

2.2. SYNCHROTRON RADIATION

$$P = (1 - dp)(\cos^2 2\theta \sin^2 \kappa + \cos^2 \kappa) + dp(\cos^2 2\theta \cos^2 \kappa + \sin^2 \kappa)$$

or

$$P = \frac{(\cos^2 2\theta \sin^2 \kappa + \cos^2 \kappa) + rp(\cos^2 2\theta \cos^2 \kappa + \sin^2 \kappa)}{1 + rp},$$

where κ is the azimuthal angle (zero in the vertical direction) (Rowles *et al.*, 2012).

2.2.5.2. Radiation damage

The intensity of the incident beam can be so high that radiation damage becomes a real concern, particularly for samples containing organic molecules, such as pharmaceuticals, or organometallic materials. Radiation damage manifests itself by progressive shifts (often anisotropic) in the peak positions, a general reduction in peak intensities and peak broadening as the sample's crystallinity degrades. With high-resolution data, the effects are easily seen and can appear after only a few seconds in the worst cases. In such circumstances it may be better to use a 1D or 2D PSD to collect data of sufficient statistical quality before the damage is too severe. However, if the highest-resolution data are required, *via* scanning an analyser crystal, then the problem can be alleviated by filling a long capillary with sample and translating it between scans to expose fresh sample to the beam, thus acquiring multiple data sets which can be summed together. Such an approach necessarily requires a sufficient amount of disposable sample. If attempting to study the evolution of a particular part of the sample, *e.g.* undergoing heat treatment in the beam, then substituting fresh sample is not necessarily an option, and radiation damage can be a frustrating hindrance.

2.2.5.3. Beam heating

With a photon intensity of the order 10^{12} photons $\text{mm}^{-2} \text{s}^{-1}$ incident on the sample – a possible value for the unfocused beam on a beamline based on an insertion device at a modern third-generation source – the power in the beam corresponds to a few mW mm^{-2} . If a small fraction is absorbed by the sample this can represent a significant heat load that becomes troublesome when trying to work with samples at cryogenic temperatures, where heat capacities are relatively low.

As an example, consider a sample of microcrystalline silicon, composed of cubic $1 \mu\text{m}^3$ grains irradiated by a 31 keV beam (0.4 Å wavelength) with 10^{12} photons $\text{mm}^{-2} \text{s}^{-1}$. The power of the beam is 5 mW mm^{-2} ($31 \times 10^3 \text{ e} \times 10^{12} \text{ W mm}^{-2}$). The mass absorption coefficient of Si at 0.4 Å wavelength $\mu/\rho \simeq 1.32 \text{ cm}^2 \text{ g}^{-1}$ (Milledge, 1968) leading to a linear absorption coefficient of 3.1 cm^{-1} (density of Si = 2.33 g cm^{-3}). Any problems with absorption by such a sample might usually be discounted; for a 1-mm-diameter capillary the value of μr is 0.1, assuming the powder density is 2/3 of the theoretical density.

A single $1\text{-}\mu\text{m}^3$ grain of cross section $1 \mu\text{m}^2$ is hit by 10^6 photons s^{-1} , of which a small fraction are absorbed,

$$\begin{aligned} \text{photons absorbed} &= 10^6 [1 - \exp(-3.1 \times 10^{-4})] \\ &= 310 \text{ photons s}^{-1}, \end{aligned}$$

corresponding to an absorbed power of $1.54 \times 10^{-12} \text{ W}$. Not all this energy is retained; significant amounts are lost as fluorescence, Compton scatter *etc.* Consultation of tables of mass attenuation coefficients and mass energy-absorption coefficients (Hubbell, 1982; Seltzer, 1993) indicates that for Si at 31 keV about 80% of the energy is retained, thus a net heating power of

$1.2 \times 10^{-12} \text{ W}$. The mass of the Si grain is $2.33 \times 10^{-15} \text{ kg}$. At ambient temperature, where the specific heat capacity of Si is $704.6 \text{ J kg}^{-1} \text{ K}^{-1}$, this leads to an instantaneous tendency to increase the temperature by $\sim 0.7 \text{ K s}^{-1}$. At cryogenic temperatures, *e.g.* 10 K, the specific heat capacity is over three orders of magnitude lower, $0.28 \text{ J kg}^{-1} \text{ K}^{-1}$ (Desai, 1986), leading to a very strong tendency for the temperature to rise (1840 K s^{-1}). The extent of the potential problem varies depending on the real net absorption of energy of the sample at the wavelength being used. However, it is clear that to prevent local beam-heating effects, the absorbed energy must be removed from the sample as efficiently as possible, *i.e.* by having excellent thermal contact between the grains of the sample and the external medium. At cryogenic temperatures this can be accomplished *via* the He exchange gas in the cryostat. Thus, if using a capillary sample, the capillary must either be left unsealed, to allow the He to permeate between the grains of sample, or it must be sealed under He, allowing transport of the heat to the walls of the capillary. Sealing under air, nitrogen, argon or other atmosphere leads to a loss of heat-transport capability when the gas solidifies, with consequent unpredictable behaviour for the sample caused by the beam-heating effects. This can involve significant shifts in peak positions and peak broadening depending on the instantaneous local temperature gradients. The problems tend to be worse at softer energies, where X-ray absorption is generally higher. Notwithstanding the potential problems, good-quality low-temperature data can be measured with appropriate care.

