

## 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  $\rho$  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  $\Delta E_0$  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,  $\mu_{10}$  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  $\sigma$ ,

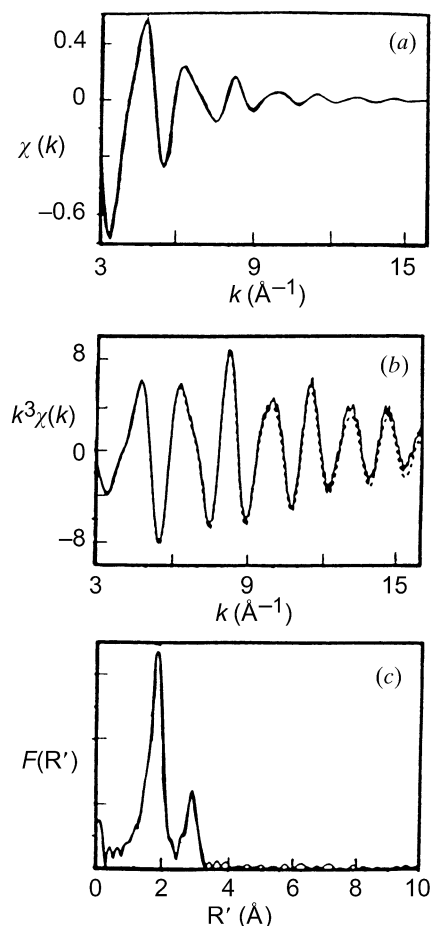


Fig. 4.2.3.4. Steps in the reduction of data from an XAFS experiment using the Fourier transform technique: (a) after the removal of background  $\chi(k)$  versus  $k$ ; (b) after multiplication by a weighting function (in this case  $k^3$ ); (c) after Fourier transformation to determine  $r'$ .