

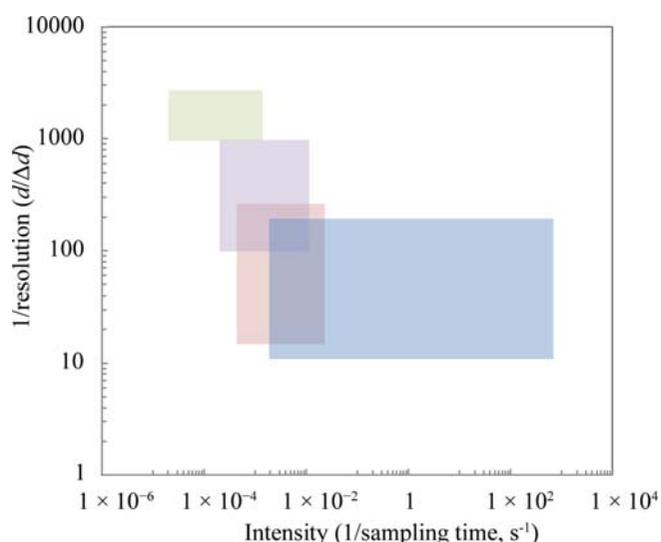
2. INSTRUMENTATION AND SAMPLE PREPARATION

Table 2.3.5

Advantages of CW and TOF instruments (modified from Kisi & Howard, 2008)

CW	TOF
(1) Incident beam may be essentially monochromatic, in which case the spectrum is well characterized	(1) The whole incident spectrum is utilized, but it needs to be carefully characterized if intensity data are to be used
(2) Large d -spacings are easily accessible for study of complex magnetic and large-unit-cell structures	(2) Data are collected to very large Q values (small d -spacings)
(3) Can fine tune the resolution during an experiment	(3) Few cold neutron instruments are available for study of complex magnetic and large-unit-cell structures
(4) More common	(4) Resolution is constant across the whole pattern
(5) Peak shapes are simpler to model	(5) Very high resolution is readily attained by using long flight paths
(6) Absorption and extinction corrections are relatively straightforward	(6) Complex sample environments are very readily used if 90° detector banks are available
(7) Data storage and reduction is simpler	(7) Simpler to intersect a large proportion of the Debye–Scherrer cones with large detector banks
(8) Extremely rapid data collection and stroboscopic measurements are feasible	(8) Very fast data collection is feasible
(9) Engineering diffractometers are very well suited for strain scanning in complex objects	(9) Engineering diffractometers use an extended diffraction pattern, ideal for <i>in situ</i> loading and/or heating
(10) Texture is straightforward to measure on engineering diffractometers	(10) Texture can be measured on universal instruments

facility (UK) or SuperHRPD at J-PARC confers a particular advantage. The CW equivalent high-resolution powder diffractometers such as D2B at ILL and ECHIDNA at ANSTO can almost match the absolute resolution of the TOF instruments, D2B achieving $\Delta d/d$ of 5.6×10^{-4} ; however, the resolution function for a CW diffractometer [equation (2.3.18)] has a strong minimum and so this resolution can only be achieved over a restricted range of d -spacing. The reflections appearing in the highest-resolution zone can be shifted by wavelength changes, which of necessity require re-recording of the pattern.

**Figure 2.3.25**

Schematic showing regions of intensity–resolution space in which different diffractometer types typically operate. High-resolution TOF diffractometers operate in the green area, engineering diffractometers (TOF or CW) in the purple area, multi-purpose TOF diffractometers such as POLARIS in the orange area and very high intensity CW diffractometers in the blue area.

The second extreme case is when rapid kinetic behaviours are to be studied. In this case, a small number of CW diffractometers (e.g. D20 at the Institut Laue–Langevin or WOMBAT at ANSTO) have a distinct advantage. Therefore at this time, processes that occur reproducibly and uniformly over a large sample on sub-1 s timescales are best suited to stroboscopic studies using one of the very rapid CW diffractometers available. There are nonetheless a great number of processes that can be studied on the timescales accessible using TOF, where near-constant resolution across the entire diffraction pattern lends considerable advantage.

If unaffected by extremes of resolution, intensity or highly specialized data types (stress, texture *etc.*), the choice between a CW or TOF instrument can be made based more casually on proximity to neutron sources and the access arrangements for national or regional neutron users.

2.3.5. Experimental considerations

2.3.5.1. Preliminary considerations

Neutron-diffraction studies are motivated by a desire to exploit the unique properties of neutrons as listed in Sections 2.3.1 and 2.3.2. As access to neutron diffraction is carefully regulated through an experiment proposal system, considerable planning is required in order to write a successful proposal. Owing to the expense of operating a neutron source and pressure on instrument time, there is an onus on the experimental team to make the best use of neutron beam time. Consideration should be given to the type of instrument required, the resolution that is needed, the d -spacing range of interest, how long each pattern will take to record, the requirement (or not) for standard samples and whether a special sample environment is needed.

