Applications of X-Ray Absorption Spectroscopy

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Abstract

This document contains the presentation materials for a seminar entitled *Applications of X-Ray Absorption Spectroscopy*. This file is suitable for presentation directly from a computer or for printing onto transparency sheets.

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The XAS Experiment

Experimental setup. Optics and detectors. Sample environments.

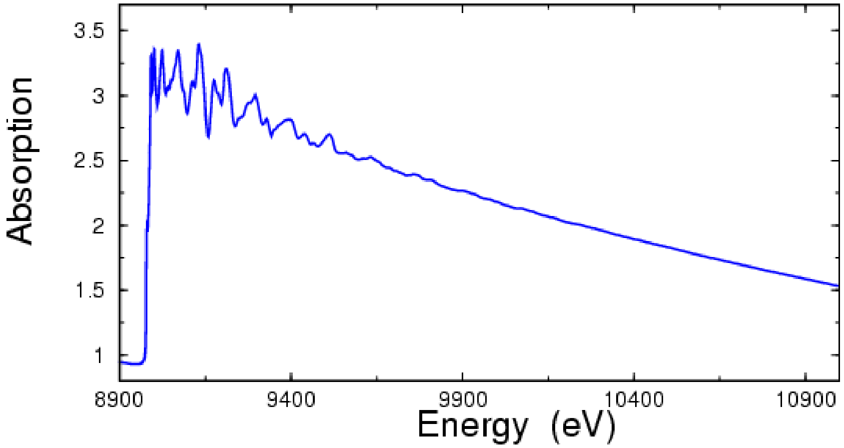
Several Example Applications of XAS

Speciation, time resolved measurements, structure determination, local symmetries

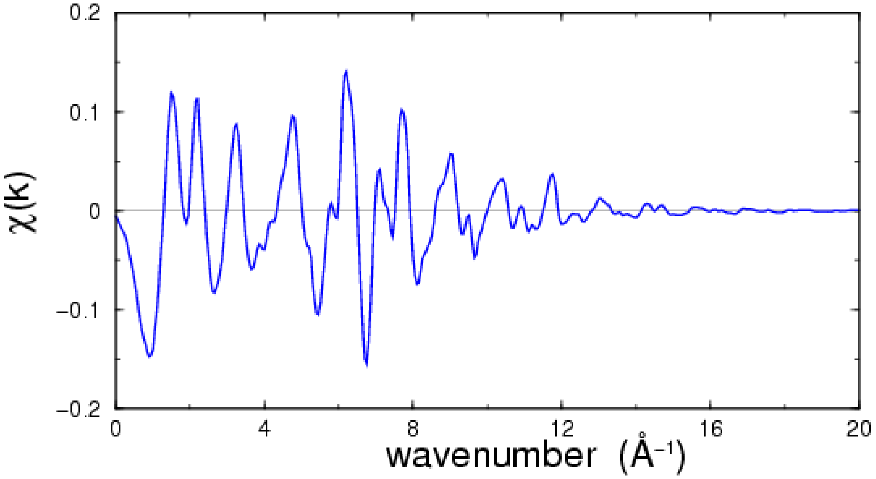
EXAFS Data

In an EXAFS experiment, one measures an absorption spectrum.

It looks something like this:



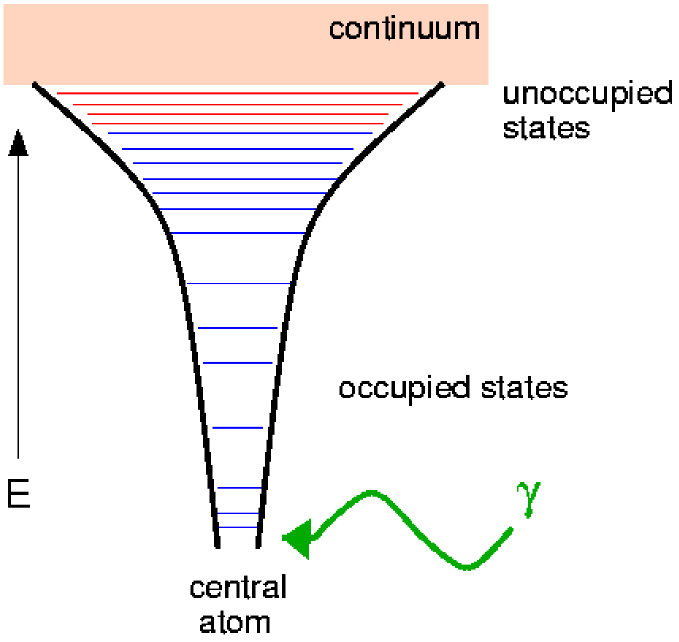
We first extract the wiggly part:

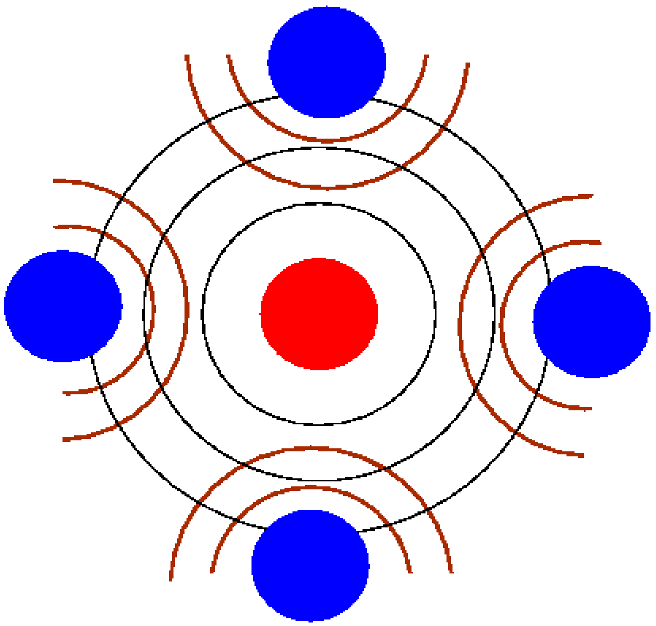


What information is contained in these data?

