

4. PRODUCTION AND PROPERTIES OF RADIATIONS

4.2.3.4. Attenuation coefficients in the neighbourhood of an absorption edge

4.2.3.4.1. XAFS

Although the existence of XAFS has been known for more than 60 years following experiments by Fricke (1920) and Hertz (1920), it is only in the last decade that a proper theoretical description has been developed. Kronig (1932*a*) suggested a long-range-order theory based on quantum-mechanical precepts, although later (Kronig, 1932*b*) he applied a short-range-order (SRO) theory to explain the existence of XAFS in molecular spectra. As time progressed, important suggestions were made by others, notably Kostarev (1941, 1949), who applied this SRO theory to condensed matter, Sawada, Tsutsumi, Shiraiwa, Ishimura & Obashi (1959), who accounted for the lifetime of the excited photoelectron and the core-hole state in terms of a mean free path, and Schmidt (1961*a,b*, 1963), who showed the influence atomic vibrations have on the phase of the back-scattered waves.

Nevertheless, neither the experimental data nor the theories were sufficiently good to enable Azaroff & Pease (1974) to decide which theory was the correct one to use. However, Sayers, Lytle & Stern (1970) produced a theoretical approach based on SRO theory, later extended by Lytle, Stern & Sayers (1975), and this is the foundation upon which all modern work has been built. Since 1970, a great deal of theoretical effort has been expended to improve the theory because of the need to interpret the wealth of data that became available through the increasing use of synchrotron-radiation sources in XAFS experiments.

A number of major reviews of XAFS theory and its use for the resolution of experimental data have been published. Contributions have been made by Stern, Sayers & Lytle (1975), Lee, Citrin, Eisenberger & Kincaid (1981), Lee (1981), and Teo (1981). The rapid growth of the use of synchrotron-radiation sources has led to the development of the use of XAFS in a wide variety of research fields. The XAFS community has met regularly at conferences, producing conference proceedings that demonstrate the maturation of the technique. The reader is directed to the proceedings edited by Mustre de Leon, Stern, Sayers, Ma & Rehr (1988), Hasnain (1990), and Kuroda, Ohta, Murata, Udagawa & Nomura (1992), and to the papers contained therein. In the following section, a brief, simplified, description will be given of the theory of XAFS and of the application of that theory to the interpretation of XAFS data.

4.2.3.4.1.1. Theory

The theory that will be outlined here has evolved through the efforts of many workers over the past decade. The oscillatory part of the X-ray attenuation relative to the 'background' absorption may be written as

$$\chi(E) = \frac{\mu_l(E) - \mu_{l0}(E)}{\mu_{l0}(E)}, \quad (4.2.3.8)$$

where $\mu_l(E)$ is the measured value of the linear attenuation coefficient at a photon energy E and $\mu_{l0}(E)$ is the 'background' linear attenuation coefficient. This is sometimes the extrapolation of the normal attenuation curve to the edge energy, although it is usually found necessary to modify this extrapolation somewhat to improve the matching of the higher-energy data with the XAFS data (Dreier, Rabe, Matzfeld & Niemann, 1984). In most computer programs, the normal attenuation curve is fitted to the data using cubic spline fitting routines.

The origin of XAFS lies in the interaction of the ejected photoelectron with electrons in its immediate vicinity. The wavelength of a photoelectron ejected when a photon is absorbed is given by $\lambda = 2\pi/k$, where

$$k = [(2m/\hbar^2)(E - E_0)]^{1/2}. \quad (4.2.3.9)$$

This outgoing spherical wave can be back-scattered by the electron clouds of neighbouring atoms. This back-scattered wave interferes with the outgoing wave, resulting in the oscillation of the absorption rate that is observed experimentally and called XAFS. Equation (4.2.3.8) was written with the assumption that the absorption rate was directly proportional to the linear absorption coefficient.