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Table 2.3.6

Suitability of problems to high-resolution or high-intensity diffractometers

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Problem	High resolution	High intensity (medium resolution)
Solve a complex crystal or magnetic structure	Essential, especially in the presence of pseudo-symmetry	Not usually suitable†‡
Refine a complex crystal or magnetic structure	Essential. Will benefit from a high Q -range if available	Not usually suitable†‡
Solve or refine small inorganic structures	Beneficial, but not usually essential unless pseudosymmetry is present	Usually adequate
Quantitative phase analysis	Only required when peaks from the different phases are heavily overlapped	Usually adequate. Allows phase quantities to be tracked in fine environmental variable steps (T, P, E, H etc.) during <i>in situ</i> experiments
Phase transitions	Depends on the nature of the transition and complexity of the structures. Essential for transitions involving subtle unit-cell distortions and pseudosymmetry	Often adequate for small inorganic structure transitions and order–disorder transitions. Allows fine steps in an environmental variable (T, P, E, H etc.)
Line-broadening analysis	Essential for complex line broadening such as from a combination of strain and particle size, dislocations, stacking faults etc.	Adequate for tracking changes in severe line broadening as a function of an environmental variable (T, P etc.) especially if the pure instrumental peak shape is well characterized
Rapid kinetic studies	Not appropriate	Essential

† In some cases the symmetry and lattice parameters are such that the diffraction peaks are well spaced and not severely overlapped even at modest resolution. ‡ May be necessary to supplement high-resolution data to observe weak superlattice reflections in the presence of very subtle or incomplete order–disorder transitions.

Table 2.3.7

Guidance on choice of wavelength/detector bank

Reproduced from Kisi & Howard (2008) by permission of Oxford University Press.

Problem	Choice	Reasons
Solve complex or low-symmetry structures	Longer wavelength	Increase d -spacing resolution to allow correct symmetry and space group to be assigned
Refine a large or complex crystal structure	Shorter wavelength	Ensure that the number of peaks greatly exceeds the number of parameters. Improve determination of site occupancies and displacement parameters
Solve or refine magnetic structures	Longer wavelength	Ensure that large d -spacing peaks are observed. Spread the magnetic form factor over the entire diffraction pattern
Quantitative phase analysis	Usually shorter wavelength	Improve the accuracy of the determination. Longer wavelengths only required if peak overlap is severe
Phase transitions	Shorter wavelength	Ensures adequate data for order–disorder or other unit-cell-enlarging transitions
	Longer wavelength	Subtle unit-cell distortion or pseudosymmetric structures

In the general case, there is competition between the resolution and the intensity of diffractometers, although some of the modern TOF diffractometers (*e.g.* POLARIS, GEM, POWGEN, NOMAD and iMATERIA) simultaneously record patterns of moderate resolution and intensity, and high-intensity patterns at low resolution, in different detector banks. For the purposes of this chapter, high resolution is defined as a minimum diffraction peak width at half maximum height corresponding to $\Delta d/d \leq 10^{-3}$. This is the resolution typically required to observe lattice-parameter differences [*e.g.* $(a - b)/a$] of as little as 4×10^{-5} or so in the absence of sample-related peak broadening. Such a diffractometer is typically of the order of 10 to 1000 times slower than corresponding high-intensity diffractometers at the same neutron source. The decision to opt for a high-resolution diffractometer or a high-intensity diffractometer will depend critically on the nature of the problem under study. This situation

was considered in Kisi & Howard (2008) and their conclusions are reproduced in Table 2.3.6.

It might be expected that the total information content in a diffraction pattern correlates with the d -spacing range covered and therefore this should be maximized. However, this expectation overlooks the different purposes for which powder-diffraction patterns are used. A greater density of diffraction peaks (*e.g.* in a CW pattern recorded using a short neutron wavelength) makes the detailed refinement of complex crystal structures more precise; however, it makes the determination of unit cell and systematic absences *more* difficult as well as reducing access to information contained within the peak shapes concerning the sample microstructure. Table 2.3.7 summarizes these effects. It should be noted that in this context parallels exist between a short-wavelength CW diffraction pattern and a low-angle-detector-bank TOF pattern; and between a longer-

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wavelength CW pattern and a high-angle-detector-bank TOF pattern, subject to limitations imposed by the wavelength distribution in the incident spectrum.

