2. INSTRUMENTATION AND SAMPLE PREPARATION

(ii) *Crystallite perfection.* For crystal-structure studies, it is preferred that the crystallites in the sample be as near perfect[19] 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

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[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).

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.
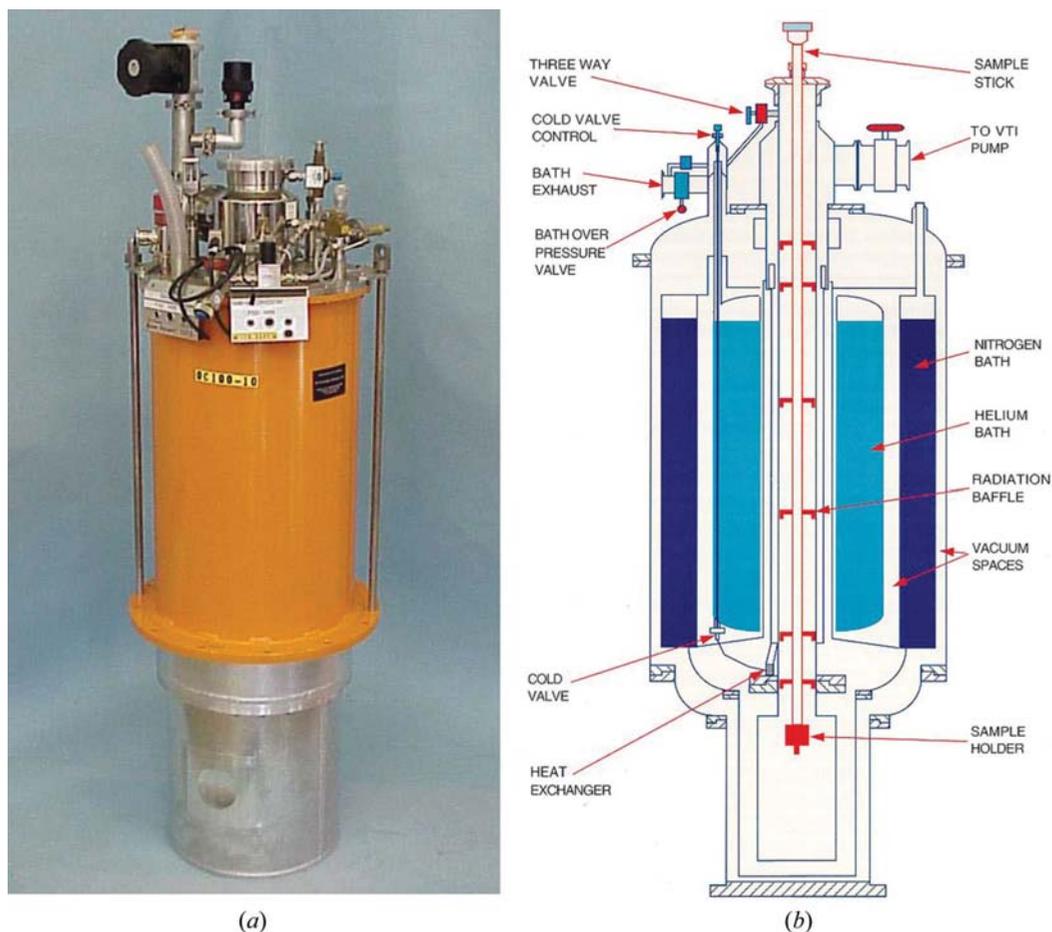
2.3.5.3.2. *Non-ambient temperature*

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 nitrogen tanks into the 'tails', which are thin-walled Al or V

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 ~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).
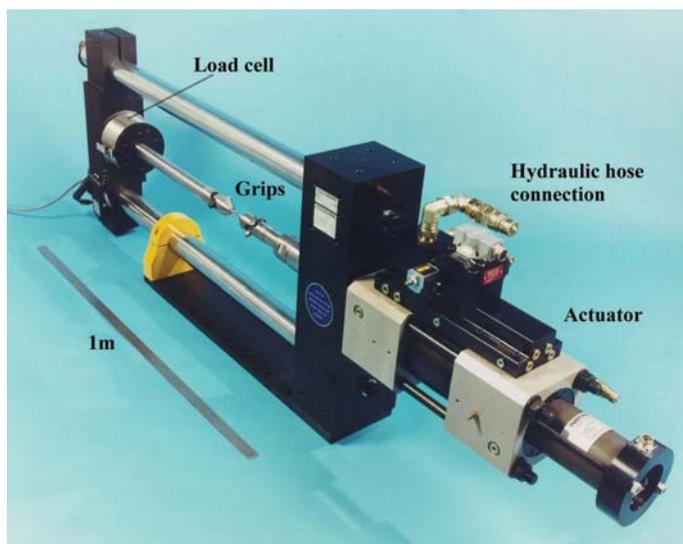
Figure 2.3.27
Elements of a typical mechanical testing machine used for applying uniaxial stress (pressure) to samples on an engineering neutron diffractometer. This example of a 100 kN device is from the instrument ENGIN-X at the ISIS facility, UK. (Credit: STFC.)
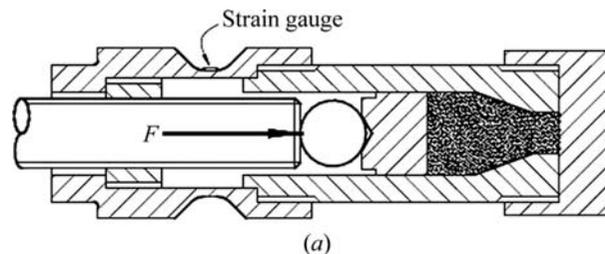

Figure 2.3.28
(*a*) Cross section and (*b*) exterior of a self-loading die for the study of stresses in granular materials.

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.
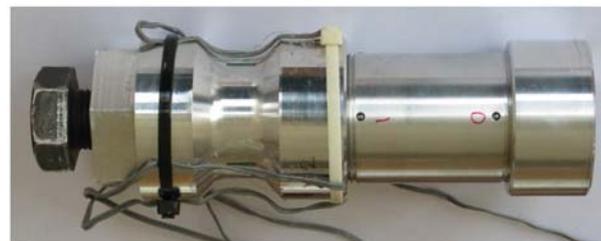
2.3.5.3.3. *Uniaxial stress*

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 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.