Heuristic Picture of EXAFS

In an EXAFS measurement, a deep core electron is excited into a state above the Fermi energy.





The photoelectron propagates as a spherical wave and scatters off the surrounding atoms. This cartoon is overly simplistic, but serves to motivate an understanding of absorption.

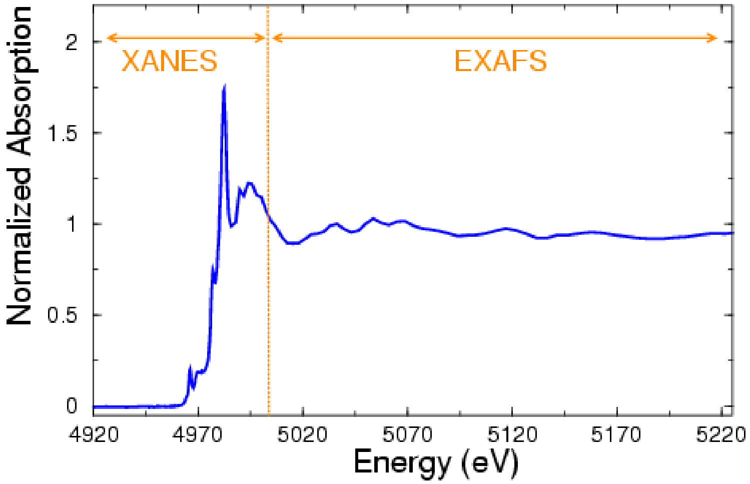
XANES and EXAFS

The x-ray absorption spectrum is typically considered in two parts.

X-ray Absorption Near Edge Structure

and

Extended X-ray Absorption Fine Structure



XANES contains information about the valence and density of states of the absorber, as well as qualitative structural information.
It is *interpreted*, often by simulation.

EXAFS contains detailed information about the local atomic structure.
It is *analyzed* by curve fitting.

Fermi's Golden Rule

In XAS we measure the dipole mediated transition of an electron in a deep core state $|i\rangle$ into an unoccupied state $|f\rangle$:

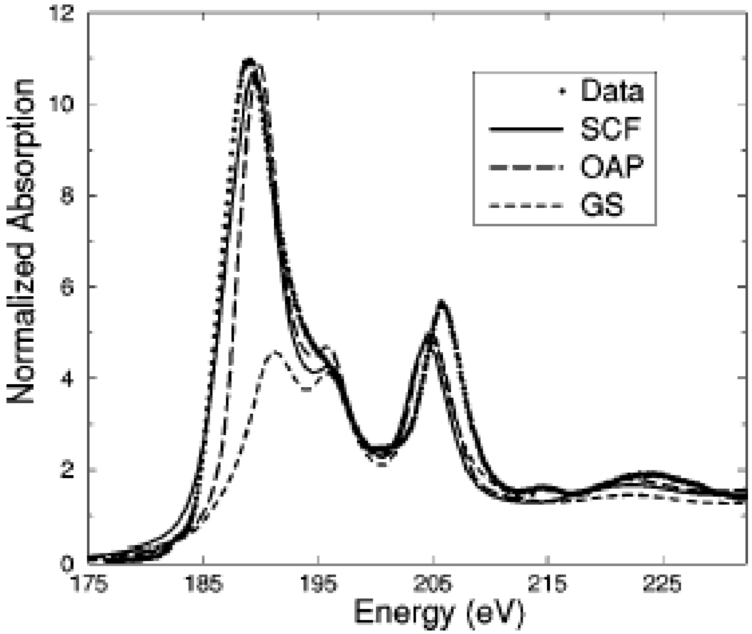
$$\mu(E) \propto \sum_{f}^{E_f > E_F} \left|\langle f|\hat{\epsilon} \cdot \mathbf{r}|i\rangle\right|^2 \delta(E_f)$$

There are two ways to solve this equation:

1. Accurately represent $|i\rangle$ and $|f\rangle$, then evaluate the integral directly. This is the approach taken, for example, by molecular orbital theory.
2. Use multiple scattering theory:

$$\mu(E) \propto -\frac{1}{\pi} \operatorname{Im} \langle \mathrm{i}|\hat{\epsilon}^* \cdot \boldsymbol{r}\, \mathbb{G}(r, r'; E) \hat{\epsilon} \cdot \boldsymbol{r}'|\mathrm{i}\rangle \Theta(E - E_F).$$

Simulating the XANES Spectrum: cubic BN



The XANES spectrum probes the final state density of states above the Fermi energy. Along with some electronic structure information about the absorber, the XANES contains information about the local structural environment. Combined with good theory, XANES is a powerful structural tool applicable to a wide variety of scientific problems.