A decision must be made on how long to spend recording each diffraction pattern, such that the greatest number of patterns (samples) may be studied without compromising the information content of each pattern. Since counting is governed by Poisson statistics, the statistical precision of N counts in a radiation detector (X-ray, electron or neutron) is represented by the standard deviation σ :

$$\sigma = N^{1/2}. \quad (2.3.23)$$

This is true regardless of whether a single count is made or multiple counts are summed to give an integrated intensity or a total count from several detectors. For a relatively constant arrival rate of neutrons, the precision of each data point will increase with counting time t in proportion to $t^{1/2}$, and this will be reflected in the agreement indices (*e.g.* R_{wp} ; Chapter 4.7) between the observed and calculated neutron intensities during structure refinements (*e.g.* Rietveld refinement) as well as in the estimated standard deviation (e.s.d.) of the refined crystal structure and other parameters. It has been shown by Hill & Madsen (1984) using CW X-ray powder-diffraction patterns that this is the case for small counting time; however, the agreement and e.s.d.'s quickly attain a plateau for counting times where 2000–5000 counts are recorded at the top of the largest diffraction peak. Beyond this, systematic errors in the models used for peak shapes, background *etc.* begin to dominate the fitting procedure. An important consequence is that since the expected values of the parameter e.s.d.'s fall in proportion to $t^{-0.5}$ whereas their actual values plateau, the statistical χ^2 increases for patterns recorded beyond the limit suggested by Hill & Madsen. A number of recommendations may be derived from these results:

- (i) It is of no benefit for routine crystal structure refinements to record data beyond the point where the strongest peak has 5000 or so counts at its apex and to do so may render parameter e.s.d.'s invalid.
- (ii) Counting for longer times *is* however recommended for problems that hinge upon weak superlattice or magnetic peaks. Similarly, it may be of benefit when minor phases are of interest, such as in complex engineering materials, in samples undergoing phase transitions or in multi-component geological materials.
- (iii) An equally important result from Hill & Madsen is that respectable refined parameter estimates could be obtained using powder-diffraction patterns with only 200–500 counts at the apex of the strongest peak. This is extremely useful when assessing counting times in rapid kinetic studies where the shortest acceptable counting time is preferred. Modern data-acquisition electronics are often configured to allow very short acquisition times or 'event-mode operation' (Section 2.3.4.2.2) with patterns subsequently added together to obtain the required statistical and/or time resolution. In this case, the shortest time step available should be used provided sufficient data storage capacity is at hand.

In CW measurements with a detector bank scanned in small angular steps, similar arguments to those above apply to the sampling interval. This too has been investigated by Hill & Madsen (1986) and again, improvements to the agreement between the calculated and observed patterns and indeed improvements to refined parameter e.s.d.'s were only observed

until systematic errors begin to dominate the fit. As a general rule of thumb, once the applicable counting *time* has been established, the counting interval should be adjusted to give at least 2 (but typically around 5) sampling points in the top half of the diffraction peak for routine crystal structure refinements. Finer sampling intervals are however beneficial in the case of:

- (i) subtle symmetry changes that manifest in the peak shape well before peak splitting is observable,
- (ii) following the evolution of a minor phase during an *in situ* experiment, or
- (iii) peak-shape analyses to explore the sample microstructure (crystallite size, strain distribution, dislocation density, stacking-fault probability *etc.*).

CW measurements using instruments with a fixed position-sensitive detector and TOF measurements both have their raw sampling interval fixed by the instrument architecture, which cannot be varied. The recorded patterns can be subsequently rebinned to a larger sampling interval, although this would usually only be considered to reduce serial correlations during profile refinement (Hill & Madsen, 1986).

2.3.5.2. Sample-related factors

Recording a neutron powder-diffraction pattern is in itself a simple operation. There are, however, a number of sample-related variables that can affect the accuracy or the precision of the resulting patterns, or the ability to analyse them. It is worth mentioning here that neutron-diffraction samples are often large, in the range 1–40 g, to compensate for the lower incident fluxes and scattering cross sections as compared with the X-ray case. Large sample size has a strong mitigating effect on many of the sample-induced problems to be discussed in Chapter 2.10 and below.

The absolute *accuracy* of the position, intensity and shape of neutron powder-diffraction peaks is primarily determined by:

- (i) *How representative the whole sample is of the whole system.* Known as disproportionation, this problem results from any non-random factor during sampling. For example, within rocks there is spatial variability in the mineral content (where to sample), hardness differences (different mineral particle sizes) and differing density (settling effects). Similar considerations apply to multiphase ceramic materials and metal alloys. With highly penetrating neutrons, this can be greatly reduced by using the polycrystalline solid sample provided that the crystallite size is relatively small [see (iii) below]. Disproportionation primarily influences quantitative phase analysis studies. Crystal-structure results are unaffected provided there is enough of each phase of interest to give a high-quality diffraction pattern.
- (ii) *How representative the irradiated part of the sample is of the whole system.* Although ideally the entire sample is bathed in the incident beam, for highly focused neutron beams on high-intensity and/or strain-scanning diffractometers, the beam-sample interaction volume is smaller than the whole sample. In such cases, if a gradient in an experimental variable such as temperature, pressure or composition is present, then the irradiated portion of the sample can be quite unrepresentative and this needs to be addressed in the overall experiment plan.
- (iii) *How representative the diffracting part of the sample is of the whole sample.* There are two circumstances in which the observed diffraction pattern may be unrepresentative of the irradiated portion of the sample. First, very large crystallite

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size leads to the phenomenon of *granularity*, which is dealt with in detail in Section 2.10.1.1. Crystallites diffract only when the Bragg condition is met, so if the crystallite size is a sizable fraction of the irradiated part of the sample, only a small number of crystallites are aligned for diffraction. With only relatively few crystals diffracting, the peak shapes, intensities and apparent *d*-spacings are strongly distorted. Second, when there is amorphous material present, it is visible in the diffraction pattern only as structure in the background signal and is not analysed using standard crystallographic techniques.

