Elements of XAFS

Grant Bunker
Physics Department, Illinois Institute of Technology
Chicago, Illinois

Introduction

Over the last two decades X-ray Absorption Fine Structure (XAFS) spectroscopy has emerged as an incisive probe of the local structure around selected atomic species in solids, liquids, and molecular gases[1]. Foremost among its strengths are its applicability to amorphous materials and its "tunability" – the ability to probe the environments of different elements in the sample by selecting the incident x-ray energy.

Although the phenomenon and its basic explanation in terms of a quantum mechanical interference effects have been known since the 1930's, the phenomenon did not become a practical experimental tool until two events occurred: the distillation by Stern, Sayers, and Lytle[2] of the essential physics of the process into the standard XAFS equation and their proposal of a simple method of data analysis; and the availability of tunable, high flux, high energy-resolution synchrotron radiation beamlines. The number of XAFS experiments performed has grown exponentially since 1970 as a consequence of these developments.

The amount of information available from a single XAFS spectrum (typically 10-20 or so parameters) is small compared to that available from x-ray diffraction, but the information available from a well-chosen experiment can be particularly incisive and may be inaccessible by any other technique. XAFS (a short-range order technique) is particularly powerful when intimately combined with complementary techniques such as x-ray diffraction (a long range order technique). Recent developments in theory and experiment show great promise for extending the range and power of the XAFS.

The purpose of this article is to provide a basic introduction to XAFS as it has been traditionally practiced and to provide a brief survey of important recent advances in the field.

The XAFS phenomenon

The simplest XAFS experiments are done in transmission mode. Polychromatic x-rays are produced by a synchrotron radiation source or by bremsstrahlung from a conventional laboratory source, and a desired energy band of approximately 1 eV bandwidth is then selected by diffraction from a silicon double crystal monochromator. Only those x-ray photons that are of the correct wavelength λ ($\lambda = hc/E$, where h is Planck's constant and c is the speed of light) to satisfy the Bragg condition $n\lambda = 2d \sin\theta$ at the selected angle θ will be reflected from the first crystal; the others are absorbed. The parallel second crystal

---

[1] For a broad review of XAFS, see the book *"X-ray Absorption"*, D.C. Koningsberger and R. Prins, eds, John Wiley and sons, NY, (1989); recent developments can be surveyed in Proceedings of the XAFS VII Conference, Jpn. J. Appl. Phys. **32**, Suppl. 32-2 (1993)

[2] D.E. Sayers, E.A.Stern, and F.W. Lytle, Phys. Rev. Lett. **27,** 1204 (1971)

is used as a mirror to restore the beam to its original direction. The monochromatic x-rays are then allowed to pass through the sample, which should absorb approximately 50%–90% of the incident x-rays. The incident and transmitted x-ray fluxes are monitored, usually with gas ionization chambers.

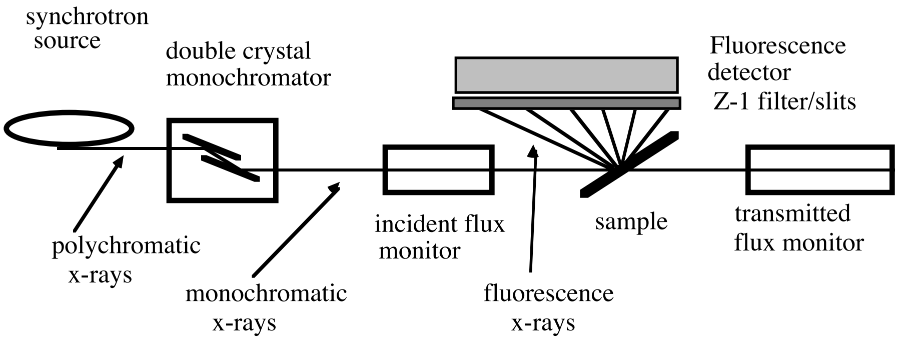


Figure 1 – Schematic XAFS experiment

For a homogeneous sample of uniform thickness x, the absorption coefficent $\mu(E)$ is related to the transmitted (I) and incident (I_0) fluxes by[3] $I/I_0 = \exp(-\mu(E)x)$. The absorption coefficient is related to the cross section σ (cm^2/g) and the density ρ (g/cm^3) by $\mu = \rho\sigma \approx \sum_i \rho_i\sigma_i = \rho \sum_i (m_i/M)\sigma_i$, where the sum is over the elements i in the sample of mass fraction m_i/M. This expression is approximate – indeed the utility of XAFS is based on the fact that the total absorption is *not* simply the sum of the atomic absorption coefficients; the proximity of neighboring atoms strongly modulates the absorption coefficient as a function of energy.