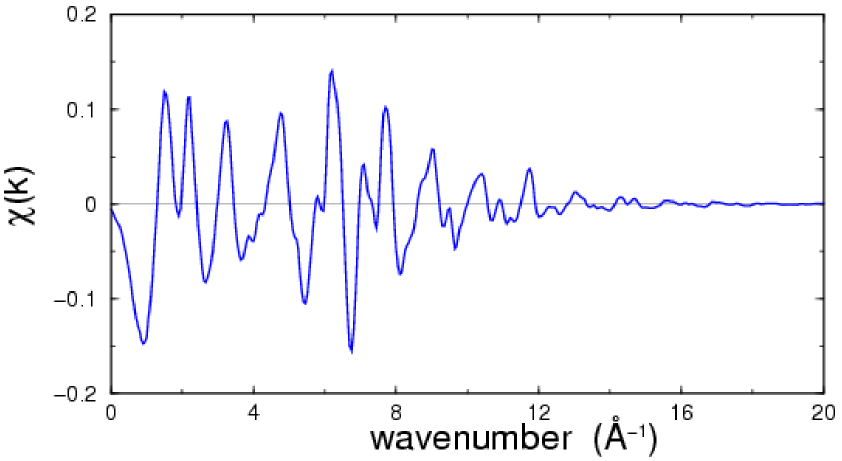
Real-space multiple-scattering calculation and interpretation of x-ray-absorption near-edge structure
A.L. Ankudinov, B. Ravel, J.J. Rehr, and S.D. Conradson

Physical Review **B58**, #12 pp. 7565–7576

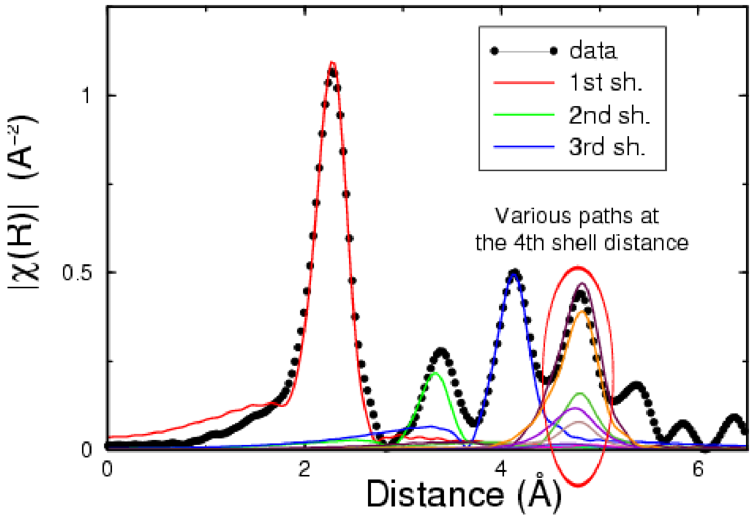
Fitting EXAFS Data

The EXAFS can be analyzed using curve fitting, yielding quantitative information about the structural environment of the absorber.

This is the background-subtracted data in photoelctron wavenumber.



This is the magnitude of the complex Foruier transform with parts of the fit

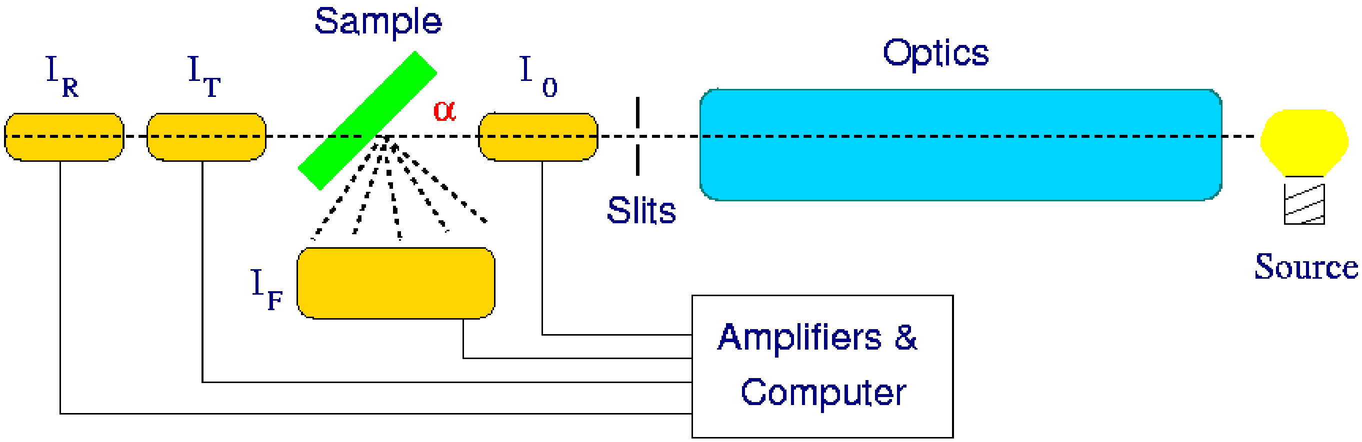


The Information Content of the XAS Spectrum

XANES	EXAFS
1. Fermi energy	1. Bond lengths
2. Projected DOS for absorber	2. RMS displacements about bond lengths
3. Local coordination geometry	3. Coordination
4. Charge transfer (from theory)	4. Partial pair distributions
5. Total DOS (from theory)	5. Three-body effects