(iv) *How representative the recorded pattern is of the sample.* There are two other factors that can affect accuracy of the diffraction pattern.

The first is that the crystallites may have preferred (rather than random) orientations, so that some sets of atomic planes are overrepresented and others underrepresented in the diffraction pattern. This effect and the means to overcome it in X-ray diffraction measurements are covered in Section 2.10.1.2. Neutron powder diffraction, by using large samples on a rotating sample holder in transmission geometry, is generally far less susceptible to preferred orientation than X-ray diffraction. In cases where preferred orientation is unavoidable, it is generally of a simple axial form due to the sample rotation. Quite good analytical means for modelling preferred orientation of this type are available in the various refinement programs described in Chapter 4.7.

The second effect is attenuation. For most materials, thermal neutrons are attenuated comparably by true absorption and scattering, the overall effect being very minor. For a small number of elements (*e.g.* B, Cd, Gd – see Table 2.3.2) the absorption is high, and in an even smaller number of isotopes (*e.g.* H) the incoherent scattering is high enough to give significant attenuation. Details of these processes are dealt with in Section 2.10.2.4 as well as in Sections 2.4.2 and 3.5.3 of Kisi & Howard (2008). In summary, when using transmission geometry and absorbing samples, diffraction peaks at low angle (CW) are attenuated more than those at higher angles. An additional linear dependence on neutron wavelength occurs in TOF patterns. Therefore the relative intensities are incorrect and during structure refinements unreasonable (often negative) displacement parameters will result. When strongly attenuating elements or isotopes are present three approaches are available; the data can be recorded in reflection geometry, the capillary-coating method can be adapted from X-ray diffraction, or the sample can be diluted with a large amount of a weakly absorbing material. The latter two methods are explained in Section 2.10.1.4.2.2.

Sample-related factors that interact with the precision of various crystallographic and microstructural parameters determined from a given diffraction pattern are:

(i) *The crystallite size within the sample.* As discussed at length in Chapter 2.10, the ideal size for crystallites in a powder-diffraction measurement is 2–5 μm . The upper limit is determined by onset of granularity [see (iii) above]. The lower limit is set by the onset of detectable crystallite size broadening (Chapter 5.1). To first order, the broadening of diffraction peaks due to small crystallite size is well understood. It has negligible effect on the measured intensity of diffraction peaks and does not affect the numerical value of the peak positions (hence *d*-spacings); however, the precision

or standard error of such measured positions is strongly affected. In addition, the precision (standard error) of measurements of other microstructural features such as strain distributions, dislocation density or stacking-fault probability are strongly affected. Powdered samples should be sized to lie within the range 2–5 μm with the lower limit being the more important in this case. The crystallite size within solid polycrystalline samples is an inherent part of the system. Forming a material with a fine grain size is a universal method for strengthening metals and ceramics alike. In systems undergoing phase transitions the crystallites typically subdivide into small portions during the transition. Consequently, crystallite size broadening is often an inevitable part of a powder-diffraction experiment.

(ii) *How ideal the crystal structure is within the crystallites.* The preparation of powder samples can induce several types of lattice defects (dislocations, stacking faults, twin faults *etc.*) into the material under study. Each of these leads to changes to the peak positions, shapes and breadths. Likewise, in solid polycrystalline samples, thermal-expansion anisotropy and mismatch between different phases cause intergranular strains which manifest themselves in broadened peaks. Each new source of broadening strongly affects the precision with which other microstructural features of the sample can be determined from peak-shape analysis. In ground powders, it is sometimes possible to relieve stresses and repair defects by annealing, but only if it is certain that no detrimental changes to the material occur under the annealing conditions.

A common prerequisite for the detailed analysis of diffraction patterns is a good understanding of the instrument's characteristic peak shapes and widths, *i.e.* the resolution function (Sections 2.3.4.1.4 and 2.3.4.2.1). The parameters of the resolution function are needed to enable Rietveld (Chapter 4.7) or whole-pattern (Chapter 3.6) analysis of the diffraction patterns. A good description for the instrument resolution function is important in the study of sample microstructure (*e.g.* crystallite size, strain distribution or dislocation studies) and may be established using standard samples. Early versions of the NIST LaB₆ lattice-parameter and peak-shape standards (SRM 660) were unsuitable because of the high neutron absorption of natural boron. More recently, NIST has developed LaB₆ standards SRM 660b and 660c made with ¹¹B that can be used for neutron diffraction (see Section 3.1.4). Suitable air- and moisture-stable alternatives with a closely regulated crystallite size and a moderate density of diffraction peaks include Al₂O₃, CeO₂, Y₂O₃ and some intermetallic compounds such as Cu₉Al₄ and Cu₅Zn₈.