The absorption coefficient decreases as the energy E increases, approximately as $1/E^3$, except for sudden increases in absorption coefficient called absorption edges that occur at energies characteristic of the elements which make up the sample. Figure 2 shows a transmission XAFS spectrum of cubic ZnS (Sphalerite). Note the rapid rise in absorption and the rapidly oscillating fine structure above the edge.

---

[3] In normal XAFS experiments $\mu(E)$ is determined only *modulo* a smooth background which varies slowly when plotted vs energy. This additive background is subtracted out in subsequent data processing. Also an arbitrary scale factor is divided out in the normalization step. The energy dependence of detector sensitivity and the absorption of other materials in the beam path cause the detected signals to be multiplied by a slowly varying function, which is transformed into an additive background when the logarithm is taken. Thus such effects can be neglected in determining $\mu(E)$ in transmission experiments. They cannot be neglected in fluorescence and other detection modes however because no logarithm is taken.

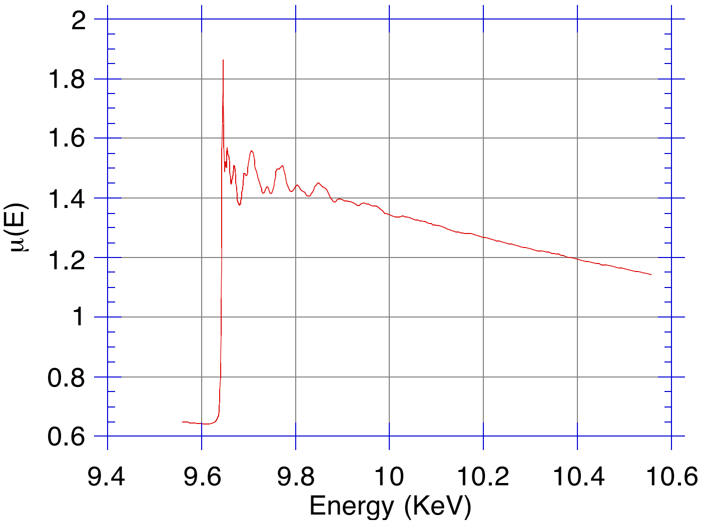


Figure 2 – Transmission XAFS spectrum of ZnS

The sudden rise in absorption at the edge occurs when an incident x-ray photon has just sufficient energy to cause transition of an electron from the $1S$ state of some element in the sample (in this case Zn) to an unfilled state of predominantly p-character (i.e. angular momentum $l = 1$ with respect to the central absorbing atom). In the near edge region, sometimes called the "X-ray Absorption Near Edge Structure" (XANES), transitions may occur to unfilled bound states, nearly-bound states (resonances), or continuum states of the appropriate symmetry. Well above the absorption edge ($\geq$ 30 eV), in the "Extended X-ray Absorption Fine Structure" (EXAFS) region, transitions are to continuum states. Edges due to transitions from less deeply bound levels (e.g. 2S, $2P_{1/2}$,$2P_{3/2}$, 3S..., which are designated L_I, L_{II}, L_{III}, M_I... edges) also occur at lower x-ray energies. These contribute a smooth background absorption to the K-edge spectrum. The L-edges are themselves suitable for measuring XAFS, particularly for higher atomic number elements for which the K-edge energies may be experimentally difficult to reach. Furthermore the L_{II} and L_{III} edges are of particular interest for transition metals because they probe d-symmetry states. In this article we shall concentrate on K-edge absorption for simplicity.

