

4. PRODUCTION AND PROPERTIES OF RADIATIONS

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).

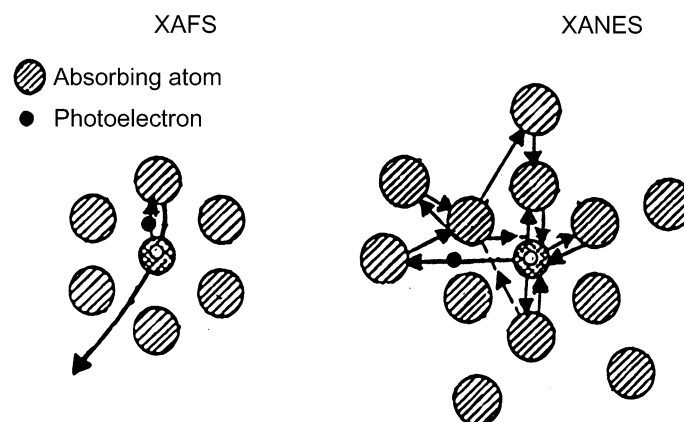


Fig. 4.2.3.5. Schematic representations of the scattering processes undergone by the ejected photoelectron in the single-scattering (XAFS) case and the full multiple-scattering regime (XANES).