One's ability to successfully analyse a diffraction pattern is then strongly affected by:

(i) *Smooth and locally monotonic peak shapes.* The two primary causes of failing to meet this requirement are granularity (crystallites significantly above the preferred 2–5 μm size) and unusual sample shapes such as hollow samples. Examples of the former may be seen in Figs. 2.10.2 and 2.10.3, where large single crystals in the sample each give a discrete diffraction peak, the composite of which looks nothing like the true powder peak shape. The case of hollow samples is rarely seen unless the 'capillary-coating' technique (see Section 2.10.1.4.2.2) is adopted for a highly absorbing sample or diffraction peaks from a hollow sample container are also to be analysed. In this case, the peak shape will have a depression in the centre due to the non-uniform distribution of diffracting matter across the specimen.

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- (ii) *Crystallite perfection.* For crystal-structure studies, it is preferred that the crystallites in the sample be as near perfect¹⁹ as possible. However, materials of interest are often far from perfect, containing stacking faults, domain walls, antiphase boundaries, compositional gradients, strain gradients *etc.* Fig. 9.22 in Kisi & Howard (2008) illustrates this for a ferroelectric material. Here the individual crystallites are subdivided into ferroelectric domains with different orientations defined by the symmetry relationship between the parent (cubic) and daughter (tetragonal) structures. Where differently oriented domains abut, there is a strain gradient over a finite portion of crystal. This is visible in the diffraction pattern as a plateau between twin-related pairs of peaks such as the 200/002 pair shown, because in the strain gradient all d -spacings between d_{200} and d_{002} are present.
- (iii) *Sample perfection.* The major types of imperfection in sampling are described under *accuracy* in the preceding discussion. Our main interest here is in the preferred orientation of crystallites, which means some diffraction peaks are exaggerated and others underrepresented in the diffraction pattern. Methods for avoiding or reducing preferred orientation are dealt with in Section 2.10.1.2. In addition, whole-pattern fitting and reasonably robust mathematical models for preferred orientation, principally the March–Dollase model (Dollase, 1986) and models based on spherical harmonics (Ahtee *et al.*, 1989), have reduced the effect of preferred orientation on crystal-structure parameters and quantitative phase analyses derived from powder-diffraction patterns. In a small number of cases of severe and/or multi-axis preferred orientation, these models can fail and efforts to reduce the effect within the sample need to be revisited.

2.3.5.3. Sample environment and in situ experiments

It is more often the case with neutron diffraction than with X-ray or electron diffraction that the purpose is an experimental study involving rather more than a simple room-temperature data collection.²⁰ As such, there are a great variety and complexity of sample environments available, relating to studies: at room temperature, cryogenic temperatures, high temperature and high pressure; under magnetic fields, electric fields or applied stress; during gas–solid, liquid–solid, solid–solid or electrochemical reactions; and almost any combination of these. There are several other chapters in this volume that include descriptions of sample environments for neutron powder-diffraction experiments under high (hydrostatic) pressure (Chapter 2.7), electric and magnetic fields (Chapter 2.8) and chemical and electrochemical reactions (Chapter 2.9). Some general guidance on the mounting of samples is also given in Chapter 2.10. Additional information concerning sample containers for non-ambient studies, as well as sample environments not expressly covered in these chapters, will be presented briefly below.

2.3.5.3.1. Sample containers

Solid polycrystalline samples can be directly mounted on the diffractometer; however, powder samples require careful containment. Powder spillage must be avoided because samples

may become activated in the neutron beam and spilled powders present a radiological hazard. Owing to the low neutron attenuation by most materials, neutron diffraction patterns are generally recorded in transmission (Debye–Scherrer) geometry. Therefore sample containers that do not contribute significantly to the diffraction pattern are required. Fortunately there are several materials that have essentially zero coherent neutron scattering length, *i.e.* they give no discernible diffraction peaks and minimal contribution to the background. Most versatile is elemental vanadium, which has a scattering length of just -0.3824 fm (Table 2.3.2), making its diffraction pattern 100–750 times weaker than most other metals. Coupled with excellent room-temperature resistance to atmospheric corrosion, it is not surprising that it is the material that is used most often for neutron powder diffraction sample holders. Typical designs are discussed in Section 2.10.2.3. Another useful material for room-temperature containment is Al, which has very low attenuation and few diffraction peaks of its own. This is especially useful in cases where only the large d -spacing peaks are of interest, for example with magnetic materials or large-scale structures, or where a fine radial collimator is able to exclude diffraction from the sample container.

