School on Synchrotron and FEL Based Methods and their Multi-Disciplinary Applications

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XAS data analysis

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Introduction to the EXAFS data analysis

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Material almost integrally taken from Carlo Meneghini: EXAFS tutorial at Synchrotron Radiation school of Duino 2011
Characteristics of a XAS spectrum

Pre-edge background

Post edge atomic background

Edge Energy

Pre-edge background

XANES
XAFS study: from experiment to results

Data collection

Extraction of XAFS structural signal: $\chi(k)$

Structural refinement

Check the results

END

Preliminary data treatment

Structural model(s)

Revision
XAFS study: from experiment to results

1. **Data collection**
2. **Preliminary data treatment**
3. **Extraction of XAFS structural signal: \( \chi(k) \)**
4. **Structural refinement**
5. **Check the results**
6. **Structural model(s)**

The process includes iteration via revisions at each step.
Data collection

Considerations:

1) Proposal submission + proposal evaluation + beamtime scheduling = 6 to 12 months
2) Difficult to have new beamtime in case of proposal failure

- Check the proposal submission deadlines
- Discuss your experiment with local contacts

Choose properly the experimental set-up & sample preparation

Check data quality constantly during the experiment

Optimize your beamtime!

Measure reference samples

Choose properly data collection strategy
Data collection

Choose properly the experimental set-up & sample preparation

• For massive concentrated samples: **TRANSMISSION**

  Jump \[ 0.5 \leq \Delta \mu t \leq 1.5 \]
  Total absorption \[ \mu t \leq 2 \]

  ![Warning] inhomogeneities, holes, not parallel surfaces, etc...

• For thin concentrated or thin diluted samples: **FLUORESCENCE**

  ![Warning] Self absorption, detector linearity, Bragg reflections
Choose properly the data collection strategy

- Acquisition time per point
- Single scan or repeated scans
- $\Delta E$ or $\Delta k$ step

**Constant $\Delta k$ acquisition**
- Optimizes the number of collected points
- More efficient
- Faster
Data collection

Measure reference samples

\[ \mu_{\text{ref}} = \ln \frac{I_1}{I_2} \]

\[ \mu_{\text{exp}} = \ln \frac{I_0}{I_1} \]

Normalized Absorption

Energy (eV)
Data collection

**Check data quality constantly during the experiment**

- Evaluate signal/noise ratio

\[ \sigma = 1.1 \times 10^{-4} \]

\[ S/N \sim J/\sigma \]

**S/N ratio should be less than** \(10^{-3}\)
Data collection

Check data quality constantly during the experiment

- Check for:
  - Glitches
  - Discontinuities
  - Edge shift
XAFS analysis: from experiment to results

Data collection

Preliminary data treatment

Extraction of XAFS structural signal: \( \chi(k) \)

Structural refinement

Check the results

Structural model(s)

END
Preliminary data treatment

Choose the best spectra and useful data regions

do not use the blue one!

do not use data beyond 13000 eV!
Preliminary data treatment

De-glitch
Preliminary data treatment

Align
Preliminary data treatment

Average
Preliminary data treatment is boring, it may be long...
While you are waiting for your data collection to finish...

Do it on already collected data!!
You will save your time at home!!
XAFS analysis: from experiment to results

Data collection

Preliminary data treatment

Extraction of XAFS structural signal: $\chi(k)$

Structural refinement

Check the results

END
Extraction of the EXAFS signal

\[ \alpha(E) \]

- pre-edge line + post-edge line

Normalized data

- \( \mu_0 \) calculation

\[ \chi(k) = \frac{\mu - \mu_0}{\mu_0} \]

structural signal \( \chi(k) \)

Fourier Transform

Fourier Filtering

Structural refinement

revise preliminary treatment
Extraction of the EXAFS signal

pre-edge line + post-edge line

Normalized data
Extraction of the EXAFS signal

$\mu_0$ calculation

structural signal $\chi(k)$
Extraction of the EXAFS signal

**μ₀ calculation**

1) Define $E_0$

$E_0$ will allow to set the starting point of $\chi(k)$. It is generally taken at the maximum of the 1st derivative of the absorption.