Experimental Setup

Here is a schematic of the XAS experiment

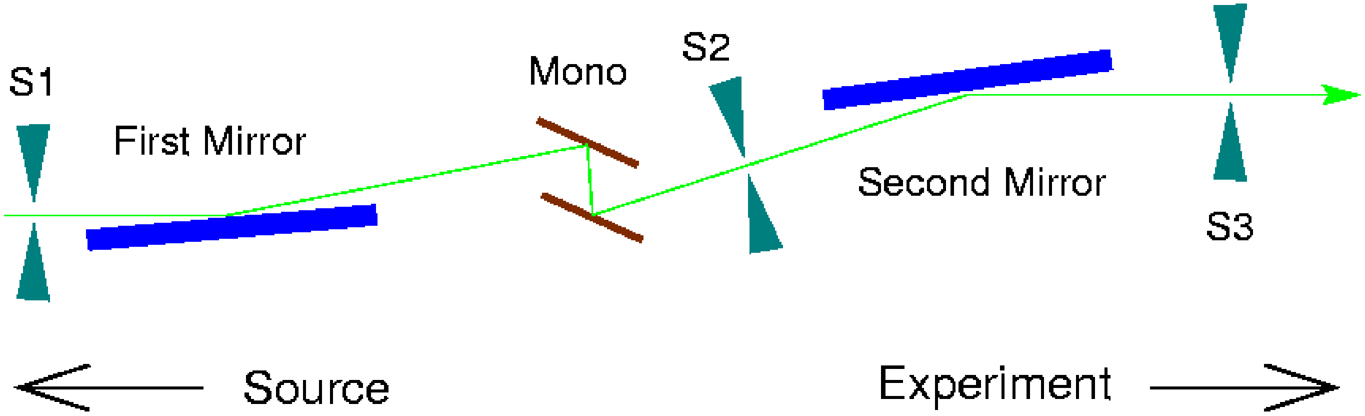


The five parts of the experiment are (1) the source, (2) the optics, (3) the sample, (4) the detectors, and (5) the electronic and computer.

transmission	fluorescence
$\mu(E) = \ln\left(\frac{I_0}{I_t}\right)$	$\mu(E) = \frac{I_f}{I_0}$

Optics and Detectors

Here is a common type of optics, which includes a monochromator and mirrors for harmonic rejection.



Several kinds of detectors are commonly used, including

1. ion chambers
2. diodes
3. energy discriminating
4. wavelength dispersive

Sample Environments

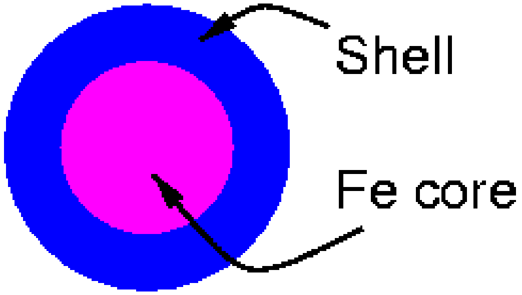
Any sample environment which allows photons to reach the sample and pass through (or fluoresce out of) the sample can be used in an XAS experiment. Here is an incomplete list:

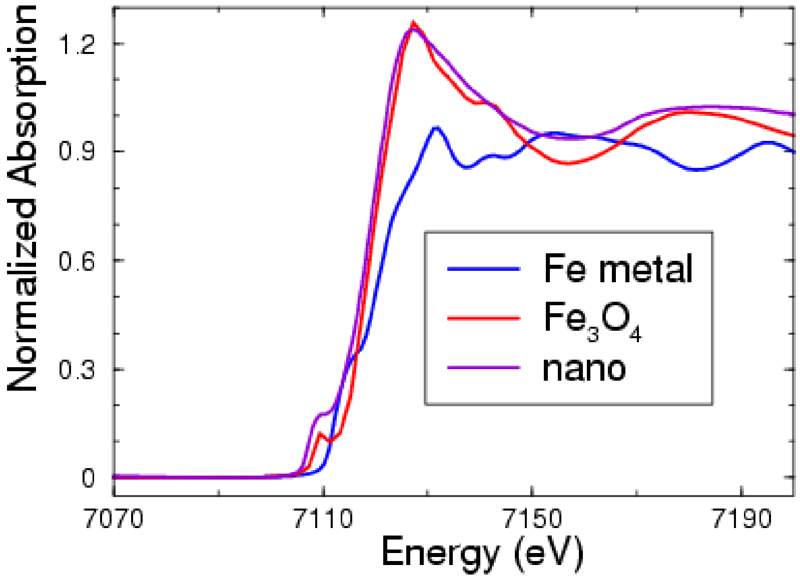
1. Furnace
2. Cryostat
3. Pressure cell
4. UHV chamber
5. Electrochemical cell
6. External electric or magnetic field

. . . and a whole bunch I didn't think of the day I wrote this slide.

Characterizing Nanoparticles

In 6342 there is an effort to produce nanoparticulate, metallic iron for use in biosensor applications. The idea is to cover an iron core with an antioxidation layer.



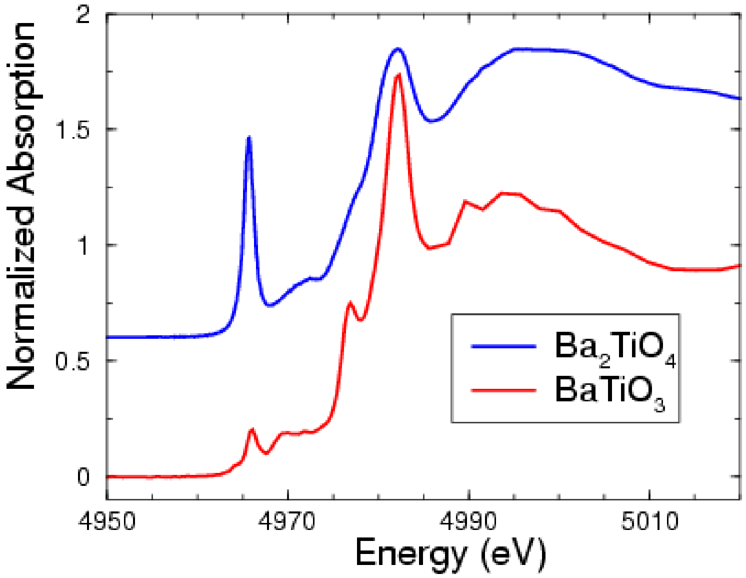


Unfortunately the effort to date has not been successful. The XAS clearly shows that the iron portion of the sample is well oxidized.

XAS is a useful tool for speciation.