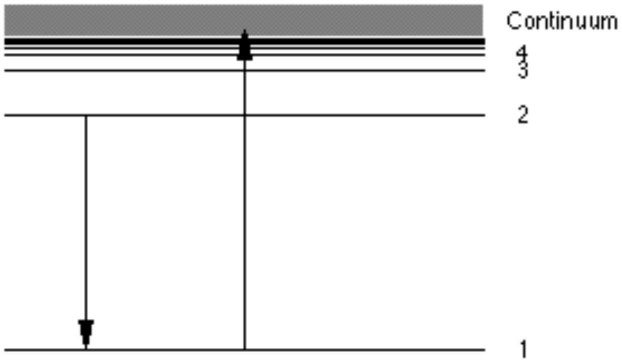


Figure 3 – Excitation of photoelectron from 1S state to continuum

It has become clear in recent years that there is no fundamental distinction between the physics of EXAFS and XANES; the distinction is only one of complexity of the spectra. For example, effects such as multiple scattering and the energy dependence of the central atom absorption ($\mu_0(E)$ – see below) are more important in the XANES region. Modern theories appear capable of explaining the entire spectral range within the context of multiple scattering theory. For this reason EXAFS and XANES are now referred to jointly under the term "XAFS".

It should be noted however that the structure in the pre-edge region and on the rising part of the edge often is rather sensitive to details of the local site symmetry, bond length, charge state, and orbital occupancy. This XANES information can often be exploited to provide information on the chemical state of the sample, even in case where EXAFS spectra cannot be obtained with adequate signal to noise ratio.

The absorption probability $\mu(E)$ is given in time dependent perturbation theory[4] as the square of the transition matrix element $\left| < \psi_f | \hat{\epsilon} \cdot \vec{r} e^{i\vec{\kappa}\cdot\vec{r}} | \psi_i > \right|^2$, where $|\psi_i>$ and $|\psi_f>$ are respectively the initial and final state wavefunctions, and $\hat{\epsilon}$ and $\vec{\kappa}$ are the x-ray electric polarization and wave vector. In the dipole approximation the exponential is neglected[5] and the absorption probability is independent of the direction of propagation of the x-ray, and depends only on the relative orientation of the sample axes with respect to $\hat{\epsilon}$. The absorption coefficient is a second rank tensor.

In an isolated atom, such as a monatomic gas, the continuum final state wavefunction ψ_f consists of a spherical wave emerging from the central absorbing atom, and the spectrum shows little fine structure. However, if the atom is placed into condensed matter, the final state wavefunction consists of both an outgoing part and a part that is scattered from neighboring atoms. The outgoing and backscattered parts of the final state wavefunction interfere either constructively or destructively, depending on the electron wavelength and the distance to the backscattering atom. As the incident x-ray energy E is scanned above the absorption threshold E_0, the kinetic energy of the photoelectron $E - E_0$ is varied, and consequently its momentum $\hbar k$ and wavelength $2\pi/k$, which, by conservation of energy are related by $\hbar^2 k^2/2m = E - E_0$. This interference modulates the matrix element and the absorption probability, which gives rise to oscillations in the absorption coefficient which are periodic in the wavenumber k. In this way the absorption coefficient literally records an interferogram of the spatial distribution of neighboring atoms.

---

[4] P.A.M. Dirac, *"The Principles of Quantum Mechanics"*, fourth edition, Oxford at the Clarendon Press, 1981

[5] Dipole selection rules apply to a good approximation; for K-edges, quadrupole corrections are smaller than dipole by a quantity of order $(Z\alpha)^2$, where Z is the atomic number and $\alpha \approx 1/137$ is the fine structure constant. Quadrupole transitions are often observed in the near edge region of transition metal compounds when they are not masked by larger dipole transitions.

