

## 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.

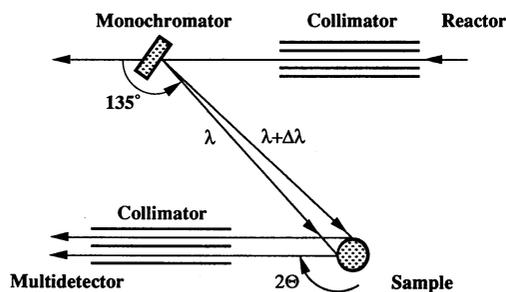


Fig. 2.4.2.1. Schematic drawing of the high-resolution neutron powder diffractometer D2B at ILL, Grenoble.

## 2.4. POWDER AND RELATED TECHNIQUES: ELECTRON AND NEUTRON TECHNIQUES

However, a PSD may be scanned to increase the profile definition. The minimum scan angle is clearly the angle between elements, from  $0.2^\circ$  for a PSD to  $2.5^\circ$  or more for a multidetector in steps of from  $0.025$  to  $0.1^\circ$ . If larger scans are performed, it is most convenient to reduce the data to a single profile by averaging the counts from different detector elements at each point in the profile, after correcting for relative efficiencies and angular separations.

The resolution, of either machine, should be no better than really necessary for a particular sample: additional resolution merely reveals problems with sample perfection and line shape, making Rietveld refinement difficult, and of course reducing effective intensity. In any case, resolution is ultimately limited by the powder particle size and strain broadening (Hewat, 1975). As an order of magnitude, if  $D = 1000 \text{ \AA}$  is the effective size of the perfect crystallites that make up a much larger (1 to  $10 \mu\text{m}$ ) powder grain, then for lattice spacing  $d = 1 \text{ \AA}$ , the best resolution that one can hope to obtain is of the order  $\Delta d/d = d/D = 10^{-3}$ , corresponding to a line width of  $\Delta(2\theta) \simeq 0.1^\circ$ . A few more perfect materials (usually those for which single crystals can be grown!) will produce higher-resolution patterns, but then primary extinction may not be negligible.

It is not even necessary to have the best possible resolution for all  $d$  spacings: ideally, the resolution should be proportional to the density of lines, and this increases with the surface area of the Ewald sphere of radius  $1/d$ . Then we want  $\Delta d/d = d^2$  or  $\Delta(2\theta) = \lambda^2/\sin 2\theta$ . This has a minimum near  $2\theta = 90^\circ$ . In fact, the full width at half-height is (Cagliotti, Paoletti & Ricci, 1958)

$$\Delta^2(2\theta) = U \tan^2 \theta + V \tan \theta + W.$$

The parameters  $U$ ,  $V$ , and  $W$  are functions of the monochromator mosaic spread and collimation, from which it follows that the minimum in  $\Delta(2\theta)$  occurs for scattering angles  $2\theta \simeq 2\theta_M$ . The monochromator take-off angle should then be at least  $90^\circ$ ; in practice, since  $\Delta^2(2\theta)$  increases quadratically with  $\tan \theta$  for angles larger than this focusing angle, the monochromator take-off should be even greater than  $90^\circ$ . A value of  $120$  to  $135^\circ$  is recommended.

For this focusing geometry, the different wavelengths  $\lambda + \Delta\lambda$ , reflected at different angles from the monochromator, are brought back parallel to the primary beam, and the line width becomes simply the convolution of the primary and detector collimations  $\alpha_1$  and  $\alpha_3$ :

$$\Delta^2(2\theta) = \alpha_1^2 + \alpha_3^2.$$

The collimators  $\alpha_1$  and  $\alpha_3$  should then be equal and small. Such fine collimators are now made routinely from gadolinium oxide-coated stretched plastic foil (Carlile, Hey & Mack, 1977). The collimator  $\alpha_2$  should simply be large enough to pass all wavelengths reflected by the mosaic spread  $\beta$  of the monochromator, *i.e.*  $\alpha_2 \simeq 2\beta$ .

Neutron crystallographers have been reluctant to use large take-off angles because they seem to imply greatly reduced beam intensity. Indeed, large  $\theta_M$  means small waveband  $\Delta\lambda/\lambda$  since  $\Delta\lambda/\lambda = \Delta d/d = \Delta(\theta_M) \cot \theta_M = \beta \cot \theta_M$ . However,  $\Delta\lambda/\lambda$  and therefore beam intensity can be recovered simply by increasing  $\beta$ . This has no effect on the resolution at focusing, but it does increase the line width at low angles where there are few lines. When large  $d$  spacings are needed, for example for magnetic structures, it is best for both resolution and intensity to retain the same high take-off geometry and increase the wavelength to bring these lines closer to the focusing angle. A large take-off angle also gives a large choice of high-index reflections and wavelengths up to  $6 \text{ \AA}$ !

A fixed take-off angle greatly simplifies machine design: the multidetector collimation  $\alpha_3$  is also necessarily fixed, but the single primary collimator  $\alpha_1$  can readily be changed. It is useful to have a second choice, much larger than  $\alpha_3$ , to boost intensity for poor samples or exploratory data collection. The resolution at low angles, largely determined by  $\beta$  (or  $\alpha_2$ ), is not much affected by increasing  $\alpha_1$ .

Finally, the machine should be designed around the sample environment, since this is one of the strengths of neutron powder diffraction. There is no point in building a neutron machine with superb resolution and intensity (these can much more readily be obtained with X-rays) if it cannot produce precise results for the kind of experiments of most interest – those for which it is difficult to use any other technique (Hewat, 1986b).