Sample containers for specialized sample environments vary greatly. Low-temperature studies routinely use V or Al cans, as for room-temperature studies. High-temperature studies of powders can use V cans up to approximately 1073 K provided that an inert gas or vacuum environment is present. At higher temperatures, thin-walled fused silica (silica glass) can be used as it has several advantages: it is amorphous and therefore gives no sharp diffraction peaks; it is vacuum tight and relatively easy to seal to vacuum fittings *via* O-rings outside or graded glass–metal seals within the hot zone of the furnace; it is transparent, so the state of the sample can be viewed during loading and after the experiment; and it is immune to thermal shock. Silica can survive at temperatures up to 1473 K and for short periods can resist temperatures up to 1673 K, although some devitrification may occur. Care should be exercised since although fused silica has no sharp diffraction peaks, its short-range order does give a structured background which has to be carefully treated in subsequent analyses. Containers for still higher temperatures can be made from other ceramics such as alumina or from refractory metals such as Nb, Ta or W in increasing order of temperature resistance. Noble metals such as Pt may seem to have some advantages; however, they are extremely weak and fragile after high-temperature annealing. All high-temperature sample-container materials are able to chemically react with *some* samples at high temperature and great care must be taken when selecting them. If possible, a trial heating should be conducted off-line prior to the experiment.

2.3.5.3.2. Non-ambient temperature

As neutron powder diffraction is routinely conducted in transmission geometry, non-ambient sample environments have many common features. They are typically cylindrical in shape, with the sample can loaded centrally from above on a ‘sample stick’, which goes by various names in different fields.

An example is the liquid-helium cryostat developed at the Institut Laue–Langevin, shown in Fig. 2.3.26. The internal space is evacuated and heat is removed from the sample *via* conduction through the sample stick to cold reservoirs in contact with the liquid-helium tank. The sample protrudes below the helium and neutron tanks into the ‘tails’, which are thin-walled Al or V

¹⁹ If the crystallites are too perfect, then diffracted intensities might be affected by ‘extinction’ (Sabine, 1985), so an ‘ideally imperfect’ crystallite is to be preferred.

²⁰ For example, more than 90% of recent neutron powder-diffraction proposals to Oak Ridge have requested non-ambient conditions (Kaduk, personal communication).

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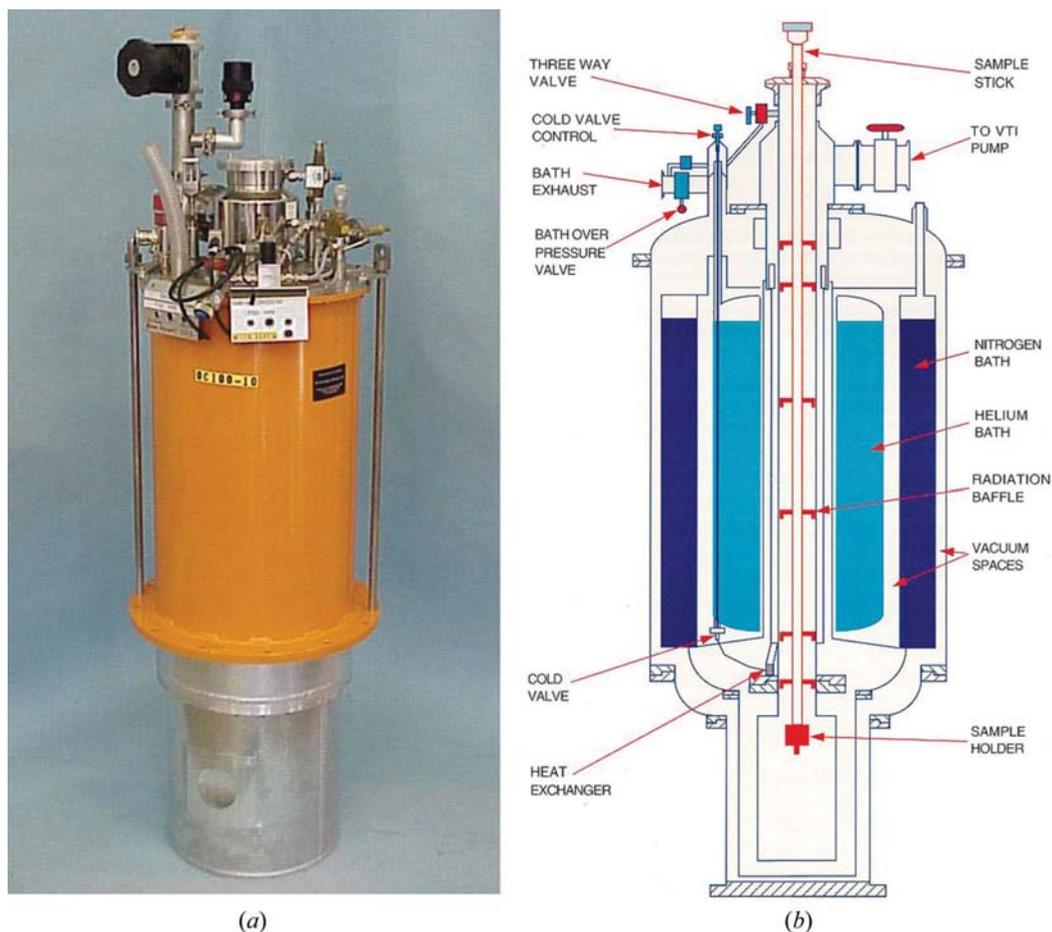