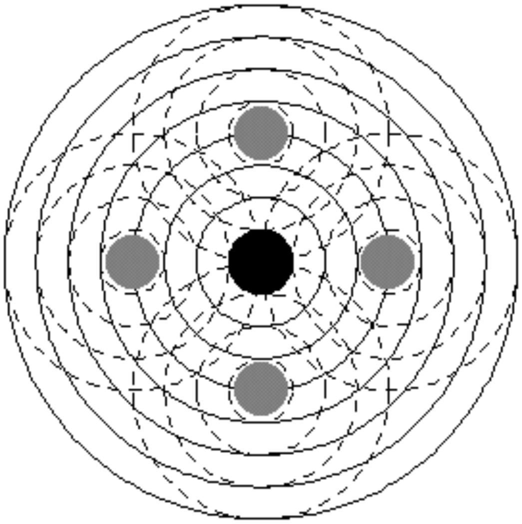


Figure 4 – Outgoing and backscattered portions of final state wave function

Basic Theory

The transition matrix element can be expressed in terms of the Green's function: $\mu(E) \propto \langle\psi_i|H_{\text{int}}GH_{\text{int}}|\psi_i\rangle$, where $G = \sum_n |n\rangle\,(E-\hbar\omega+i\epsilon)^{-1}\,\langle n|$ and H_{int} is the interaction hamiltonian. The Green's function can be expanded as a series of terms corresponding to zero, single, double and higher order scatterings from neighboring atoms: $G = G_0 + G_0TG_0 + G_0TG_0TG_0...$, where G_0 is the Green's function of the central atom alone and T is the total scattering matrix of the surrounding atoms. Because the absorption coefficient depends linearly on the Green's function, $\chi(k)$ can similarly be expressed as a sum of contributions corresponding to increasing numbers of scattering events. Experiment and theory have shown that in most cases relatively low orders of multiple scattering are needed to obtain agreement with experiment.

It is convenient to express the total absorption coefficient $\mu(E)$ as the isolated atom absorption $\mu_0(E)$ times a correction factor χ: $\mu = \mu_0(1+\chi)$. χ is the fractional change in absorption coefficient that is induced by neighboring atoms. Within the context of the single scattering approximation (and others discussed below), Stern, Sayers and Lytle[2] derived a very simple and useful expression for χ, which has come to be called the standard EXAFS equation. According to this theory, for K-edge excitation, an atom (index i) at relative distance r_i makes a contribution to the EXAFS

$$\chi(k) = -\sum_i \frac{3\cos^2\theta_i}{kr_i^2}\,|f_i(k)|\,S_0^2 e^{-2r_i/\lambda_e}\sin(2kr_i + 2\delta_1(k) + \arg(f_i(k)),$$

where $k = \sqrt{2m(E-E_0)/\hbar^2}$ ($\approx \sqrt{.263(E-E_0)}$ in eV,Å units), θ is the angle between the x-ray polarization vector $\hat{\epsilon}$ and the vector $\vec{r_i}$ connecting the central atom with the atom in question. $|f_i(k)|$ and $\arg(f_i(k))$ are the modulus and phase of the complex electron scattering amplitude for each atom; $\delta_1(k)$ is the $l = 1$ partial wave phase shift of the central absorbing atom; and S_0^2 and the photoelectron mean free path λ_e account for losses of coherence due to multielectron excitations. The $1/r^2$ factor accounts for the $1/r$

decrease in intensity of the photoelectron wave propagating out to the scatterer and then back to the central atom.

Several approximations underpin the simple theory: the potential energy of the photoelectron propagating through the solid is approximated as that of spherically symmetric atoms with a constant region between them (the "muffin tin approximation"); only a single electron is directly excited, which interacts with the electron gas in the solid; only backscattering from each neighboring atoms is included, i.e. multiple scattering is neglected; and in the scattering process the photoelectron is approximated as a plane wave.

The plane wave and single scattering approximations are known to be inadequate, and modern theory properly takes account of them. When spherical wave effects are included, the basic structure of the EXAFS equation can be preserved if the plane wave scattering amplitude $f(k)$ is replaced by an effective scattering amplitude[6] $f_{\text{eff}}(k, r)$ – the scattering amplitude acquires a weak r dependence. Also, in the case of oriented samples, additional terms proportional to $\sin^2 \theta$ also appear at low k which may not always be negligible.

The neglect of multiple scattering implies that the total $\chi(k)$ is a simple linear sum of contributions from backscattering atoms. This is a useful first approximation, but it is known that multiple scattering can be important, particularly when the absorbing atom and scatterers are collinear. The overall structure of the simple equation is that of a sum of damped sine waves: a k-dependent amplitude prefactor times the sine of a phase which is approximately linear in k. In other words each atom contributes a sinusoidal signal which, when plotted vs k, oscillates more rapidly the larger the distance – rapid oscillations in the EXAFS mean long distances. The stronger the scattering amplitude, the larger the signal. In an oriented sample, the signal from a given atom is largest when its radius vector lies along the direction of the x-ray polarization vector.

The contributions from multiple scattering also oscillate more rapidly the longer their path length. For this reason single scattering contributions from higher shells may oscillate at about the same frequency as multiple scattering contributions of similar path length. This complicates interpretation of higher shell data. This problem may be essentially solved by recent theoretical advances.

