

## 2. DIFFRACTION GEOMETRY AND ITS PRACTICAL REALIZATION

(c) Compositional information may be obtained by use of X-ray microanalysis (or electron-energy-loss spectroscopy) performed in the electron microscope and this provides an effective additional guide to identification.

(d) Electron diffraction data often extend to smaller  $d$  spacings than X-ray data because there is no wavelength limitation.

(e) The electron diffraction  $d$ -spacing information is rarely more precise than 1% and the uncertainty may be 5% for large  $d$  spacings.

With these points in mind, databases specially designed for use with electron diffraction have been developed. The NIST/Sandia/ICDD Electron Diffraction Database follows the design principles of Carr, Chambers, Melgaard, Himes, Stalick & Mighell (1987). The 1993 version contains crystallographic and chemical information on over 81 500 crystalline materials with, in most cases, calculated patterns to ensure that diagnostic high- $d$ -spacing reflections can be matched. It is available on magnetic tape or floppy disks. The MAX-d index (Anderson & Johnson, 1979) has been expanded to 51 580 NSI-based entries (Mighell, Himes, Anderson & Carr, 1988) in book form for manual searching.

## 2.4.2. Neutron techniques (By A. W. Hewat)

Neutrons have advantages over X-rays for the refinement of crystal structures from powder data because systematic errors (Wilson, 1963) are smaller, and the absence of a form factor means that information is available at small  $d$  spacings. It is also easy to collect data at very low or high temperature; examining the structure as a function of temperature (or pressure) is much more useful than simply obtaining 'the' crystal structure at STP (standard temperature and pressure). In some cases, 'kinetics' measurements at intervals of only a few seconds are needed to follow chemical reactions.

A neutron powder diffractometer need not separate all of the Bragg peaks, since complex patterns can be analysed by Rietveld refinement (Rietveld, 1969), but high resolution will increase the information content of the profile, and permit the refinement of larger and more complex structures. Doubling the unit-cell volume doubles the number of Bragg peaks, requiring higher resolution, but also halves the average peak intensity. Resolution must not then be obtained at the expense of well defined line shape, essential for profile analysis, nor at the expense of intensity.

Two types of diffractometer are required in practice: a high-resolution machine with data-collection times of a few hours (or days) for Rietveld structure refinement, and a high-flux machine with data-collection times of a few seconds (or minutes) for kinetics measurements. In both cases, the data-collection rate depends on the product of the flux on the sample, the sample volume, and the solid angle of the detector (Hewat, 1975). The

flux on the sample can be increased with a focusing monochromator, the sample volume by using large sample-detector distances or Soller collimators, and the detector solid angle by using a large multidetector.

The focusing monochromator is usually made from horizontal strips of pyrolytic graphite or squashed germanium mounted on a vertically focusing plate 100 to 300 mm high. A large beam can thus be focused on a sample up to 50 mm high. Vertical divergence of  $5^\circ$  or more can be tolerated even for a high-resolution machine; the peak width is only increased (and made asymmetric) far from scattering angles of  $90^\circ$ , where most of the peaks occur. The effect is in any case purely geometrical, and can readily be included in the data analysis (Howard, 1982).

To increase the wavelength spread  $\Delta\lambda/\lambda$ , and hence intensity, monochromator mosaic can be large ( $20'$ ) even for high resolution, since all wavelengths are focused back into the primary-beam direction at scattering angles equal to the monochromator take-off angle (Fig. 2.4.2.1).

Rather long wavelengths (1.5 to 3 Å) are favoured, to spread out the pattern, and to reduce the total number of reflections excited (increasing their average intensity). Data must then be collected at large scattering angles with good resolution to obtain sufficiently small  $d$  spacings, and this implies a large take-off angle. A graphite filter to remove  $\lambda/2$  and higher-order contamination is a popular choice for a primary wavelength of 2.4 Å (Loopstra, 1966). Since germanium reflections such as  $hhl$  with  $h, l = 2n + 1$  do not produce  $\lambda/2$  contamination, a filter is not needed for primary wavelengths below about 1.6 Å with high-take-off-angle geometry, but is still necessary for longer wavelengths.

The multidetector can be an array of up to 64 individual detectors and Soller collimators for a high-resolution machine (Hewat & Bailey, 1976; Hewat, 1986a), or a position-sensitive detector (PSD) for a high-flux machine (Allemand *et al.*, 1975). Gas-filled ( $^3\text{He}$  or  $\text{BF}_3$ ) detectors are usual, though scintillator and other types of solid-state detector are increasingly used; the PSD may be either a single horizontal wire with position-detection logic comparing the signals obtained at either end, or an array of vertical wire detectors within a common gas envelope. The vertical aperture of the single-wire detector seriously limits the efficiency of what is otherwise a very cheap solution, and of course large angular ranges cannot be covered by a single straight wire.

The vertical aperture should match the vertical divergence from the monochromator ( $\sim 5^\circ$ ). Composite detectors can be constructed by stacking elements both vertically to increase the aperture, and horizontally to increase the angular range. Construction of a wide-angle ( $160^\circ$ ) multiwire detector is difficult and expensive, but a solid angle of more than 0.1 sr may be obtained. The solid angle for a collimated multidetector, even if it covers  $160^\circ$ , may be less than 0.01 sr.

The sample volume limits the resolution of the PSD, since the detector resolution  $\alpha_3$  (typically  $0.2^\circ$ ) is the mean of the element width and the sample diameter (typically 5 mm) divided by the sample-to-detector distance (typically 1500 mm). For a Soller collimator,  $\alpha_3$  can be as little as  $5'$ , and does not depend on the sample volume, which can be large (20 mm diameter) even for high resolution. The PSD also requires special precautions to avoid background from the sample environment, while the collimated machine can handle difficult sample environments, especially for scattering near  $90^\circ$ .

The definition of the detector is the number of data points per degree. For profile analysis, unless the peak shape is well known *a priori*, about five points are needed per reflection half-width, which is more than usually available from a multiwire PSD.

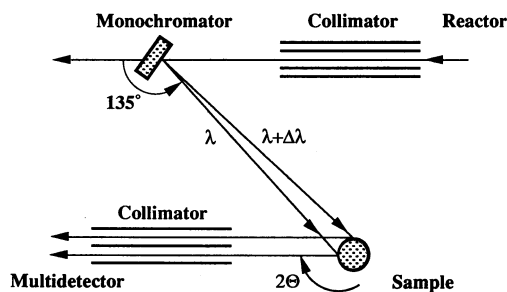


Fig. 2.4.2.1. Schematic drawing of the high-resolution neutron powder diffractometer D2B at ILL, Grenoble.