Transition Metal Coordination Environments

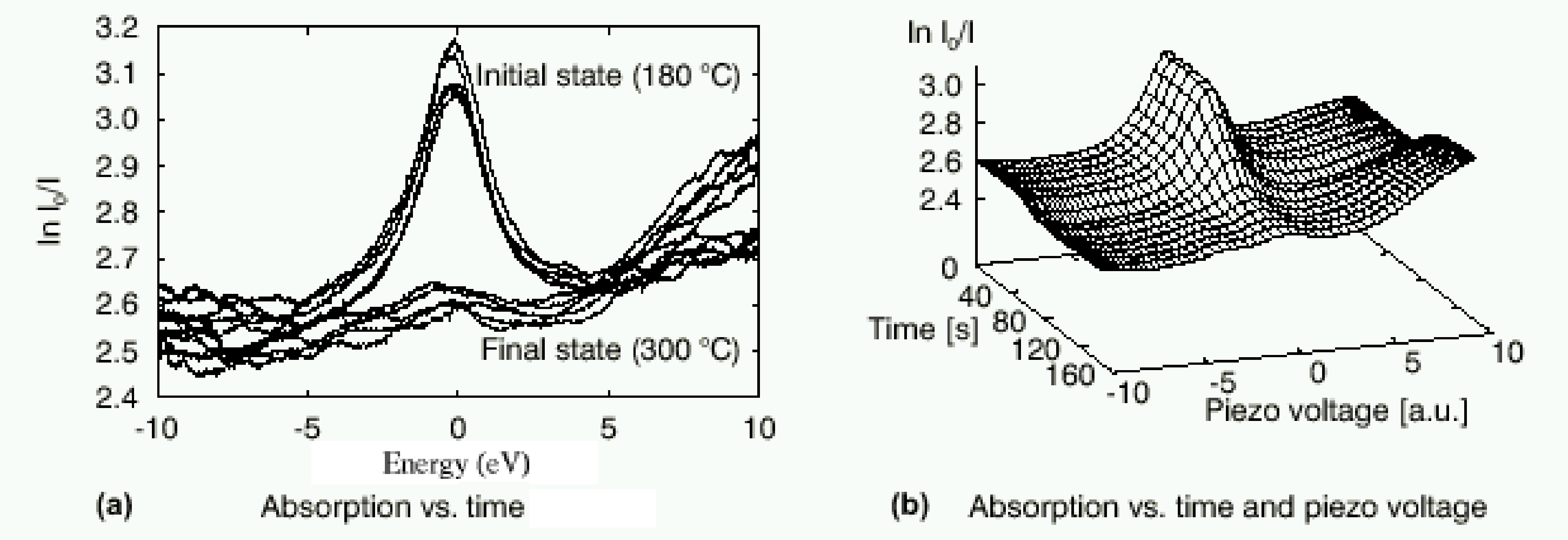
Speciation is a key application of XAS. It is particularly useful for transition metal compounds where different coordination geometries lead to distinct near-edge spectra.



A tetrahedral transition metal environment (i.e. not inversion symmetric) shows a characteristic sharp peak just above the Fermi energy.

Time Resolution of Chemical Reaction

The notion of speciation can be extended by considering the time evolution of a reaction.



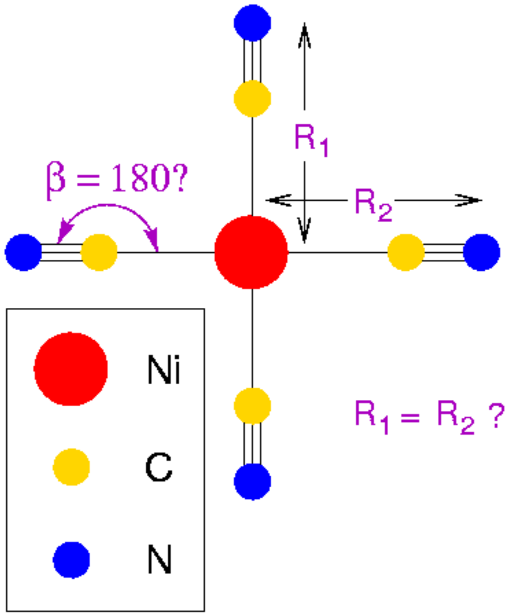
In this example tetrahedral Cr^{VI} is reduced to octahedral Cr^{III}.
The large peak evolves into a much smaller one.

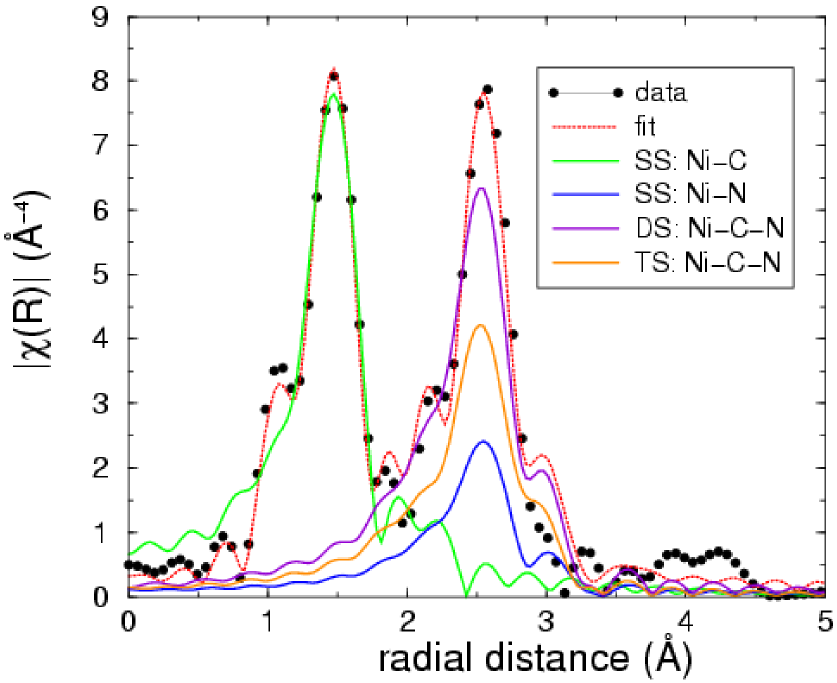
Piezo-XAFS for the investigation of solid-state transformations in the millisecond range,
J.-D. Grundwaldt, D. Luetzenkirchen-Hecht, M. Richwin, S. Grundmann, B.S. Clausen, and R. Frahm,

J. Phys. Chem., submitted.

Molecules in Solution

$[\mathrm{Ni(CN)_4}]^{2-}$ is a square planar molecule soluble in water.