It is conventional to express $\chi(E)$ in terms of the momentum of the ejected electron, and the usual form of the theoretical expression for $\chi(\mathbf{k})$ is

$$\chi(\mathbf{k}) = \sum_i (N_i/k r_i^2) |f_i(k)| \exp(\sigma_i^2 k^2 - r_i/\rho) \sin[2k r_i + \varphi_i(k)]. \quad (4.2.3.10)$$

Here the summation extends over the shells of atoms that surround the absorbing atom, N_i representing the number of atoms in the i th shell, which is situated a distance r_i from the absorbing atom. The back-scattering amplitude from this shell is $f_i(k)$ for which the associated phase is $\varphi_i(k)$. Deviations due to thermal motions of the electrons are incorporated through a Debye-Waller factor, $\exp(-\sigma_i^2 k^2)$, and ρ is the mean free path of the electron.

The amplitude function $f_i(k)$ depends only on the type of back-scattering atom. The phase, however, contains contributions from both the absorber and the back-scatterer:

$$\varphi_i^l(k) = \varphi_i^j(k) + \varphi_i(k) - l\pi, \quad (4.2.3.11)$$

where $l = 1$ for K and L_I edges, and $l = 2$ or 0 for L_{II} and L_{III} edges. The phase is sensitive to variations in the energy threshold, the magnitude of the effect being larger for small electron energies than for electrons with considerable kinetic energy, *i.e.* the effect is more marked in the neighbourhood of the absorption edge. Since the position of the edge varies somewhat for different compounds (Azaroff & Pease, 1974), some impediment to the analysis of experimental data might occur, since the determination of the interatomic distance r_i depends upon the precise knowledge of the value of $\varphi_i(k)$.

In fitting the experimental data based on an empirical value of threshold energy using theoretically determined phase shifts, the difference between the theoretical and the experimental threshold energies ΔE_0 cannot produce a good fit at an arbitrarily chosen distance r_i , since the effect will be seen primarily at low k values ($\sim 0.3r\Delta E_0/k$), whereas changing r_i affects $\varphi_i(k)$ at high k values ($\sim 2k\Delta r$). This was first demonstrated by Lee & Beni (1977).

The significance of the Debye-Waller factor $\exp(-\sigma_i^2 k^2)$ should not be underestimated in this type of investigation. In XAFS studies, one is seeking to determine information regarding such properties of the system as nearest- and next-nearest-neighbour distances and the number of nearest and next-nearest neighbours. The theory is a short-range-order theory, hence deviations of atoms from their expected positions will influence the analysis significantly. Thus, it is often of value, experimentally, to work at liquid-nitrogen temperatures to reduce the effect of atomic vibrations.

Two distinct types of disorder are observed: vibrational, where the atom vibrates about a mean position in the structure, and static, where the atom occupies a position not expected theoretically. These terms can be separated from one

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another if the variation of XAFS spectra with temperature is studied, because the two have different temperature dependences. A discussion of the effect of a thermally activated disorder that is large compared with the static order has been given by Sevillano, Meuth & Rehr (1978). For systems with large static disorders, *e.g.* liquids and amorphous solids, equation (4.2.3.10) has to be modified somewhat. The XAFS equation has to be averaged over the pair distribution function $g(r)$ for the system:

$$\chi(k) = \frac{F(k)}{k} \int_0^{\infty} g(r) \exp(-2r/\rho) \frac{\sin(2kr + \varphi_k)}{r^2} dr. \quad (4.2.3.12)$$

Other factors that must be taken into account in XAFS analyses include: inelastic scattering (due to multiple scattering in the absorbing atom and excitations of the atoms surrounding the atom from which the photoelectron was ejected) and multiple scattering of the photoelectron. Should multiple scattering be significant, the simple model given in equation (4.2.3.10) is inappropriate, and more complex models such as those proposed by Pendry (1983), Durham (1983), Gurman (1988, 1995), Natoli (1990), and Rehr & Albers (1990) should be used. Several computer programs are now available commercially for use in personal computers (*EXCURVE*, *FEFF5*, *MSCALC*). Readers are referred to scientific journals to find how best to contact the suppliers of these programs.

4.2.3.4.1.2. Techniques of data analysis

Three assumptions must be made if XAFS data are to be used to provide accurate structural and chemical information:

- (i) XAFS occurs through the interaction of waves *singly* scattered by neighbouring atoms;
- (ii) the amplitude function of the atoms is insensitive to the type of chemical bond (the postulate of transferability), which implies that one can use the same amplitude function for a given atom in problems involving compounds of that atom, whatever the nature of its neighbours or the nature of the bond; and
- (iii) the phase function can be transferred for each pair of absorber-back-scatterer atoms.