Figure 2.3.26

(a) Exterior and (b) interior of the standard ILL liquid-helium cryostat for cooling samples in the range 1.8–295 K. An internal heater allows samples to be studied without interruption from 1.8–430 K. Reproduced with permission from the ILL.

cylindrical sections that allow ready transmission of neutrons but preserve the vacuum and exclude radiant heat from the outside world. Liquid-helium cryostats can generally attain base temperatures of 4.2 K (He alone) or 1.9 K if pumped. Liquid-nitrogen cryostats are limited to 77 K. A second type of low-temperature device is the closed-cycle He refrigerator, commonly referred to by the trade name Displex. These are more compact than a liquid-helium cryostat and do not require refilling. Depending on the number of stages and internal design, refrigerators with base temperatures as low as 4 K are available.

Samples are typically first cooled to base temperature and then studied at the chosen sequence of increasing temperatures. This is achieved through a small electric resistance heater and control system. As heat transfer to and from the sample is deliberately poor in these devices, sufficient time should be allowed for the (often large) sample to reach thermal equilibrium before recording its neutron-diffraction pattern. It is worth noting that the attainment of thermal equilibrium does not guarantee that the sample has attained thermodynamic equilibrium. Some phase transitions are notoriously slow, for example the ordering of hydrogen (or deuterium) in Pd metal at 55 K and 75 K, which can take up to a month (Kennedy *et al.*, 1995; Wu *et al.*, 1996), or the ordering of C in TiC_x ($0.6 < x < 0.9$) around 973 K, which can take a week to complete (Moisy-Maurice *et al.*, 1982; Tashmetov *et al.*, 2002).

Raising samples to above ambient temperature is, for X-ray diffraction, the subject of a separate chapter (Chapter 2.6); however, neutron-diffraction high-temperature devices are somewhat different. Most commonly used and most versatile is

the foil element resistance furnace, in which Cu bus bars transfer electric current to a cylindrical metal foil which heats up as a result of its electrical resistance. Foil elements are typically 30–60 mm in diameter and up to 200 or 250 mm long so as to provide a long hot zone of uniform temperature within the furnace. The sample is located, *via* a sample stick from above or occasionally *via* a pedestal support from below, in the centre of the foil heating element, ensuring that it is uniformly bathed in radiant heat. Concentric metal-foil heat shields greatly reduce heat loss to the exterior by radiation, while convective losses are avoided by evacuating the interior of the furnace to $\sim 10^{-5}$ mbar. Metals for manufacture of the foil elements include V, which has almost no coherent diffraction pattern and can operate continuously up to 1173 K or intermittently to 1273 K. For temperatures above this, progressively more refractory metals are chosen such as Nb (<1773 K), Ta (<2473 K) or W (2773 K). These materials will contribute some small diffraction peaks to the observed patterns, which requires the recording of reference patterns from the empty furnace before commencing. Owing to the internal vacuum, some types of sample are at risk of subliming, decomposing or disproportioning during the experiment. In such cases, sample cans that extend outside the hot zone, where they can be coupled to a gas-handling system and filled with an internal atmosphere of air, an inert gas or a reactive gas of interest as required, are used.

Alternatives to foil furnaces include variations of the wire-wound laboratory furnace with a split winding and reduced insulating material in the neutron beam path, Peltier devices, hot-air blowers and induction heaters. The first three of these are discussed by Kisi & Howard (2008).

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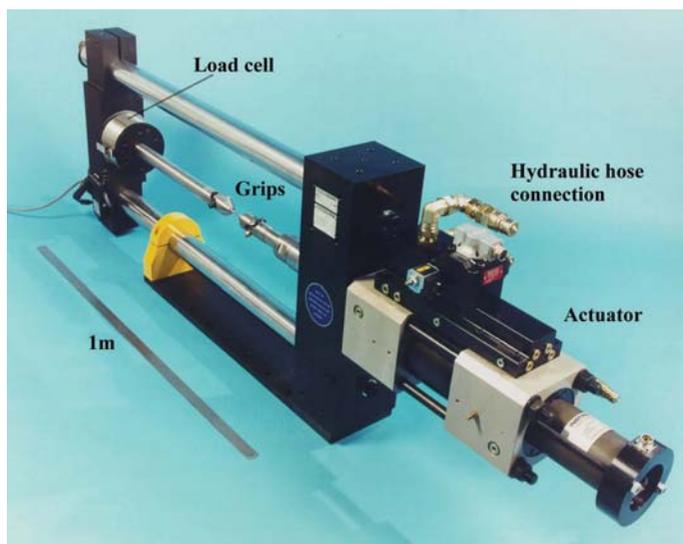


