X-RAY ABSORPTION SPECTROSCOPY (XAS)

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OUTLINE

- Background X-ray absorption spectroscopy
- Fundamentals of atoms and electronic transitions
- X-ray absorption near edge spectra (XANES) process
- XANES examples
- Extended X-ray absorption fine structure (EXAFS) fundamentals
- EXAFS examples
Absorption of X-Rays.-This paper contains an account of an experimental investigation concerning the discontinuity in the X-ray absorption corresponding to the K-series for the chemical elements from magnesium to chromium inclusively. The method followed was the same as that devised and employed by de Broglie. A specially designed vacuum spectrograph was used. Fine Structure of Absorption.-The spectrograms show that the discontinuity has a rather complex structure, a result in advance of those obtained by earlier investigators. A photometric study of the plates was made in order to obtain a more accurate knowledge of the detailed structure of the absorption limits. Results. These are recorded in tables which give for each element the wave-lengths of the different remarkable points in the structure of the discontinuities. The theoretical bearing of the new observations is briefly discussed. © 1920 The American Physical Society.

We have applied Fourier analysis to our point-scattering theory of x-ray absorption fine structure to invert experimental data formally into a radial structure function with determinable structural parameters of distance from the absorbing atom, number of atoms, and widths of coordination shells. The technique is illustrated with a comparison of evaporated and crystalline Ge. We find that the first and second neighbors in amorphous Ge are at the crystalline distance within the accuracy of measurement (1%).
ACRONYMS

▪ General terms:
  – XAS: X-ray absorption spectroscopy
  – XAFS: X-ray absorption fine structure

▪ Specific terms:
  – EXAFS: Extended x-ray absorption fine structure
  – XANES: x-ray absorption near edge structure
ELECTRONIC STRUCTURE OF AN ATOM

▪ Electronic structure described by 4 quantum numbers:
  – Principal: \( n \)
  – azimuthal: \( \ell = 0, 1, 2, \ldots n-1 = s, p, d, f \)
  – total angular momentum: \( j = \ell + s \), spin = +1/2 or -1/2

▪ K shell, \( n=1; 1s \)
▪ L shell, \( n=2; 2s, 2p_{1/2}, 2p_{3/2} \)
▪ M shell, \( n=3; 3s, 3p_{1/2}, 3p_{3/2}, 3d_{3/2}, \) and \( 3d_{5/2} \)

▪ Electronic transitions due to X-ray absorption must follow dipole selection rule requires conservation of angular momentum
  – Transitions are allow for \( \ell = +/- 1 \)
XANES: ELECTRONIC TRANSITIONS

- XANES directly probes the angular momentum of the unoccupied electronic states: these may be bound or unbound, discrete or broad, atomic or molecular.

- Dipole selection rules apply*: \( \Delta l = \pm 1 \)

- Primary transition will be:
  - \( s \rightarrow p \) for K (1s core electron) and L\(_1\) (2s core electron initial state) edges
  - \( p \rightarrow d \) for L\(_2\) (2p\(_{1/2}\)) and L\(_3\) (2p\(_{3/2}\)) edges

- But…..final state usually not atomic-like and may have mixing (hybridization) with other orbitals. This is often the interesting part of the XANES!

* Some transitions are true quadrupolar transitions. These are usually very weak.
METAL K-EDGE XANES

- Absorption edge: dipole $1s \rightarrow 4p$ transition ($\Delta l = \pm 1$)
- Pre-edge: mixing of $3d-4p$ opens $1s \rightarrow 3d$ transition
OXIDATION STATE OF Mn OXIDES

Mn K-edge XANES

- Many edges of many elements show significant edge shifts (binding energy shifts) with oxidation state.
- First observation was by Berengren for phosphorus in 1920*!

**PT XANES DURING IN SITU REDUCTION**

Direct in situ measurement of Pt reduction

- Pt L$_3$-edge p-$\rightarrow$d transition
- Pt electrons: [Xe]4f$^{14}$5d$^{6}$s$^{1}$
- Pt white line intensity decreases as temperature increases due to 5d electrons filling
- Rate of decrease is fastest at ~270°C.

![Pt XANES](image)

**Pt White Line Height**

- Fastest rate of decrease

![Graph](image)
BEER’S LAW: ABSORPTION OF X-RAYS BY MATTER

- $\mu x$ is the absorption length of a material
- One absorption length, $I_t = 37\% \ I_0$
- Two absorption lengths, $I_t = 13\% \ I_0$

$$I_t = I_0 e^{-\mu x}$$
MEASUREMENT OF X-RAY ABSORPTION COEFFICIENT

Transmission

\[ \mu = \log \frac{I_0}{I_t} \]

Fluorescence

\[ \mu \propto \frac{I_f}{I_0} \]
DEFINITION OF EXAFS

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

Background

Edge Step

Pt Foil in energy

\[ \Delta \mu \]

Energy (eV)
FERMI’S GOLDEN RULE

\[ \mu(E) \propto |\langle i | H | f \rangle|^2 \]

- Initial State: atom with core electron
- Interaction term: incident x-ray
- Final State: atom with core hole, photo-electron

- Transition between two quantum states
- Initial state is well localized at the absorbing atom
- Final state is not, but can be written in terms of two parts

\[ |f\rangle = |f_0\rangle + |\Delta f\rangle \]

