Introduction to X-ray Absorption Spectroscopy
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Part 1:
• What is XAFS?
• What does it tell us?
• The EXAFS equation

Part 2:
• Basic steps in the analysis
• Quick overview of typical analysis
• Example for Co doped ZnO films
What is XAFS?

XAFS stands for X-ray Absorption Fine Structure and appears in the vicinity of absorption edges.

EXAFS – Extended XAFS

XANES – X-ray Absorption Near Edge Structure

What is an absorption edge?
Cu example

EXAFS

XANES

E (eV)

Absorption

Absorption

E (eV)
EXAFS sensitive to local atomic structure

Nearest neighbor information:
- Distance
- Atomic type
- Coordination number
- Vibrational amplitude

Typically useful for the first few coordination shells

DiCicco et al. PRB 54, 9086
XANES sensitive to chemical state and valence

Fe compounds

Normalized absorption

E (ev)

Fe2O3
FeO
Fe3O4
Fe metal
hematite
Why is x-ray absorption useful?

- Short range order probe - crystallinity not required
- Element specific (Fe – 7111 eV, Cu – 8980, etc.)
- Near edge sensitive to chemistry
  - Valence
  - Site symmetry
- Extended structure sensitive to atomic neighbors
  - Number and type of neighbors
  - Distance to neighbors
  - Disorder in neighbors
  - Orientation of bonds (using x-ray polarization)
- Can be applied to dilute systems
Calculation of Absorption

From Fermi’s golden rule

\[
\mu = \frac{4\pi \omega e^2}{c} N |\langle i | r | f \rangle|^2 \rho(E_f)
\]

\(i\) – Initial state: 1s or 2p electron localized in the core of the atom

\(f\) – Final state: outgoing photoelectron wave + interactions with the neighboring atoms

\(\rho(E_f)\) – Density of final states
The XAFS equation

\[ \chi(k) = \frac{\mu(k) - \mu_0(k)}{\mu_0(k)} = \sum_j \frac{N_j}{kR_j^2} A_j(k) p_j(e) \sin\left[ 2kR_j + \psi_j(k) \right] \]

\[ k = \frac{\sqrt{2m_eE}}{\hbar} \]  The electron wavevector, \( E = E_{x-ray} - E_{edge} \)

- \( \mu_0 \) - "atomic" absorption
- \( R \) - distance to atoms of shell j
- \( N \) - number of atoms in shell j
- \( A \) - amplitude factor
- \( p \) - polarization factor
- \( \psi \) - phase factor
Cu EXAFS

![Cu EXAFS Graph](image-url)
Fourier Transform can separate the shells
The amplitude factor

\[ \chi(k) = \sum_j \frac{N_j}{kR_j^2} A_j(k) p_j(e) \sin \left[ 2kR_j + \psi_j(k) \right] \]

\[ A_j(k) = S_0^2 F_j(k) Q_j(k) e^{-2R_j/\lambda} \]

- \( S_0^2 \)- amplitude reduction due to multi-electron excitation
  - Typically 0.7 - 0.9 (almost constant with \( k \))
- \( F_j(k) \)- magnitude of the complex backscattering amplitude \( f_j(k,\pi) \)
- \( Q_j(k) \)- disorder term
- \( \lambda \)- mean free path of photoelectron (includes contribution from core hole lifetime)

\( f_j(k,\pi) \) calculated with theory such as FEFF
Backscattering Amplitude

$k (\text{Å}^{-1})$

- **C**
- **Cu**
- **Si**
- **Pt**
The Phase factor

\[ \chi(k) = \sum_j \frac{N_j}{kR_j^2} A_j(k) p_j(e) \sin\left[ 2kR_j + \psi_j(k) \right] \]

\[ \psi_j(k) = 2\phi_c + \theta_j(k) + \varphi_j(k) \]

\( \phi_c \) - p-wave (for K-edge) phase shift due to central atom potential

\( \theta_j(k) \) - the phase of the backscattering factor \( f_j(k,\pi) \)

