Chapter 4.1

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Spectral distortions and pre-processing of experimental data

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This part of *International Tables for Crystallography Volume I* is dedicated to the description of the main causes of spectral distortions and how they can be corrected. The goal of any X-ray absorption fine-structure (XAFS) measurement is to record, as a function of the photon energy, a quantity which is directly proportional to the linear attenuation coefficient of the sample under study (or the cross section of the excited atom). Since XAFS obtains information fron the spectral lineshape (XANES/NEXAFS) or from the relative variation of the attenuation coefficient (EXAFS), an absolute measurement of the attenuation coefficient is not generally required; however, a direct proportionality is, in principle, required and since no measurement is free from nonlinearities and distortions, an understanding of their origins and a quantification of their amount is of paramount importance.

Crystal and grating monochromators transmit not only the fundamental wavelength but also higher order harmonics; for Si(111) crystal monochromators the third-order harmonic is generally present. The presence of harmonics is well known to induce nonlinearities and spectral distortions due to incomplete compensation between the transmitted (or fluorescence/electron yield) and incident beam detectors; if the harmonic content is not constant during a scan, the problem may be even more severe. The presence of harmonics induces spectral distortions of XANES spectra and a reduction of the amplitude of the EXAFS oscillations. Hence, it is of paramount importance to quantify and reduce the harmonic content of the impinging beam. Similar problems can be caused by the misalignment of slits. These topics are covered in Chapter 4.2 (Abe, 2024).

The sample properties, both intrinsic and related to preparation, may adversely affect the quality of XAFS spectra. In fluorescence (and, to a lesser degree, electron-yield) measurements the variation of the penetration depth of the sample with photon energy, known as 'self-absorption', can lead to spectral distortions; this problem is particularly severe when the concentration of the absorbing element is above a few percent, and various approaches have been proposed to quantify, experimentally reduce and/or correct spectra for this effect. In the transmission geometry, inhomogeneities in the sample thickness (or, worse, the presence of pinholes in the sample) are known to induce spectral distortions. When the sample is a high-quality crystal, or is a thin film deposited on a single crystal, two effects may distort fluorescence-detected XAFS spectra at specific combinations of sample orientation and incident beam wavelength: (i) Bragg diffraction peaks may enter the detector (causing distortion

Related chapters

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and saturation) and (ii) X-ray standing waves may be excited in the sample or substrate, inducing a variation of the fluorescence intensity which is due to the local enhancement of the electric field. All of these sample-related issues are discussed in Chapter 4.3 (De Panfilis & Bardelli, 2024).

Several aspects related to the detectors used in all types of measurement modes have to be carefully considered. Ion chambers used as incident and transmitted beam monitors must be constructed and operated under conditions which reduce nonlinearities to acceptable levels. The signal-to-noise ratio of such detectors is known to be affected by acoustic and electrical disturbances; the readout electronics must be optimized, with particular attention to the amplifier rise time. In fluorescence-yield mode a significant background signal can be generated by elastic and inelastic scattering; several approaches have been developed to reduce this unwanted background, including an optimized detector–sample geometry, the use of filters and slits, and grazing incidence. Finally, since counting electronics are most often used for fluorescence detection, dead-time corrections must be understood and applied. These issues are described in Chapter 4.4 (Ciatto *et al.*, 2024).

Fine-structure spectra from thin films and flat surfaces may be recorded in a grazing-incidence geometry by measurement of the reflectivity as a function of impinging photon energy. However, reflectivity is due to both the real and imaginary components of the index of refraction. Special data-treatment procedures have been developed to analyse these spectra and are described in Chapter 4.5 (d'Acapito, 2024).

Chapter 4.6 (Chantler, 2024*a*) discusses the determination of the precision of each data point via repeated measurements; also discussed in this contribution are the estimation of correlation between signals upstream and downstream of the sample, the propagation of uncertainties and the combination or comparison of different data sets. Finally, the various issues related to absolute measurement of X-ray absorption spectra are quantitatively summarized in Chapter 4.7 (Chantler, 2024*b*). A partial list of sources of systematic errors discussed here includes ion-chamber dark current, air paths, sample, scattering, harmonic content, counting detector dead time and sample roughness; an extensive reference list is also included.

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