EXAFS equation

In a real experiment one averages over many sites in the sample, and the instantaneous positions of atoms may differ because of thermal and quantum zero point motion, and structural heterogeneity. XAFS essentially takes a snapshot of the instantaneous configurations of atoms, because the lifetime of the excited state is limited by the lifetime of the core hole (i.e. the vacancy in the initial (1S) state), and core hole level widths ΔE are 1 eV or greater, corresponding to time scales of $\tau = \hbar/\Delta E < 10^{-15}$ sec, approximately 10^3 times shorter than periods of interatomic vibration.

For randomly oriented polycrystalline or solution samples an isotropic average over angles must be performed. In this case the contributions from atoms of the same atomic number and at similar distances from the absorbing atom may not be resolvable from each other, and the atoms must be conceptually grouped together into "coordination shells".

---

[6] J.J. Rehr, J. Mustre de Leon, S.I. Zabinsky, J. Am. Chem. Soc., **113**, 5135 (1991)

For small variations in distance within a shell[7], the equation becomes:

$$\chi(k) = -\sum_j \frac{N_j}{kR_j^2}|f(k)|e^{-2R_j/\lambda_e}e^{-2k^2\sigma_j^2}\sin(2kR_j + 2\delta_1(k) + \arg(f(k))),$$

where N_j is the number of atoms in the coordination shell, and σ_j^2 is the mean square variation of distances about the average R_j to atoms in the j_{th} shell. This is the classic EXAFS equation of Stern, Sayers, and Lytle[1].

There are numerous exact expressions for the full multiple scattering $\chi(k)$, and most of them involve computationally inefficient nested sums over angular momenta up to high order. Rehr and Albers[8] have recently shown that the simplicity of the path by path approach is retained if the scattering amplitudes at each vertex of a scattering path are replaced by matrices F; six by six matrices seem to provide essentially exact results. Their expression for a path , (either single or multiple scattering) is

$$\chi_\Gamma(p) = \mathrm{Im}\, S_0^2 \frac{e^{i(\rho_1+\rho_2+\cdots+\rho_N+2\delta_1)}}{\rho_1\rho_2\cdots\rho_N} e^{-\sigma_\Gamma^2 p^2/2} \times \mathrm{Tr}\, MF^N \cdots F^2F^1,$$

where M is a termination matrix, $\vec{\rho}_i = p(\vec{R}_i - \vec{R}_{i-1}$, $p^2/2m = E - V_{\mathrm{MT}}$ and V_{MT} is the zero energy of the muffin tin potential. The effects of disorder are approximated by the debye waller-like factor, where σ_Γ is the mean square variation in total length of path , .

Elementary Data Analysis

The EXAFS equation contains structural parameters (N,R,σ^2) as well as functions which are characteristic of atoms in the sample ($f(k)$,$\delta_1(k)$,$\lambda(k)$). These scattering amplitudes and phases can be obtained to a good approximation by comparing the "unknown" sample with standard compounds of known structure; the scattering amplitudes and phases are said to be "transferable"[9]. Historically this has been the preferred method of analyzing EXAFS data because the accuracy of theoretical EXAFS programs has been marginal. The situation has recently improved dramatically with the introduction of Rehr's FEFF programs, as discussed below.

---

[7] "Small" disorder in this case means $k_{\mathrm{max}}\sigma << 1$ where k_{max} is the maximum k used in fitting. When this condition fails marginally, additional terms involving higher order moments (or cumulants) of the distribution can be added to the basic EXAFS equation. For large disorder either model-dependent or regularized inverse methods must be used.

[8] J.J. Rehr and R.C. Albers, Phys. Rev. B **41**, 8139 (1990)

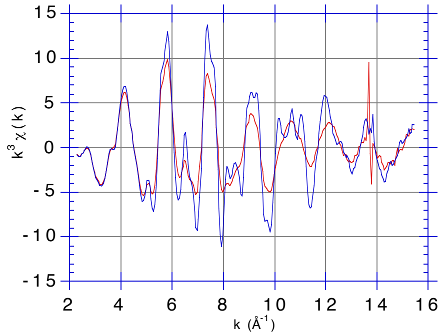
[9] The reason that the transferability concept works well is that the backscattering amplitude is relatively insensitive to the potential in the periphery of the backscatterer (one way to see this is that the large momentum transfer involved in backscattering can only be caused by high spatial fourier components of the scattering potential, which occur in the core region of the backscatterer). Since it is the outer regions of the scatterer that are affected most by chemical bonding and solid state effects, the scattering amplitudes and phases are not strongly sensitive to chemical effects in the EXAFS region. This is somewhat less true for multiple scattering, particularly forward scattering.