- Depends on neighboring atoms
- Depends on adsorbing atom
X-RAY ABSORPTION PROCESS

1) X-ray with energy below the binding energy of the core level does not interact with the atom.
2) X-ray with energy just above the binding energy of the core level has a probability of being adsorbed producing a low energy photo-electron.
3) X-ray with higher energy have a probability of being adsorbed and producing higher energy photo-electron.

\[ \lambda = (E - E_0)^{-\frac{1}{2}} \]
Interference between outgoing and scattered photoelectron at the absorbing atom causes modulations in the probability for absorption.
ATOMIC PHASE SHIFT $\delta(k)$

$\chi(k) \propto \psi_{scatt}(k, r = 0)$

$\propto \frac{e^{ikR}}{kR} \left[ F(k)e^{-i\delta(k)} \right] \frac{e^{ikR}}{kR}$

$\chi(k) \propto \frac{F(k)}{k^2 R^2} \sin(2kR + \delta(k))$

- Atomic Phase shift has two parts. One part from the absorbing atom and another part from the scattering atom.
- Typically corrections to the FT for atomic phase shift takes into account only the absorbing atom component.
LIFETIME OF PHOTOELECTRON AND CORE HOLE

- X-ray absorption fine structure requires a core hole and a coherent photoelectron.
- The mean free path $\lambda$ of the photoelectron limits the contributions to EXAFS to the first few neighbors.

Probability for a coherent photoelectron to travel the distance $2R$ is given by

$$e^{-\frac{2R}{\lambda_j}}$$
PASSIVE ELECTRON REDUCTION FACTOR

\[ S_0^2 = \left| \left\langle \phi_f^{N-1} \middle| \phi_i^{N-1} \right\rangle \right|^2 \]

- The initial and final states include all the passive electrons of the absorbing atom.
- If the electrons do not react to the creation of the core hole, then there is no difference in these passive electrons and the initial and final states are identical giving \( S_0^2 = 1 \), indicating a screened potential.
- If the electrons do react (they only have \( 10^{-15} \) seconds to do so) then the final state will be slightly different from the initial state. The final state will have the electrons pulled in slightly due to the core hole and the value for \( S_0^2 \) can be as small as \( \sim 0.7 \), indicating an unscreened potential.
- Value for \( S_0^2 \) depends only on the adsorbing atom and can be transferred from a standard material such as a foil.
- \( S_0^2 \) often contains experimental affects such as energy resolution so it is best to measure a foil under the same experimental conditions as the unknown sample.
EXAFS signal is the sum of many individual scattering events \( j \).

It is convenient to group scattering events from shells of atoms, \( i \), of the same type at the same radial distance from the adsorbing atom. Then we need to multiply the scattering contribution by the number of atoms in each shell (\( N_i \)).
Summing over shells introduces an error because not all of the atoms in a shell are at exactly the same radial distance from the adsorbing atom.

The scattering process takes place in $10^{-15}$ seconds. Atomic vibrations occur in $10^{-12}$ to $10^{-13}$ seconds.

Neighboring atoms are frozen at some position about their equilibrium position.
THE EXAFS EQUATION

\[ \chi(k) = \sum_i \chi_i(k) \]

with

\[ \chi(k) = \sum_j \frac{N_j S_0^2 F_j(k) e^{-2k^2 \sigma_j^2} e^{-\frac{2R}{\lambda}}}{k R_j^2} \sin[2kR_j + \delta_j(k)] \]

\[ R_i = R_0 + \Delta R \]
\[ k^2 = 2 m_e (E - E_0) / \hbar \]

Theoretically calculated values
- \( F_j(k) \) effective scattering amplitude
- \( \varphi_j(k) \) effective scattering phase shift
- \( \lambda(k) \) mean free path

Starting values
- \( R_0 \) initial path length

Parameters determined from a fit to data
- \( N_i \) degeneracy of path
- \( S_0^2 \) passive electron reduction factor
- \( \sigma_i^2 \) mean squared displacement of half-path length
- \( E_0 \) energy shift
- \( \Delta R \) change in half-path length
PT EXAFS OF REFERENCE MATERIALS

Pt EXAFS: unique information about the average local atomic environment of Pt

- Pt-O, Pt-Cl, and Pt-Pt signals are unique and are readily distinguished.
LOW TEMPERATURE REGION

- Large changes in Pt EXAFS with reduction temperature
- Pt-O and Pt-Cl bonding readily distinguished
- Pt-Pt cluster formation observed by 250°C
EXAFS AND STEM: AS RECEIVED

Direct in situ measurement of Pt reduction

- STEM Images show isolated atoms and few dimers*
- Good agreement with EXAFS

PT CLUSTER SIZE AND EXAFS PT-PT CN

Pt-Pt Coordination Number is related to Pt cluster size

<table>
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<th>Atoms</th>
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EXAFS AND STEM: 350°C REDUCTION

350°C Reduced: Isolated atoms and 6Å clusters

- STEM Images:
  - Isolated Pt atoms
  - Small groups of Pt atoms
  - ~ 4 Å – 6 Å diameter Pt clusters

- EXAFS: ~ 6 Å diameter Pt clusters