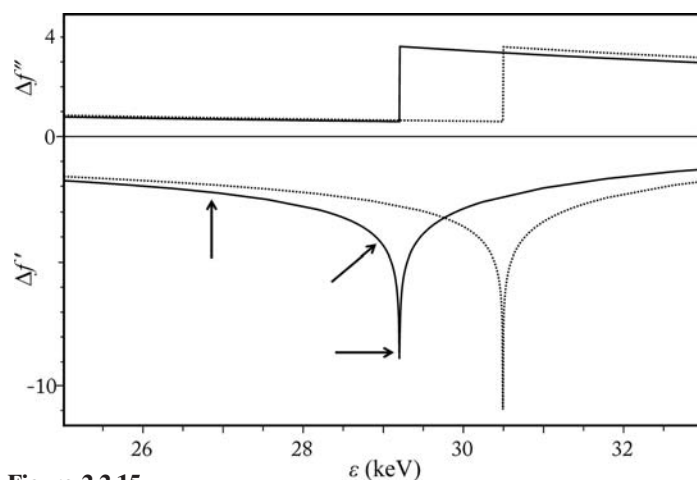## 2. INSTRUMENTATION AND SAMPLE PREPARATION

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 $Q > 25$ Å^{-1} ($d < 0.25$ Å) or more are required, with patterns of good statistical quality. Such Q values are not possible with Mo or Ag radiation (Ag $K\alpha$, $\lambda = 0.56$ Å, $Q \simeq 22$ Å^{-1} at $2\theta = 160°$), but are easily accessible at $\lambda = 0.4$ Å (31 keV) by scanning to $2\theta = 106°$. At 80.7 keV (0.154 Å, ten times shorter than Cu $K\alpha$) patterns to $Q \simeq 35$ Å^{-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 mono-chromator 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 Å 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 diffract-ometer 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. Alter-natively, 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

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