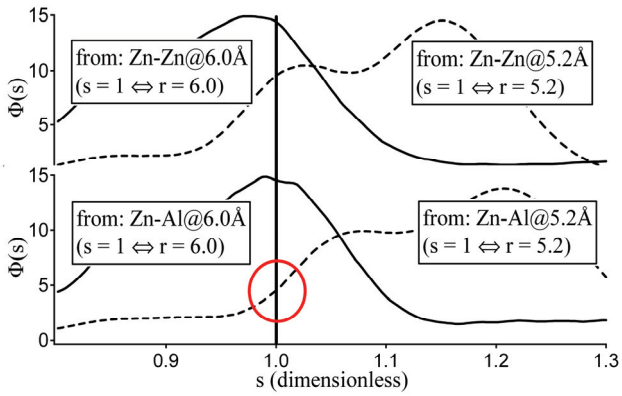

FIGURE 6. Four PDF's in the region ≈ 4.8 - 6.6 Å, see text.

Results

With the previously used Morlet wavelet, it was possible to distinguish Zn and Al in the first shell (~3 Å). However, it was not possible to resolve the two more distant shells at 5.2 and 6 Å simultaneously with respect to wavenumber k (element identity) and the distance r. This problem is now overcome with the newly developed FEFF-Morlet wavelet.

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