2) Calculate $\mu_0$

$\mu_0$ is the bare atom atomic background. It is calculated empirically as a smooth curve across the data. Different XAFS data analysis softwares apply different (equivalent) approaches.

3) Subtract $\mu_0$ from $\mu$
Extraction of the EXAFS signal

Fourier Transform

FT shows more intuitively the main structural features in the real space: the FT modulus represent a pseudo-radial distribution function (RDF)

$|\text{FT}|$ peaks represent interatomic correlation

Peak position are not the true correlation distances due to the phase shift effect.
Minor effects are given by type of windows (Hanning, Kaiser-Bessel, Sine) and apodization.
Extraction of the EXAFS signal

**DO NOT REMOVE TRUE STRUCTURAL FEATURES**

**DO NOT DO THE OPPOSITE ERROR**

Large $|FT|$ contributions at low (unphysical) distances may signify "wrong $\mu_0".\]
Extraction of the EXAFS signal

Fourier Filtering

Fourier filtering allows isolating contributions of selected regions of the FT.
XAFS analysis: from experiment to results

Data collection

Preliminary data treatment

Extraction of XAFS structural signal: $\chi(k)$

Structural refinement

Check the results

END

Structural model(s)

revision
**Structural refinement**

- **Theoretical $\chi(k)$**
  
  \[
  \chi(k) = \sum_j N_j S_j^2 f_j(k) e^{-2R_j/k\chi(k)} e^{-2k^2\sigma_j^2} \sin[2kR_j + \delta_j(k)]
  \]

- **Experimental $\chi(k)$**

- **Choose a model**
- **Define the relevant structural contributions**

  - **Refine the structural parameters: $N$, $R$, $\sigma^2$**
    - **add new contributions?**
      - **Y**
        - **Change the model?**
        - **Y**
          - **Revise your data extraction?**
          - **Y**

  - **Y**

- **Require data analysis programs**

- **END**
Structural refinement

How to find a model structure

How to visualize the structure

How to calculate distances and geometries

Choose a model

ICSD database

http://database.iem.ac.ru/mincryst/

ATOMS on the Web

http://millenia.cars.aps.anl.gov/cgi-bin/atoms/atoms.cgi
XAFS data analysis softwares

http://www.xafs.org/

http://cars9.uchicago.edu/ifeffit/

Click DOWNLOADS

Click ifeffit-1.2.11.exe
Install Ifeffit.exe

1. athena GUI for Data Processing with Ifeffit
2. artemis GUI for XAFS Fitting with Ifeffit
3. hephaestus GUI for general x-ray properties of the elements
4. sixpack GUI for XAFS Processing and Fitting with Ifeffit
5. feff6 Stand-alone program for ab initio EXAFS calculations
6. atoms Stand-alone, command line crystallography->feff.inp
7. autobk Stand-alone background removal program
8. feffit Stand-alone FEFF fitting program
9. ifeffit command-line version of Ifeffit
Inside the Ifeffit directory

Extract $\chi(k)$
data fitting

Manuals and tutorials

Info on the proposed example

Configuration files: NOT FOR NEWBIES

Database of crystallographic structures: *.inp files for Atoms
Data collection

Preliminary data treatment

Extraction of XAFS structural signal: $\chi(k)$

Structural refinement

Check the results

END
Preliminary data treatment &
Extraction of XAFS structural signal: \( \chi(k) \)

List of files (group) opened into Athena
Plot highlighted files
Plot (several) marked files
Options for plot
Example 1: Cu 10 K

Open cu010k.dat into ATHENA

1: Look at the results obtained using the automatic extraction playing with plot options
Takes the value from the cursor on the graph window

1: Look at the effects of changing background subtraction parameters

- Change Eo
- Change R_{bkg}
- ...