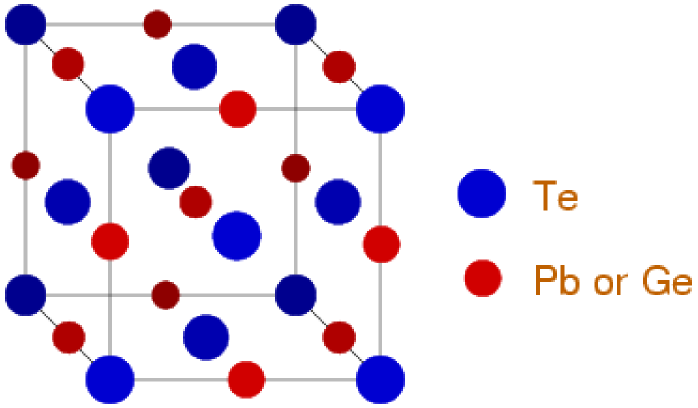


These data may be analyzed in detail, yielding quantitative results regarding lengths interatomic distances and bond angles.

S. Díaz-Moreno, PhD. Dissertation

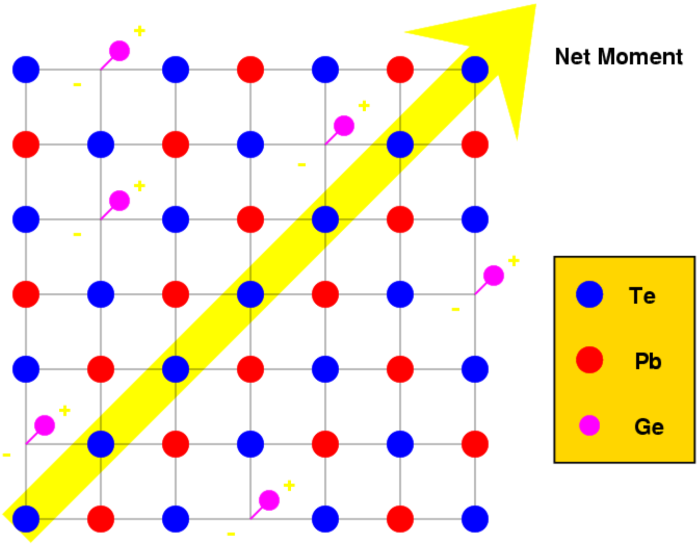
University of Sevilla, Spain

Complex Structures: Lead Germanium Telluride



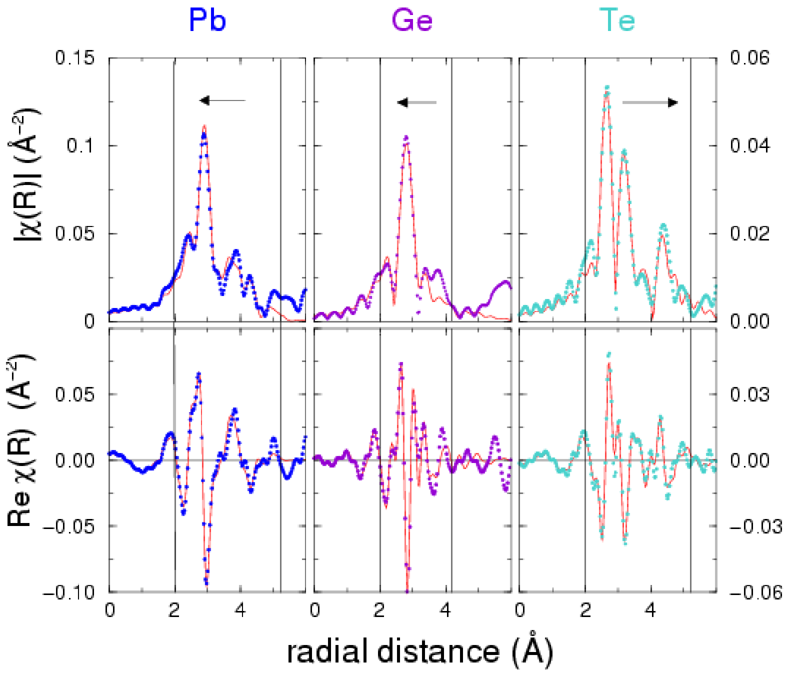
$Pb_{1\text{-}x}Ge_xTe$ is solid solution of two rock salt structure intermetallics. The Ge atoms is much smaller than the Pb atoms that it randomly substitutes for.