The traditional method of data analysis involves a sequence of steps: correction for instrumental effects such as detector dead time losses and energy resolution; spectrum averaging and removal of monochromator "glitches" (see figure below); normalization of the spectrum to unit edge step to compensate for variations in sample thickness or concentration; selection of the energy threshold E_0 and interpolation to k-space; subtraction of smooth background (typically using cubic spline functions) to generate $\chi(k)$; fourier transformation and filtering to produce single shell amplitude and phase; determination of model parameters using the "ratio method" or nonlinear least squares fitting of data using empirical or theoretical standards.

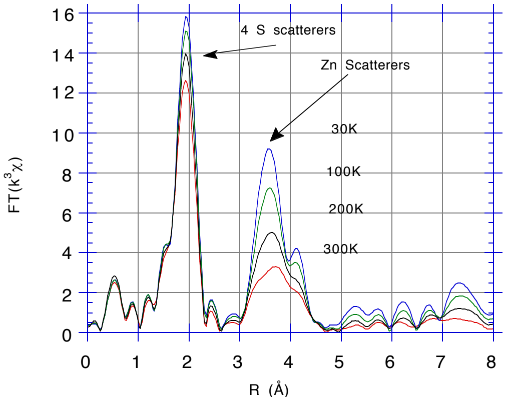
None of the numerical operations is particularly difficult - they are straightforward to implement using standard subroutine libraries or programming packages such as *Mathematica*. However, when writing a general purpose analysis package, it is important to pay attention to certain details in order to obtain reliable results for a variety of experimental data. Furthermore, some aspects of data analysis, such as fourier filtering and nonlinear least squares fitting of the data require some experience to use correctly. In particular, care must be taken to match fourier filtering windows of the standard and the unknown so that fourier filtering distortions cancel out. The most problematic aspect of nonlinear least squares fitting is parameter correlation and multiple minima. Special attention must be paid to avoiding over-fitting of the data. Specifically, the information content of XAFS data is limited by the fact that the data extend over a finite range in k-space Δk and r-space ΔR (the r-space range is limited primarily because of the photoelectron mean free path and core-hole lifetime). Nyquist's sampling theorem implies that only $2\Delta k \Delta r/\pi$ independent parameters can be determined from the data. Fortunately, however arcane the data analysis procedure, the correctness of the results ultimately can be independently checked by reconstructing simulated data based on the refined model parameters.

It is reasonable to wonder why such a complex procedure of data analysis traditionally has been used, when it would certainly be much easier conceptually to just fit the data directly using theoretical expressions including all multiple scattering processes. There have been several good reasons for the traditional procedure, however. First, comparison of empirical spectra tends to cancel out instrumental effects such as amplitude suppression at low k due to instrumental resolution (this has the unfortunate effect of allowing experimenters and beamline designers to be less careful than they might be). Second, until recently, theoretical calculations have not been sufficiently reliable to directly analyze experimental data without the use of empirical corrections. But if it is possible to determine empirical corrections, the empirical amplitudes and phases might as well be used directly. This has been the favored approach. When good empirical standards are available, theoretical data mainly have been useful for interpolating gaps (e.g. in atomic number) in one's array of empirical amplitude and phase functions.

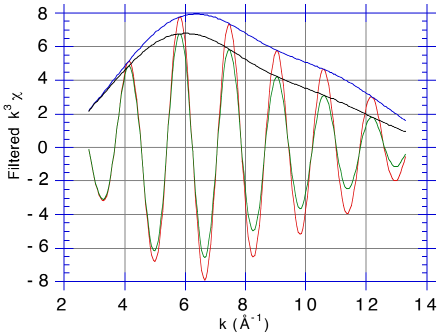
Since even simple backscattering processes could not be calculated reliably *ab initio*, experimenters have had to be rather circumspect about the reliability of theoretical multiple scattering calculations. Because of the difficulty of analyzing multiple scattering processes accurately, it has been possible to determine first shell structural parameters much more accurately than higher shells, because the signal from single scattering among first shell atoms can usually be fourier isolated from the multiple scattering. In other words, when multiple scattering processes are important, analysis of the first shell is much more reliable than it is for higher shells. In certain structures (e.g. the diamond-like structures of many semiconductors) one can be confident that the single scattering contributions from certain higher shells are not significantly contaminated by multiple scattering contributions of similar path length. In this case, fourier filtering to isolate the contributions from particular shells is a valid procedure. To do this reliably one must have some a priori knowledge of the structure, however.