\( \varphi_j(k) \) - phase factor related to the disorder of the \( j^{th} \) shell
Graph showing the relationship between $2\phi_c$ (radians) and $k$ (Å$^{-1}$) for different materials:

- **C** (solid line)
- **Cu** (dashed line)
- **Si** (dotted line)
- **Pt** (dash-dotted line)
Polarization Factor

$$\chi(k) = \sum_j \frac{N_j}{kR_j} A_j(k) p_j(e) \sin[2kR_j + \psi_j(k)]$$

Synchrotron radiation generally linearly polarized

For the K-shell the photoelectron emitted with p-wave symmetry:

$$p_j(e) = 3<\cos^2 \theta>$$

$$\langle \cos^2 \theta \rangle = \frac{1}{N_j} \sum_i \cos^2 \theta_i$$

3-fold or higher symmetry $$<\cos^2 \theta> = 1/3$$, p=1

Uniaxial symmetry (i.e. surface):

$$\chi(\Theta) = \frac{[2\chi_0 \cos^2(\Theta) + \chi_{90} \sin^2(\Theta)]}{3}$$
**YBa\(_2\)Cu\(_3\)O\(_7\) structure**

Sample is oriented powder: c-axis of all grains are aligned, no alignment of a-b axes.

Two types of Cu sites:
- Planes – have bonds in a-b plane
- Ribbons – have bonds along c axis

Consider the Cu-O near neighbor bonds:
- Polarization in **a-b plane** both sites contribute, but dominated by Plane sites
- Polarization along **c axis** the signal is dominated by the Ribbon sites
Polarization dependence of YBa$_2$Cu$_3$O$_7$

**XANES**

**EXAFS Fourier Transform**
Disorder terms

\[ \psi_j(k) = 2\phi_c + \theta_j(k) + \varphi_j(k) \]

\[ A_j(k) = S_0^2 F_j(k) Q_j(k) e^{-2R_j/\lambda} \]

\[ Q_j(k) \exp[i\varphi_j(k)] = \int dr P_j(r) \exp[i2k(r - R_j)] \]

\[ P_j(r) \] - real space distribution of atoms in shell j

Simplest case is Guassian disorder (i.e. thermal motion)
To lowest order:
\[ Q_j(k) = \exp(-2k^2\sigma_j^2) \] (Debye-Waller factor)
\[ \varphi_j(k) = 0 \]

\[ \sigma_j^2 \] - mean squared vibrational amplitude of bond length

Different from the diffraction DW factor

Non-symmetric distributions can be handled with the cumulant method
Change in disorder with temperature
Choice of Absorption edge

- Low energies require high vacuum and x-ray penetration small
- At high energies lifetime broadening washes out the spectra
- Most convenient to work in range 4-30 keV

K edges:
  - Ca \rightarrow Sn

L edges:
  - Sn \rightarrow U

For lighter elements must work at low energies
L edges

L₁ - 2s initial state - Same symmetry as K edge

L₂,₃ - 2p initial state - can have transitions to s or d final states

Three possible contributions to χ(k): χ_{ss}, χ_{sd}, χ_{dd}

\[ \chi = \left( M_{21}^2 \chi_{dd} + M_{01}^2 \chi_{ss} + 2M_{01}M_{21} \chi_{sd} \right) / \left( M_{21}^2 + M_{01}^2 / 2 \right) \]

Each contribution has its own polarization dependence

\[ p_{22}^j = \frac{1}{2} \left( 1 + 3 \langle \cos^2 \theta \rangle_j \right) \]
\[ p_{00}^j = \frac{1}{2} \]
\[ p_{02}^j = \frac{1}{2} \left( 1 - 3 \langle \cos^2 \theta \rangle_j \right) \]
L edges (cont.)