Of these three assumptions, (ii) is of the most questionable validity. See, for example, Stern, Bunker & Heald (1981).

It is usual, when analysing XAFS data, to search the literature for, or make sufficient measurements of, μ_{10} remote from the absorption edge to produce a curve of $\mu_{10}(E)$ versus E that can be extrapolated to the position of the edge. From equation (4.2.3.8), it is possible to produce a curve of $\chi(E)$ versus E from which the variation of $\chi(k)$ with k can be deduced using equation (4.2.3.9).

It is also customary to multiply $\chi(k)$ by some power of k to compensate for the damping of the XAFS amplitudes with increasing k . The power chosen is somewhat arbitrary but k^3 is a commonly used weighting function.

Two different techniques may be used to analyse the new data set, the *Fourier-transform technique* or the *curve-fitting technique*.

In the *Fourier-transform technique* (FF), the Fourier transform of the $k^n \chi(k)$ is determined for that region of momentum space from the smallest, k_1 , to the largest, k_2 , wavevectors of the photoelectron, yielding the radial distribution function $\rho_n(r')$ in coordinate (r') space.

$$\rho_n(r') = \frac{1}{(2\pi)^{1/2}} \int_{k_1}^{k_2} k^n \chi(k) \exp(i2kr') dk. \quad (4.2.3.13)$$

The Fourier spectrum contains peaks indicating that the nearest-neighbour, next-nearest-neighbour, *etc.* distances will differ from the true spacings by between 0.2 to 0.5 Å depending on the elements involved. These position shifts are determined for model systems and then *transferred* to the unknown systems to predict interatomic spacings. Fig. 4.2.3.4 illustrates the various steps in the Fourier-transform analysis of XAFS data.

The technique works best for systems having well separated peaks. Its primary weakness as a technique lies in the fact that the phase functions are not linear functions of k , and the spacing shift will depend on E_0 , the other factors including the weighting of data before the Fourier transforms are made, the range of k space transformed, and the Debye-Waller factors of the system.

In the *curve-fitting technique* (CF), least-squares refinement is used to fit the spectra in k space using some structural model for the system. Such techniques, however, can only indicate which of several possible choices is more likely to be correct, and *do not prove* that that structure is the correct structure.

It is possible to combine the FF and CF techniques to simplify the data analysis. Also, for data containing single-scatter peaks, the phase and amplitude components can be separated and analysed separately using either theory or model compounds (Stern, Sayers & Lytle, 1975).

Each XAFS data set depends on two sets of strongly correlated variables: $\{F(k), \sigma, \rho, N\}$ and $\{\varphi(k), E_0, r\}$. The elements of each set are not independent of one another. To determine N and σ ,

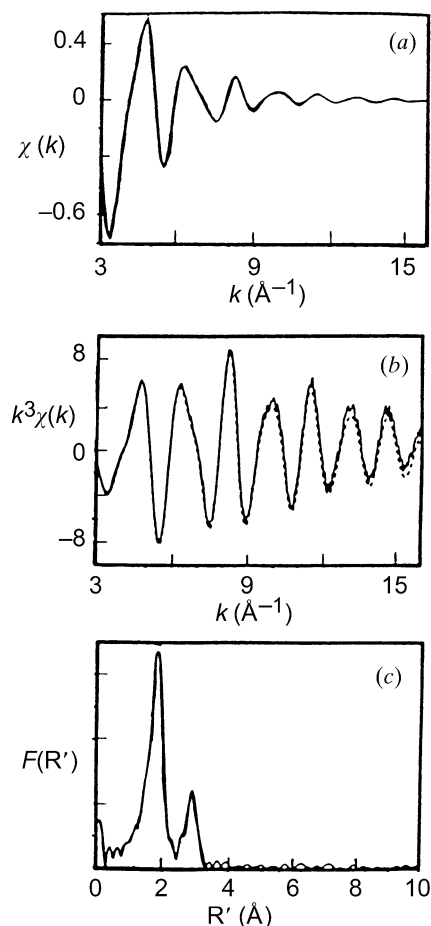


Fig. 4.2.3.4. Steps in the reduction of data from an XAFS experiment using the Fourier transform technique: (a) after the removal of background $\chi(k)$ versus k ; (b) after multiplication by a weighting function (in this case k^3); (c) after Fourier transformation to determine r' .