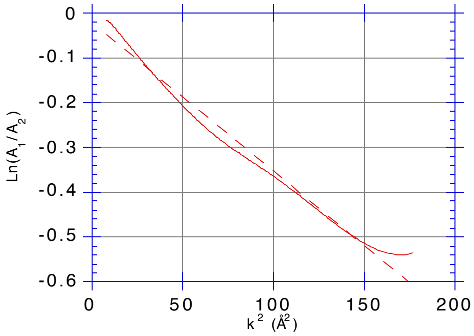
$k^3\chi$, 300K vs 30K



Fourier transforms



Filtered $k^3\chi$



$\ln(A_{300}/A_{30})$

Fortunately there has been very substantial progress in recent years[10]. It appears that the recent development of accurate, computationally efficient codes for theoretical calculation of XAFS spectra including multiple scattering, principally the FEFF5 and forthcoming FEFF6 programs by Rehr *et al* will substantially simplify and improve methods of data analysis. These codes offer the tantalizing prospect of accurately and efficiently calculating the near edge region as well. The direct approach of nonlinear least squares fitting of the data using FEFFX is now practical. One still has the inherent problem of limited information content in the EXAFS data, so complete determination of the three

---

[10] For a concise recent review, see J.J. Rehr, Jpn. J. Appl. Phys. **32**, 8 Suppl. 32-2 (1993)

dimensional structure from EXAFS still is not possible in general. However, by combining *a priori* information into XAFS modeling valuable structural information can be obtained which may not be accessible by any other technique.

Experimental Modes

In additional to dramatic improvements in theory, and promising developments in data analysis, significant progress has been made in experimental technique. A number of methods for measuring XAFS spectra and related quantities have been developed.

Some of the experimental modes and their beneficial attributes are: X-ray fluorescence (dilute species); conversion electron detection (surface sensitive), total external reflection XAFS (surface sensitive), optical luminescence (site selective), photoconductivity, EELS (microprobe, low Z in high Z matrix), X-ray Raman effect (low Z in high Z matrix), high resolution fluorescence (suppression of core hole broadening), and Diffraction Anomalous Fine Structure (DAFS).

One of the most recently discovered methods is Diffraction Anomalous Fine Structure (DAFS)[11]. DAFS is essentially a method of measuring XAFS via anomalous scattering. The intensity of selected bragg reflections from a crystalline sample are measured as a function of energy over an absorption edge and above – essentially the same energy range as XAFS. In the vicinity of an absorption edge, the x-ray scattering form factor $F(q)$ becomes complex: $F(q, E) = F_0(q) + \Delta F(q, E)$ where $\hbar q$ is the momentum transfer in the photon scattering event, F_0 is the real atomic scattering form factor, and $\Delta F(q, E) \equiv F'(q, E) + iF''(q, E)$ is zero far from the absorption edge. ΔF expresses the amplitude and phase changes that occur when a photon is resonantly scattered from the atom. Because ΔF is a response function, causality (the absence of response before stimulus) implies that ΔF is an analytic function, and its real and imaginary parts F' and F'' are related by a Kramers-Kronig (KK) transform. In other words, if one knows either F' or F'' the other can be determined.

The interesting point is that F'' is directly related to the x-ray absorption coefficient $\mu(E)$, and in DAFS one measures $F'(E)$. If there is only one crystallographic site for the element of interest, then the DAFS directly gives the XAFS by KK transform. This can be of use when one has a mixture of different crystalline forms in a sample which are averaged over with conventional XAFS. If one has multiple inequivalent crystallographic sites, the DAFS is a linear combination of the $F'(E)$ for the various sites. In that case determine the XAFS for each of the sites separately, which can provide information about the chemical state, correlated motion, bond strengths, and other information inaccessible by diffraction alone.

Summary

XAFS has developed into a mature technique with numerous applications in physics, chemistry, materials science, biology, and environmental science. The range of application of XAFS will be further extended when third generation synchrotron radiation sources come on-line. Significant advances recently have been made in theory, experimental methods, and data analysis which promise to extend the range and power of the technique.

---

[11] See articles by L. Sorenson, and I. Pickering in Proceedings of XAFS VII (ref#1)