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:

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

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_{I0} remote from the absorption edge to produce a curve of $\mu_{I0}(E)$ *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 radical distribution function $\rho_n(r')$ in coordinate (r') space.

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

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,
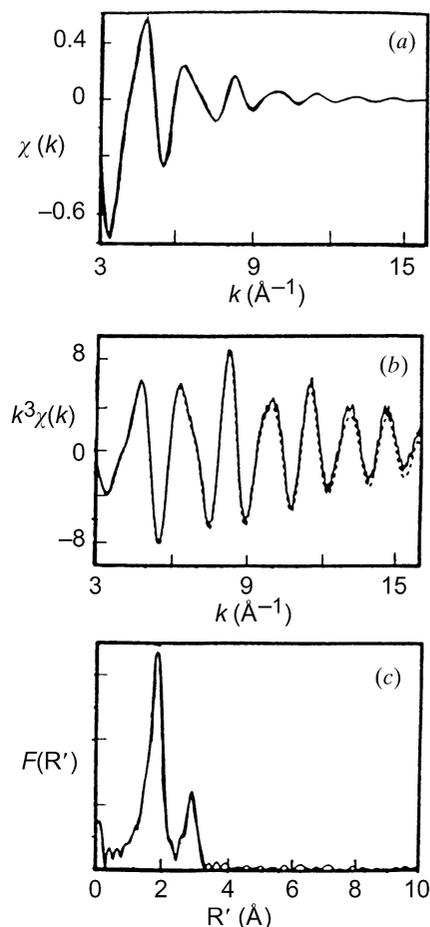

Fig. 4.2.3.4. Steps in the reduction of data from an XAFS experiment using the Fourier transform technique: (*a*) after the removal of background $\chi(k)$ *versus k*; (*b*) after multiplication by a weighting function (in this case k^3); (*c*) after Fourier transformation to determine r'.

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 & Perfettii (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 epitaxic 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

references