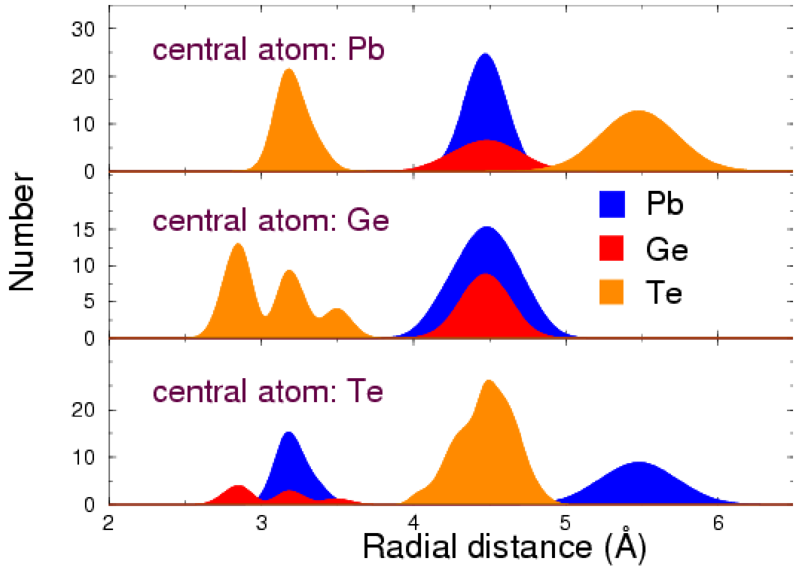
The simplest picture is that the Ge atoms displace in the direction of the net polarization vector, $\vec{P}$. However, there is a complicated relaxation of the lattice about the Ge sites and this relaxation depends on the direction of $\vec{P}$.



Complex Structures: Pair Distribution Functions

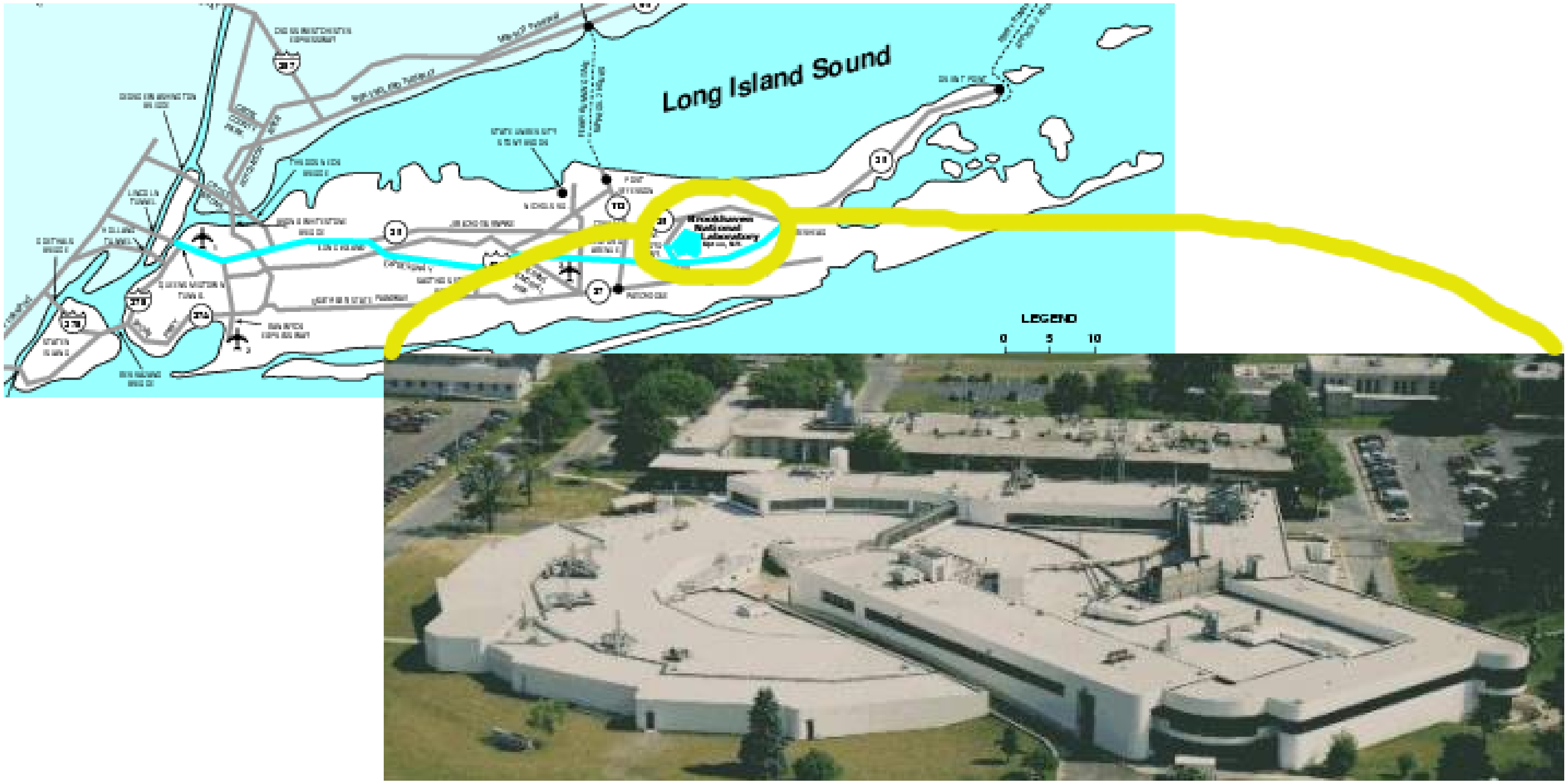
Armed with a distortion model inspired by first principles theory, I was able to parameterize these complicated distortions. In this way, I obtained excellent fits and was able to reconstruct detailed approximations to the true pair distribution functions.