2.2.5.4. Choice of wavelength

The tunability of synchrotron radiation allows the wavelength best suited to the measurements to be selected. The collimation of the beam from the source combined with a perfect crystal monochromator lead automatically to high energy resolution, with a narrow wavelength distribution about a mean value. Consequently there are no issues to contend with such as α_1 , α_2 doublets or other effects due to a composite incident spectrum, contributing to a relatively simple instrumental peak-shape function. High energy resolution is essential for high 2θ resolution, because, as shown in equation (2.2.1), the effect of the energy envelope is to broaden the diffraction peaks as 2θ increases.

In choosing the wavelength for an experiment, factors to consider include:

- The optimum operational range for the beamline to be used, which will principally depend on the characteristics of the source.
- Absorption: choosing a sufficiently hard energy generally reduces absorption and allows the use of a capillary specimen in transmission for a wide range of compounds, *e.g.* those containing transition metals or heavier elements, thus minimizing preferred orientation. Selecting the energy a little way below (in energy) the K or L_{III} absorption edge of an element in the sample may help minimize sample absorption. For any sample or series of samples, it is good practice in the planning of the experiment to calculate the linear absorption coefficient to assess the optimum capillary diameter, the wavelength to use and those to avoid.
- The use of hard energies can be advantageous for penetration through sample environments, although these should normally, as much as possible, be designed with appropriate X-ray windows *etc.* However, when absorbing environments are unavoidable, such as containing a sample in a spinning Pt

2. INSTRUMENTATION AND SAMPLE PREPARATION

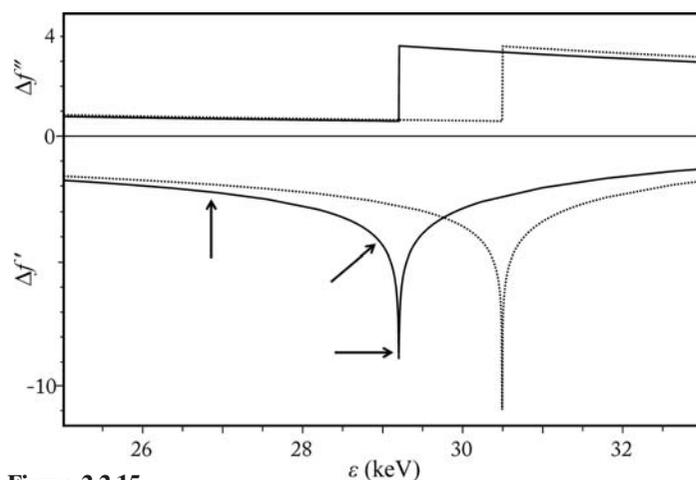


Figure 2.2.15

Variation of $\Delta f'$ and $\Delta f''$ with photon energy for Sn (solid line) and Sb (dotted line) in the vicinity of their K absorption edges (from the tables of Sasaki, 1989). An anomalous-scattering experiment seeking to distinguish the arrangement of the two elements could make measurements at the Sn edge (29.2001 keV), at a few eV below the edge and at an energy significantly removed from the edge (arrows). Equivalent measurements could be made at the Sb edge (30.4912 keV), but as this is above the energy of the Sn edge careful attention must be paid to the increase in the sample's absorption (reflected in the values of $\Delta f''$).

capillary for heating to very high temperatures, then high energy can be a major benefit.