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one must know $F(k)$ well. To determine r , $\varphi(k)$ must be known accurately.

Attempts have been made by Teo & Lee (1979) to calculate $F(k)$ and $\varphi(k)$ from first principles using an electron-atom scattering model. Parametrized versions have been given by Teo, Lee, Simons, Eisenberger & Kincaid (1977) and Lee *et al.* (1981). Claimed accuracies for r , σ , and N in XAFS determinations are 0.5, 10, and 20%, respectively.

Acceptable methods for data analysis must conform to a number of basic criteria to have any validity. Amongst these are the following:

(i) the data analysis must not give rise to systematic error in the sense that it must provide unbiased estimates of parameters;

(ii) the assumed (hypothetical) model must be able to describe the data adequately;

(iii) the number of parameters used to describe the best fit of data must not exceed the number of independent data points;

(iv) where multiple solutions exist, supplementary information or assumptions used to resolve the ambiguity must conform to the philosophy of choice of the model structure.

The techniques for estimation of the parameters must always be given, including all known sources of uncertainty.

A complete list of criteria for the correct analysis and presentation of XAFS data is given in the reports of the International Workshops on Standards and Criteria in XAFS (Lytle, Sayers & Stern, 1989; Bunker, Hasnain & Sayers, 1990).

4.2.3.4.1.3. XAFS experiments

The variety and number of experiments in which XAFS experiments have been used is so large that it is not possible here to give a comprehensive list. By consulting the papers given in such texts as those edited by Winick & Doniach (1980), Teo & Joy (1981), Bianconi, Incoccia & Stipcich (1983), Mustre de Leon *et al.* (1988), Hasnain (1990), and Kuroda *et al.* (1992), the reader may find references to a wide variety of experiments in fields of research ranging from archaeology to zoology.

In *crystallography*, XAFS experiments have been used to assist in the solution of crystal structures; the large variations in the atomic scattering factors can be used to help solve the phase problem. Helliwell (1984) reviewed the use of these techniques in protein crystallography. A further discussion of the use of these anomalous-dispersion techniques in crystallography has been given by Creagh (1987*b*). The relation that exists between the attenuation (related to the imaginary part of the dispersion correction, f'') and intensity (related to the atomic form factor and the real part of the dispersion correction, f') is discussed by Creagh in Section 4.2.6. Specifically, modulations occur in the observed diffracted intensities from a specimen as the incident photon energy is scanned through the absorption edge of an atomic species present in the specimen. This technique, referred to as diffraction anomalous fine structure (DAFS) is complementary to XAFS. Because of the dependence of intensity on the geometrical structure factor, and the fact that the structure factor itself depends on the positional coordinates of the absorbing atom, it is possible to discriminate, in some favourable cases, between the anomalous scattering between atoms occupying different sites in the unit cell (Sorenson *et al.*, 1994).

In many systems of *biological* interest, the arrangement of radicals surrounding an active site must be found in order that the role of that site in biochemical processes may be assessed. A study of the XAFS spectrum of the active atom yields structural information that is specific to that site. Normal crystallographic techniques yield more general information concerning the crystal structure. An example of the use of XAFS in biological systems is the study of iron-sulfur proteins undertaken by Shulman,

Weisenberger, Teo, Kincaid & Brown (1978). Other, more recent, studies of biological systems include the characterization of the Mn site in the photosynthetic oxygen evolving complexes including hydroxylamine and hydroquinone (Riggs, Mei, Yocum & Penner-Hahn, 1993) and an XAFS study with an *in situ* electrochemical cell on manganese Schiff-base complexes as a model of a photosystem (Yamaguchi *et al.*, 1993).

It must be stressed that the theoretical expression (equation 4.2.3.10) does not take into account the state of polarization of the incident photon. Templeton & Templeton (1986) have shown that polarization effects may be observed in some materials, *e.g.* sodium bromate. Given that most XAFS experiments are undertaken using the highly polarized radiation from synchrotron-radiation sources, it is of some importance to be aware of the possibility that dichroic effects may occur in some specimens.