Figure 2.3.27

Elements of a typical mechanical testing machine used for applying uniaxial stress (pressure) to samples on an engineering neutron diffractometer. This example of a 100 kN device is from the instrument ENGIN-X at the ISIS facility, UK. (Credit: STFC.)

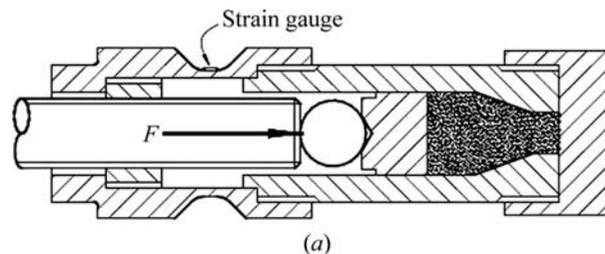
Non-ambient temperature devices are usually designed for operation either below or above ambient temperature. However, there are a large number of phase transitions and other phenomena that span from below to above ambient temperature. In order to avoid transferring samples from one sample environment to another mid-experiment, a useful hybrid device is the cryo-furnace. Cryo-furnaces are based around the liquid-helium cryostat and are equipped with more powerful heaters, allowing temperatures typically in the range 4–600 K to be covered.

2.3.5.3.3. Uniaxial stress

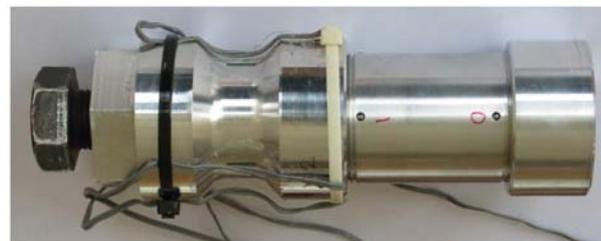
There are two major applications of *in situ* uniaxial loading. In the first, stress-induced phase transitions, ferroelasticity or simply mechanical response are studied throughout the whole sample as a function of applied stress. This may be undertaken on any powder diffractometer with a reasonable data-collection rate, depending on the resolution required. Parameters typically monitored are the relative phase proportions of parent and daughter structures, lattice parameters, individual peak shifts, which can yield the single-crystal elastic constants (Howard & Kisi, 1999), peak widths, which can indicate the breadth of strain distributions, and preferred-orientation parameters, which can indicate the degree of ferroelasticity (Kisi *et al.*, 1997; Ma *et al.*, 2001; Forrester & Kisi, 2004; Forrester *et al.*, 2005). The second application involves strain scanning using an engineering diffractometer as described in Section 2.3.4.3; however, in this instance an external load is applied to the object under study. This technique can be used to validate finite element analysis simulations of complex components with or without internal residual stresses.

Devices for the *in situ* application of uniaxial stress include adaptations of laboratory universal testing machines such as the 100 kN hydraulic load frame shown in Fig. 2.3.27. Devices such as this may be used in tension, compression, fatigue or even creep conditions depending on the sample and the problem under study.

For more specialized applications, it is sometimes possible to create a more compact device. A recent adaptation of strain



(a)



(b)

Figure 2.3.28

(a) Cross section and (b) exterior of a self-loading die for the study of stresses in granular materials.

scanning is to study the stress distribution within granular materials subjected to a variety of load cases as either the average stresses shown in Fig. 2.3.23 (Wensrich *et al.*, 2012; Kisi *et al.*, 2014), or the stress tensor in individual particles throughout a granular material bed. The latter provides insight into inhomogeneous stress distributions such as force chains (Wensrich *et al.*, 2014). The device that was used in these studies (Fig. 2.3.28) is a self-loading die within which a granular material is compacted while diffraction studies are conducted.

2.3.6. Concluding remarks

Neutron powder diffraction is just one of many neutron-scattering techniques available; however, it is one that is very commonly used. In fact, the demand for this particular neutron technique is rivalled only by that for small-angle neutron scattering. The close analogy with X-ray powder diffraction makes the technique very familiar to many practitioners of that technique. The differences from X-rays are also critical (Sections 2.3.1 and 2.3.2), since these are the means by which neutron diffraction can obtain information not otherwise accessible. In this chapter we have included descriptions of the various types of neutron source, the neutron powder diffractometers installed at these sources, and a selection of routine and more specialized applications. Demand for the technique is expected to continue, buoyed by further developments in instrumentation and the exploration of new applications.

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