Two important simplifications:

\[ M_{01} \text{ typically about } 0.2M_{21} \]

\[ \rightarrow \text{can generally ignore } M_{01}^2 \text{ term} \]

unoriented or symmetric samples: \( p_{02} = 0 \)

For unoriented or symmetric samples L edges can be treated the same as the K edge

For oriented asymmetric samples (i.e. surface site) the crossterm must be included (40% of dd term)
Multiple Scattering

- Not important for first shell
- Must be considered in analyzing all shells above first
- Dominates at large distances
- Typically limits analysis to first few shells
Multiple scattering in Cu

Calculated EXAFS for 1\textsuperscript{st} four shells

<table>
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<tr>
<th>R</th>
<th>N</th>
<th>Rel. Amp</th>
<th>Type</th>
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<td>3.615</td>
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<td>9</td>
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<td>4.428</td>
<td>24</td>
<td>55</td>
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</tr>
<tr>
<td>4.770</td>
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<td>11</td>
<td>Triangle</td>
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<td>96</td>
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<td>12</td>
<td>19</td>
<td>Single</td>
</tr>
<tr>
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<td>44</td>
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<tr>
<td>5.112</td>
<td>12</td>
<td>33</td>
<td>Collinear</td>
</tr>
</tbody>
</table>
Measuring XAFS

Need to measure absorption

Direct method:

\[ I = I_0 e^{-\mu t} \]

\[ \mu t = -\ln(I/I_0) = \ln(I_0/I) \]

Indirect methods (proportional to absorption)
- Fluorescence
- Electron Yield
- Reflectivity
- Optical emission
Fluorescence Detection

$$\mu'(E) = \frac{I_f}{I_0} = \frac{\mu(E)\sin(\theta)}{\mu_t(E)/\sin \theta + u_t(E_f)/\sin \phi}$$

$$\mu_t - \text{total absorption of sample} \ (\mu + \mu_{\text{matrix}})$$

Need to consider absorption going in and out of the sample.
Fluorescence detection - cont.

Typical case $\sin\theta = \sin\phi = 45$

**Dilute sample:** $\mu \ll \mu_{\text{matrix}}$

$$\frac{I_f}{I_0} = \frac{\mu(E)}{\mu_{\text{matrix}}(E) + \mu_{\text{matrix}}(E_f)}$$

Denominator almost constant

**Concentrated sample:** $\mu = \mu_{\text{matrix}}$

(self absorption)

$$\frac{I_f}{I_0} = \frac{\mu(E)}{\mu(E) + \mu(E_f)}$$

For K edge: $\mu(E_f) \approx \mu(E)/8$

**Thin concentrated sample:** absorption of x-rays entering and exiting sample are negligible

$$\frac{I_f}{I_0} \approx \mu(E)$$

**Glancing exit angle:** $\sin\phi \ll 1$

$$\frac{I_f}{I_0} \propto \frac{\mu(E)}{\mu_{\text{matrix}}(E_f)}$$
Self absorption

Cu metal

Re near edge

Data from R. Gordon

Normalized absorption

E (eV)

Normalized absorption

E (eV)
Fluorescence or transmission?

From statistics – $\Delta \mu x < 0.05 - 0.1$ fluorescence generally better

Many factors can influence this
    monochromator glitches
    sample uniformity
    other fluorescence lines

Often can measure both simultaneously and choose the best one
Part 2: Analyzing the EXAFS

Background removal

Fourier Transform

Normalization

Fitting to extract structural parameters
Fourier filtering
Independent Data Points

From information theory:

\[ N_i = 2\Delta k \Delta R / \pi + 1 \]

- \( \Delta k \) - range of data used in k-space
- \( \Delta R \) - range of data used in R-space

Example:

k range is 2 - 18 Å\(^{-1}\)
R space filtering or fitting window is 1.7 – 2.8 Å
Then maximum number of independent fitting parameters is 11

If data range short (kmax ~ 10) then number of possible fitting parameters will be constrained.
Example of noisy data
Typical fitting parameters

- $\Delta E_0$ – match the experimental and theoretical edge positions
- Overall amplitude factor ($S_0^2$)
- Each shell needs disorder factor ($\sigma^2$)
- May also need $\Delta R$

$\Delta E_0$ and $S_0^2$ can generally be common to all shells

Therefore, typically need 4 parameters for simple first shell and 2-3 more for each additional shell.