Because XAFS is a short-range-order phenomenon, it is particularly useful for the structural study of such *disordered systems* as liquid metals and amorphous solids. The analysis of such disordered systems can be complicated, particularly in those cases where excluded-volume effects occur. Techniques for analysis for these cases have been suggested by Crozier & Seary (1980). Fuoss, Eisenberger, Warburton & Bienenstock (1981) suggested a technique for the investigation of amorphous solids, which they call the differential anomalous X-ray scattering (DAS) technique. This method has some advantages when compared with conventional XAFS methods because it makes more effective use of low- k information, and it does not depend on a knowledge of either the electron phase shifts or the mean free paths.

Both the conventional XAFS and DAS techniques may be used for studies of surface effects and catalytic processes such as those investigated by Sinfelt, Via & Lytle (1980), Hida *et al.* (1985), and Caballero, Villain, Dexpert, Le Peltier & Lynch (1993).

It must be stressed that in all the foregoing discussion it has been assumed that the detection of XAFS has been by measurement of the linear attenuation coefficient of the specimen. However, the process of photon absorption followed by the ejection of a photoelectron has as its consequence both *X-ray fluorescence* and *surface XAFS* (SEXAFS) and *Auger electron emission*. All of these techniques are extremely useful in the analysis of dilute systems.

SEXAFS techniques are extremely sensitive to surface conditions since the mean free path of electrons is only about 20 Å. Discussions of the use of SEXAFS techniques have been given by Citrin, Eisenberger & Hewitt (1978) and Stohr, Denley & Perfetti (1978). A major review of the topic is given in Lee *et al.* (1981). SEXAFS has the capacity of sensing thin films deposited on the surface of substrates, and has applications in experiments involving epitaxial growth and absorption by catalysts.

Fluorescence techniques are important in those systems for which the absorption of the specimen under investigation contributes only very slightly to the total attenuation coefficient since it detects the fluorescence of the absorbing atom directly. Experiments by Hastings, Eisenberger, Lengeler & Perlman (1975) and Marcus, Powers, Storm, Kincaid & Chance (1980) proved the importance of this technique in analysing dilute alloy and biological specimens. Materlik, Bedzyk & Frahm (1984) have demonstrated its use in determining the location of bromine atoms absorbed on single-crystal silicon substrates. Oyanagi, Matsushita, Tanoue, Ishiguro & Kohra (1985) and Oyanagi, Takeda, Matsushita, Ishiguro & Sasaki (1986) have also used fluorescence XAFS techniques for the characterization of very

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Table 4.2.3.1. *Some synchrotron-radiation facilities providing XAFS databases and analysis utilities*

Country	Synchrotron source	Address
France	LURE	Université Paris-Sud, LURE, 91405 Orsay, France
Italy	Frascati	Laboratori Nazionali di Frascati, CP 13, 00044 Frascati, Italy
Japan	Photon Factory	Photon Factory, National Laboratory for High Energy Physics, 1-1 Oho, Tsukuba-gun, Ibaraki 305, Japan
Germany	DESY	DESY, Notkestrasse 85, 2000 Hamburg 52, Germany
United Kingdom	SRC/Daresbury	Daresbury Laboratory, Daresbury, Warrington WA4 4AD, England
USA	CHESS	CHESS, Cornell University, Ithaca, New York 14853, USA
	NLSL	NLSL, Brookhaven National Laboratory, Upton, New York 11973, USA
	SPEAR	SSRL, Stanford University, Bin 69, PO Box 4349, Stanford, California 94305, USA

thin films. More recently, Oyanagi *et al.* (1987) have applied the technique to the study of short-range order in high-temperature superconductors. Oyanagi, Martini, Saito & Haga (1995) have studied in detail the performance of a 19-element high-purity Ge solid-state detector array for fluorescence X-ray absorption fine structure studies.

A less-sensitive technique, but one that can be usefully employed for thin-film studies, is that in which XAFS modulations are detected in the beam reflected from a sample surface. This technique, *ReflexAFS*, has been used by Martens & Rabe (1980) to investigate superficial regions of copper oxide films by means of reflection of the X-rays close to the critical angle for total reflection.

