

4.2. X-RAYS

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 ,

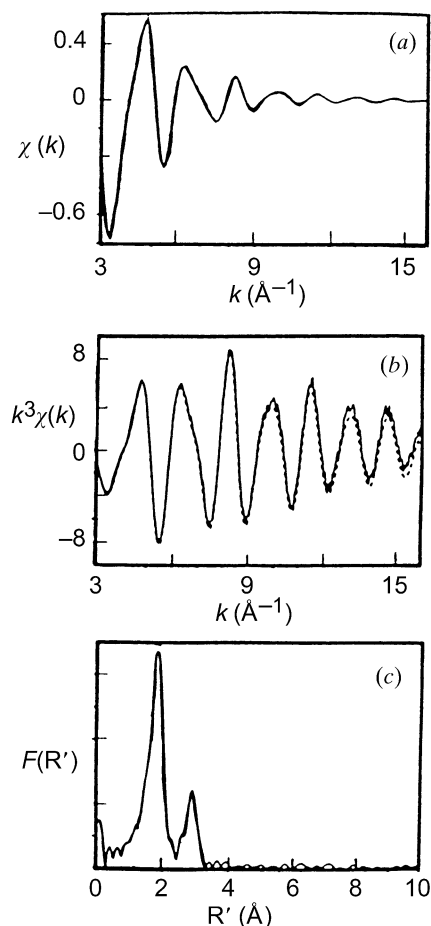


Fig. 4.2.3.4. Steps in the reduction of data from an XAFS experiment using the Fourier transform technique: (a) after the removal of background $\chi(k)$ versus k ; (b) after multiplication by a weighting function (in this case k^3); (c) after Fourier transformation to determine r' .