- (d) Hard energies are essential to measure to high Q values, where $Q = 4\pi \sin \theta / \lambda = 2\pi / d$. For pair distribution function (PDF) analysis, data to $Q > 25 \text{ \AA}^{-1}$ ($d < 0.25 \text{ \AA}$) or more are required, with patterns of good statistical quality. Such Q values are not possible with Mo or Ag radiation (Ag $K\alpha$, $\lambda = 0.56 \text{ \AA}$, $Q \simeq 22 \text{ \AA}^{-1}$ at $2\theta = 160^\circ$), but are easily accessible at $\lambda = 0.4 \text{ \AA}$ (31 keV) by scanning to $2\theta = 106^\circ$. At 80.7 keV (0.154 \AA , ten times shorter than Cu $K\alpha$) patterns to $Q \simeq 35 \text{ \AA}^{-1}$ can be obtained in minutes (even seconds) with a large stationary medical-imaging flat-panel detector (Lee, Aydiner *et al.*, 2008). Even for more classical powder-diffraction experiments, access to data for high Q values can be advantageous for Rietveld refinement of crystal structures, or for measuring several orders of reflections for peak-shape analysis in the investigation of microstructure.
- (e) Anomalous scattering: performing measurements near the absorption edge of an element in a sample and away from that edge gives element-specific changes in the diffraction intensities, enhancing the experiment's sensitivity to that element (Fig. 2.2.15). The approach can be complimentary to isotopic substitution in a neutron-diffraction experiment or may be the only option when no suitable isotope is available. Good energy resolution is important for these experiments. The values of $\Delta f'$ and $\Delta f''$ vary sharply over only a few eV at the edge, so poor energy resolution would average the abruptly changing values over too broad a range to the detriment of elemental sensitivity and sample absorption if part of the wavelength envelope strays above the edge. Moreover, it is necessary to know accurately where on the edge the measurement is being made to allow the correct values of $\Delta f'$ and $\Delta f''$ to be used in the data analysis. Tables of values have been calculated (*e.g.* Sasaki, 1989), but these do not take account of shifts in an edge due to the oxidation state(s) and chemical environment(s) of the elements. It is advisable to measure the fluorescence of the sample as the energy is scanned through the edge (by varying the monochromator angle θ_m) and then use the Kramers–Kronig

relation to calculate the variation of $\Delta f'$ and $\Delta f''$ with energy. A program such as *CHOOCH* (Evans & Pettifer, 2001) allows this to be done.

- (f) A wavelength greater than 1 \AA may be best when working with large unit cells, such as found for proteins, organic molecules or organometallic compounds. Using a long wavelength helps by moving the diffraction pattern to higher 2θ values, away from the zone most affected by background air scatter or masked by the beam stop, and to where the peak asymmetry due to axial beam divergence is less severe. Longer wavelengths are also useful when working in reflection with plate samples to minimize beam penetration and thus enhance sensitivity to the surface regions, *e.g.* in the study of surfaces or coatings.
- (g) The broad continuous spectrum available from a bending magnet or wiggler allows powder-diffraction measurements *via* the energy-dispersive approach, which is exploited when geometric considerations of the sample or environment mean that a restricted range of 2θ values is accessible or when attempting to obtain the maximum time resolution from a source, as a larger fraction of the photons from the source can be exploited.

2.2.5.5. Angular resolution

The highest angular resolution is obtained from a diffractometer equipped with an analyser crystal such as Si(111) or Ge(111). This also gives the robust parallel-beam optical configuration so that peak positions are accurately determined. For well crystallized high-quality samples, peak FWHMs of a few millidegrees are possible, thus maximizing the resolution of reflections with similar d -spacings. For less ideal samples, which represent the majority, microstructural effects broaden the peaks, and indeed high-resolution synchrotron data are exploited for detailed investigation of peak shapes and characterization of a range of properties such as crystallite size, microstrain (Chapter 5.2), defects, chemical homogeneity *etc.* Accurate high-resolution data are particularly useful for solving crystal structures from powders (Chapter 4.1), increasing the possibilities for indexing the powder diffraction pattern (Chapter 3.4), assessing the choice of possible space groups, and providing high-quality data for the structural solution and refinement steps. With a high-resolution pattern, the maximum amount of information is stored in the complex profile composed from the overlapping peaks.

2.2.5.6. Spatial resolution

Focusing the X-ray beam gives improved spatial resolution, *e.g.* for studying a small sample contained in a diamond anvil cell at high pressure. A beam with dimensions of a few μm can be obtained, though at the expense of the divergence of the beam arriving at the sample. In such cases the use of a 2D detector to record the entire Debye–Scherrer rings will be required to accumulate the diffraction pattern in a reasonable time and to reveal any problems with preferred orientation or granularity in the sample. With a very small sample only a few grains may be correctly oriented to provide each powder reflection. Alternatively, provided the intensity of the beam is high enough, simply cutting down the beam size with slits may be appropriate, *e.g.* to map residual strain in a weld or mechanical component where a spatial resolution on the 50–100 μm scale may be required. Smaller beam sizes may not be useful if they are comparable to the intrinsic grain size of the material, thus leading