Always good to constrain the fits with other knowledge about the sample.
Co doped ZnO

- Candidate material for a dilute magnetic semiconductor
- Many reports of magnetism at room temperature
- Some cases have been shown to be due to secondary phases (metallic nanoparticles)
- Some cases of well characterized single phase materials without magnetism

**EXAFS and XANES are sensitive to secondary phases**

- Element specific - allows detection of dilute dopants
- XANES can see valence change if metallic Co present
- EXAFS can identify the secondary phase (dilute nanoparticles difficult to see with diffraction)
- Bulk probe of whole film
ZnO structure (wurtzite)

- First shell tetrahedrally coordinated - no orientation dependence
- Higher shells have more orientation dependence

2 substrate orientations:
- r-plane sapphire – film grows (110)
- c-plane sapphire – film grows (001)
The Co doped ZnO samples

See Kaspar et al, PRB 77, 201303 and Heald et al PRB 79, 075202

- PLD deposited samples on r- and c-plane sapphire
- 100 nm with about 16% Co
- Some samples annealed in Zn vapor to induce magnetism
Detection of metallic Co - XANES
EXAFS for Co doped ZnO
Detection of metallic Co - EXAFS

![Graph showing EXAFS data for hcp Co, Co:ZnO - Zn, CoZn, and Co:ZnO.](image-url)
Possible magnetic forms of Co

- **HCP Co**
  - Identified previously by XRD and XAFS
  - Typically small nanoparticles
  - $1.72 \, \mu_b/Co$

- **FCC Co**
  - Stable at high temperatures
  - Can contain up to 40% Zn with accompanying lattice expansion
  - $1.72 \, \mu_b/Co$ for the pure phase

- **CoZn intermetallic**
  - $\beta$-Mn structure
  - $1.35 \, \mu_b/Co$
Fitting of near edge

Near edge inconclusive in distinguishing the metal component

Does provide an accurate estimate of the amount of metal

Near edge fits
Co EXAFS polarization dependence

**r-plane substrate**

![Graph showing Co EXAFS polarization dependence for r-plane substrate](image)

**c-plane substrate**

![Graph showing Co EXAFS polarization dependence for c-plane substrate](image)
Origin of polarization dependence - CoZn

Co near neighbors
Co – blue, Zn – gray

<table>
<thead>
<tr>
<th>Neighbor</th>
<th>N</th>
<th>Distance</th>
<th>Measured</th>
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<tbody>
<tr>
<td>Co</td>
<td>3</td>
<td>2.36 Å</td>
<td>2.34</td>
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<tr>
<td>Zn</td>
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<td>2.54</td>
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<tr>
<td>Zn</td>
<td>3</td>
<td>2.63</td>
<td>2.60</td>
</tr>
<tr>
<td>Zn</td>
<td>3</td>
<td>2.67</td>
<td>2.64</td>
</tr>
</tbody>
</table>
Fitting using CoZn model

Simultaneous fit to the two polarization directions with oriented CoZn second phase
Glancing angle XAFS - surface sensitivity

Small angles total external reflection → x-ray penetration a few nm

Compare measurements at:
0.16 deg (surface)
4 deg (bulk)
Angle dependent results

Metallic component enhanced near the surface
X-ray Absorption Spectroscopy is a powerful tool that complements scattering methods

- Element specific
- Provides both structural (EXAFS) and chemical (XANES) information
- Fluorescence detection allows extremely dilute (ppm) components to be studied
- Does not need long range order – wide range of applications
  - Operando studies of catalysts, fuel cells, and batteries
  - Detailed study of the active site in metalloproteins
  - Hazardous elements in the environment
  - Magnetism using polarized x-rays
  - High pressure studies
  - Thin film growth and characterization
  - Many others...