If a thin film is examined in a transmission electron microscope, the electron beam loses some of its kinetic energy in interactions between the electron beam and the electrons within the film. If the resultant energy loss is analysed using a magnetic analyser, XAFS-like modulations are observed in the electron energy spectrum. These modulations, electron-energy-loss fine structure (*EELS*), which were first observed in a conventional transmission electron microscope by Leapman & Cosslet (1976), are now used extensively for microanalyses of light elements incorporated into heavy-element matrices. Most major manufacturers of transmission electron microscopes supply electron-energy-loss spectrometers for their machines. There are more problems in analysing electron-energy-loss spectra than there are for XAFS spectra. Some of the difficulties encountered in producing reliable techniques for the routine analysis of EELS have been outlined by Joy &

Maher (1985). This matter is discussed more fully in §4.3.4.4.2.

A more recent development has been the observation of *topographic XAFS* (Bowen, Stock, Davies, Pantos, Birnbaum & Chen, 1984). This fine structure is observed in white-beam topographs taken using synchrotron-radiation sources. The technique provides the means of simultaneously determining spatially resolved microstructural and spectroscopic information for the specimen under investigation.

In all the preceding discussion, however, the electron was assumed to undergo only single-scattering processes. If multiple scattering occurs, then the theory has to be changed somewhat. §4.2.3.4.2 discusses the effect of multiple scattering.

4.2.3.4.2. X-ray absorption near edge structure (XANES)

In Fig. 4.2.3.2(c), there appears to be one cycle of strong oscillation in the neighbourhood of the absorption edge before the quasi-periodic variation of the XAFS commences. The electrons that cause this strong modulation of the photoelectric scattering cross section have low k values, and the electron is strongly scattered by neighbouring atoms. It was mentioned in §4.2.3.4.1 that conventional XAFS theory assumes a weak, single-scattering interaction between the ejected photoelectron and its environment. A schematic diagram illustrating the difference between single- and multiple-scattering processes is given in Fig. 4.2.3.5. Evidently, the multiple-scattering process is very complicated and a discussion of the theory of XANES is too complex to be given here. The reader is directed to papers by Pendry (1983), Lee (1981), and Durham (1983). A more recent review of the study of fine structure in ionization cross sections and their use in surface science has been given by Woodruff (1986).

The data from XANES experiments can be analysed to determine structural information such as coordination geometry, the symmetry of unoccupied valence electronic states, and the effective charge on the absorbing atom (Natoli, Misemer, Doniach & Kutzler, 1980; Kutzler, Natoli, Misemer, Doniach & Hodgson, 1981). XANES experiments have been performed to resolve many problems, *inter alia*: the origin of white lines (Lengeler, Materlik & Müller, 1983); absorption of gases on metal surfaces (Norman, Durham & Pendry, 1983); the effect of local symmetry in 3d elements (Petiau & Calas, 1983); and the determination of valence states in materials (Lerebours, Dürr, d'Huysser, Bonelle & Lenglet, 1980).

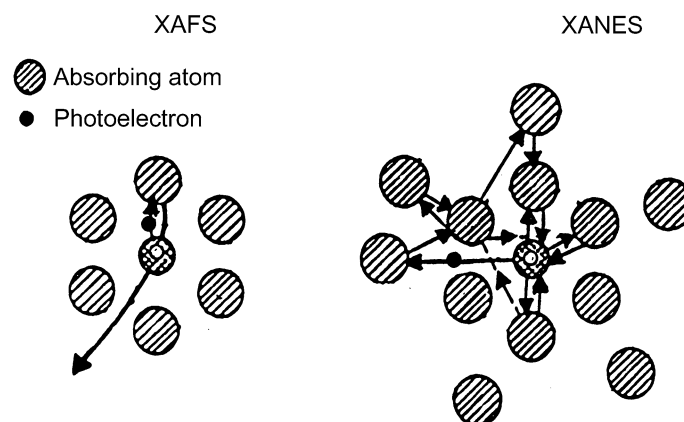


Fig. 4.2.3.5. Schematic representations of the scattering processes undergone by the ejected photoelectron in the single-scattering (XAFS) case and the full multiple-scattering regime (XANES).