R cut off for automatic background calculation

\[
\text{R}_{\text{bkg}} = 0.2
\]

\[
\text{R}_{\text{bkg}} = 1
\]

\[
\text{R}_{\text{bkg}} = 2
\]
3: Look, in R space, at the effects of changing extraction and FT parameters.
4: Look, in q (Back Fourier) space, at the effects of changing BF parameters
5: Data pre-treatment

- Calibrate energies
- Align scans
- Calibrate dispersive XAS
- Deglitch
- Truncate
- Rebin mu(E)
- Smooth mu(E)
- Convolute mu(E)
- Self Absorption
- MEE correction

Data calibration

Group: cu_foil_10k.dat
Display: deriv(E)
Smoothing: 0
Reference at: 8977.58
Calibrate to: 8979

Select a point
Find zero-crossing
Replot
Calibrate

Document section: energy calibration

Return to the main window
Save:

`cu_foil_10k.dat.chi`

\( \chi(k) \) is required for ARTEMIS
Working with several files

Go into the Fe directory

Open all the files (except README) into Athena

Temperature effect

Temperature vs. energy

All marked groups
5: Data treatment: Align $E_0$

$E_0$ appear shifted among the files.

[Graphs and data plots showing $E_0$ alignment and derivative plots.]
5: Data treatment: Merge several files

- Merge marked data in mu(E)
- Merge marked data in norm(E)
- Merge marked data in chi(k)

- Weight by importance
- Weight by chi_noise

Fe 60 are aligned
Exercise:

1. Read Fe Files
2. Align Fe files on order to have the same Eo
3. Merge files having the same T
4. Save $\chi(k)$ of merged files, these will be used for the structural analysis
Cu-fcc metal
SPG: fcc, f m 3 m (# 220)
\( a = 3.61 \text{ Å} \)
Cu 0.0 0.0 0.0

<table>
<thead>
<tr>
<th>Sh</th>
<th>R</th>
<th>N</th>
<th>( R_{Cu}(\text{Å}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>( a/\sqrt{2} )</td>
<td>12</td>
<td>2.553</td>
</tr>
<tr>
<td>II</td>
<td>( a )</td>
<td>6</td>
<td>3.610</td>
</tr>
<tr>
<td>III</td>
<td>( a\cdot\sqrt{1.5} )</td>
<td>24</td>
<td>4.421</td>
</tr>
<tr>
<td>IV</td>
<td>( a\cdot\sqrt{2} )</td>
<td>12</td>
<td>5.105</td>
</tr>
<tr>
<td>V</td>
<td>( a\cdot\sqrt{2.5} )</td>
<td>24</td>
<td>5.708</td>
</tr>
</tbody>
</table>

....
Start ARTEMIS program

Open Cu.inp file from the Cu directory

Start the refinement

Controls for plotting

Depends on what is highlighted in the Data & Paths panel

Structural model & Data refinement
It builds the cluster

<table>
<thead>
<tr>
<th></th>
<th>Sh</th>
<th>R</th>
<th>N</th>
<th>$R_{Cu}(A)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>a</td>
<td>12</td>
<td>2.553</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>a</td>
<td>6</td>
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<td></td>
</tr>
<tr>
<td>III</td>
<td>a·$\sqrt{1.5}$</td>
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<td>4.421</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>V</td>
<td>a·$\sqrt{2.5}$</td>
<td>24</td>
<td>5.708</td>
<td></td>
</tr>
</tbody>
</table>

...
Theoretical XAFS and FT for Cu fcc
Open Cu010k.chi

Using CTRL key select groups for plot

Compare model and experimental data
1st shell analysis

remove all paths or restart ARTEMIS

Right click

add 1st shell path to the list

select and Right click
The Data screen allows defining the fitting strategy and parameters.

**Path label**

**Energy shift**

**Distance correction**

**Debye Waller factor**

**Guess**: optimized in the refinement

**Def**: math expressions updated during the fit

**Set**: numbers or expressions evaluated once at the fit beginning and not updated

\[
\chi(k) = \sum_j N_j S_0^2 f_j(k) e^{-2R_j/\lambda(k)} e^{-2k^2 \sigma_j^2} \sin[2kR_j + \delta_j(k)]
\]
\[ \chi^2 = \frac{N_{\text{ind}}}{eN_{\text{pts}}} \sum_{i=1}^{N_{\text{pts}}} \left( (\Re(\chi_{\text{exp}}(r_i)) - \Re(\chi_{\text{th}}(r_i)))^2 + (\Im(\chi_{\text{exp}}(r_i)) - \Im(\chi_{\text{th}}(r_i)))^2 \right) \]

\[ \chi^2_{\nu} = \frac{\chi^2}{\nu} \quad \nu = N_{\text{ind}} - N_{\text{var}} \]