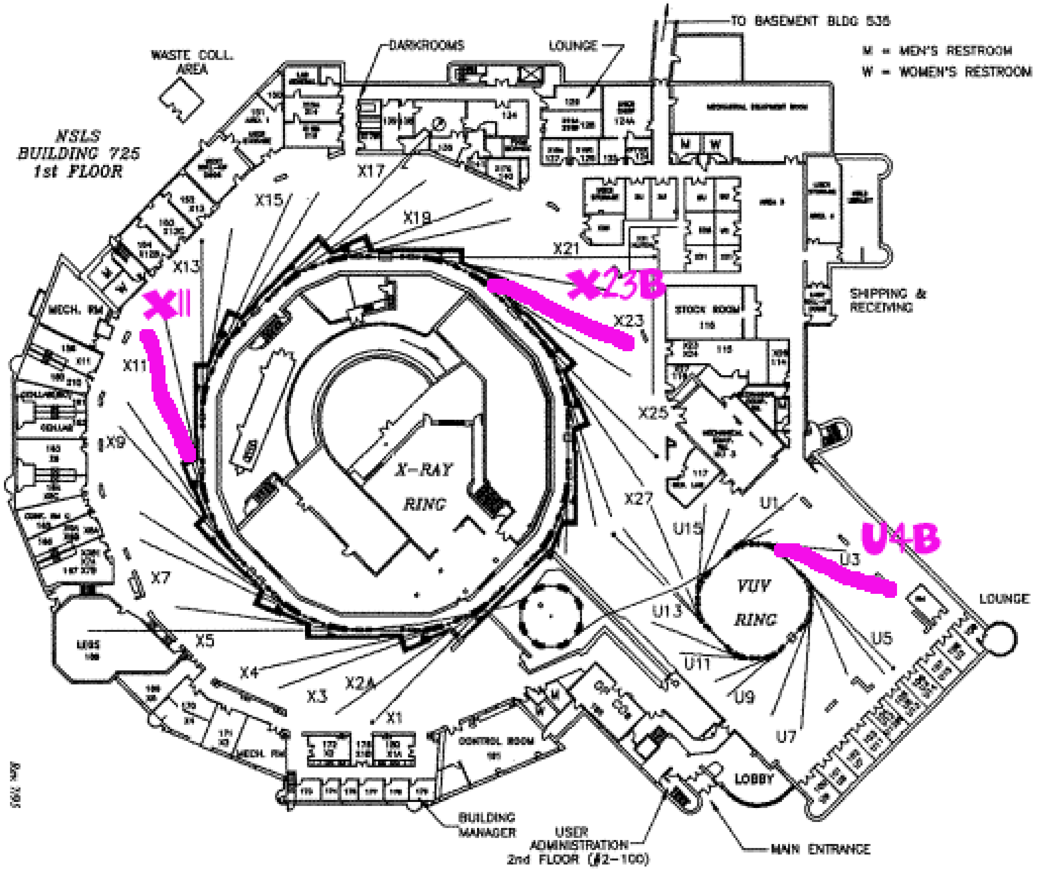


The National Synchrotron Light Source

NSLS is located on New York's Long Island, a six hour drive from the DC area.

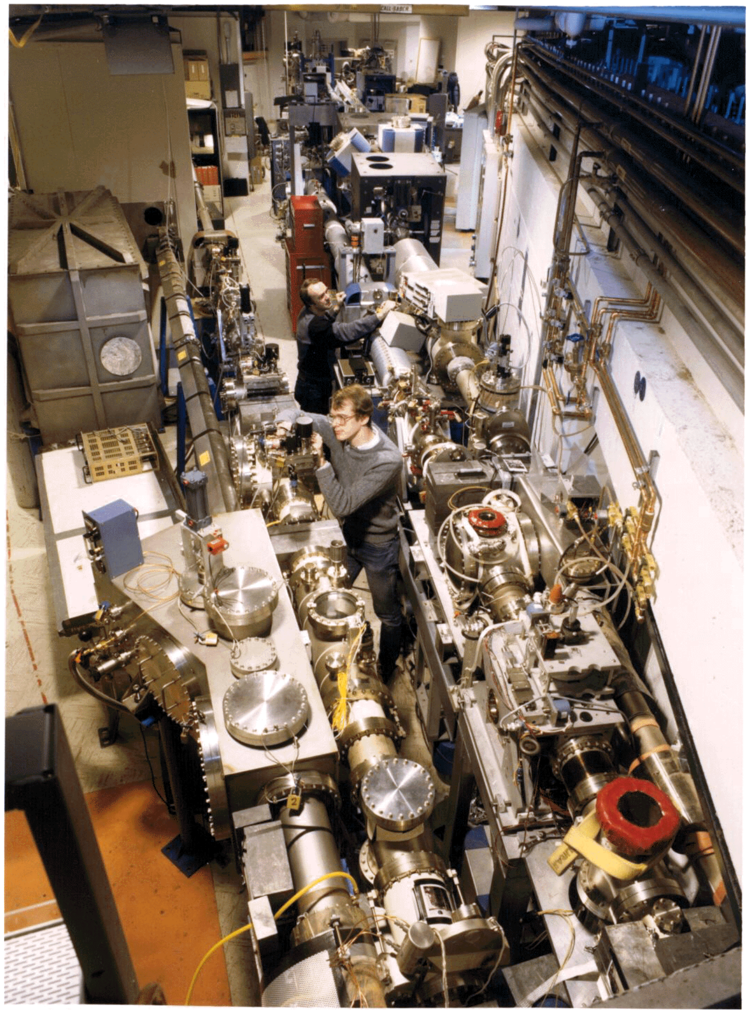


The NSLS Experimental Floor



NSLS has two storage rings providing light from the infrared through the very hard x-ray. NRL operates a UV/soft-x-ray beamline (U4B) for photoemission and magnetic scattering and dichroism studies, a hard-x-ray line (X23B) for XAS and diffraction, and a soft-x-ray line (X24C) for photoemission and reflectance spectroscopy. NRL will soon begin operating X11A and X11B extending our XAS and diffraction capabilities and adding white light capabilities.

Beamlines



This is the X23B beamline. The mirror and mono hutches are seen in the foreground. In the background is the experimental hutch containing optical tables, a 4-circle goniometer, detectors, and electronics.

Notes