The refinement is performed on the Real and Imaginary parts of the FT

\[ R^2 = \frac{\sum_{i=1}^{N_{\text{pts}}} \left( (\Re(\chi_{\text{exp}}(r_i)) - \Re(\chi_{\text{th}}(r_i)))^2 + (\Im(\chi_{\text{exp}}(r_i)) - \Im(\chi_{\text{th}}(r_i)))^2 \right)}{\sum_{i=1}^{N_{\text{pts}}} \left( (\Re(\chi_{\text{exp}}(r_i)))^2 + (\Im(\chi_{\text{exp}}(r_i)))^2 \right)} \]

Absolute misfit between experimental data and theory
Structural results

\[ \chi^2 = \sum_{i=1}^{N_{pts}} \left( \frac{\text{Re}(\chi^{exp}(r_i)) - \text{Re}(\chi^{th}(r_i))}{\epsilon} \right)^2 + \left( 3m(\chi^{exp}(r_i) - 3m\chi^{th}(r_i)) \right)^2 \]

\[ R^2 = \frac{\sum_{i=1}^{N_{pts}} \left( \frac{\text{Re}(\chi^{exp}(r_i)) - \text{Re}(\chi^{th}(r_i))}{\epsilon} \right)^2 + \left( 3m(\chi^{exp}(r_i) - 3m\chi^{th}(r_i)) \right)^2}{\sum_{i=1}^{N_{pts}} \left( \frac{\text{Re}(\chi^{exp}(r_i))}{\epsilon} \right)^2 + \left( 3m(\chi^{exp}(r_i)) \right)^2} \]
Add new contributions

Single Scattering

MS + Focusing
In principle different for each shell

In principle the same for each shell

The used path must be inside the fit range
### Table

<table>
<thead>
<tr>
<th>#</th>
<th>Name</th>
<th>Math Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>s: amp</td>
<td>0.919991</td>
</tr>
<tr>
<td>2</td>
<td>g: enot</td>
<td>5.448280</td>
</tr>
<tr>
<td>3</td>
<td>g: delr</td>
<td>-0.004</td>
</tr>
<tr>
<td>4</td>
<td>g: delr2</td>
<td>-0.004661</td>
</tr>
<tr>
<td>5</td>
<td>g: delr3</td>
<td>-0.004</td>
</tr>
<tr>
<td>6</td>
<td>g: delr4</td>
<td>-0.004</td>
</tr>
<tr>
<td>7</td>
<td>g: ss</td>
<td>0.003596 (0.000283)</td>
</tr>
<tr>
<td>8</td>
<td>g: ss2</td>
<td>0.005123 (0.001735)</td>
</tr>
<tr>
<td>9</td>
<td>g: ss3</td>
<td>0.004593 (0.000671)</td>
</tr>
<tr>
<td>10</td>
<td>g: ss4</td>
<td>0.028058 (0.043714)</td>
</tr>
<tr>
<td>11</td>
<td>g: ss5</td>
<td>0.004597 (0.000968)</td>
</tr>
<tr>
<td>12</td>
<td>g: ss6</td>
<td>0.006</td>
</tr>
</tbody>
</table>

### Correlation Analysis

- ss6 and ss7 → -0.8579
- enot and delr → 0.8206
- delr4 and ss6 → -0.6973
- enot and delr3 → 0.6235
- delr and delr3 → 0.5795
- enot and ss5 → 0.4211
- delr and delr2 → 0.3650
- delr and ss5 → 0.3464
- delr3 and delr4 → 0.3298
- delr and delr3 → 0.2970
- delr4 and ss6 → -0.2649
- enot and ss7 → 0.2621

All other correlations are below 0.25.

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### Graph

The graph shows the function `cu_foil_10k.dot.chi` in R space. The data points are represented by blue dots, and the trendline is shown in red. The window is indicated by a green line.
it's your work now!

a. amorphous Ge
b. GeO
c. Pt