2. INSTRUMENTATION AND SAMPLE PREPARATION
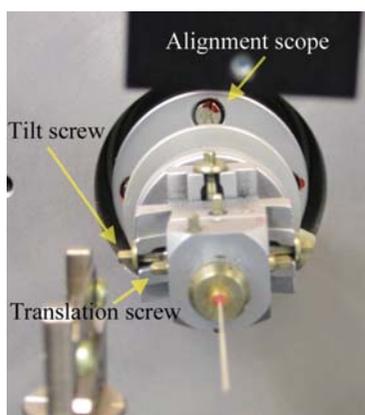

Figure 2.10.49
Goniometer head position in relation to the goniometer-mounted alignment scope.

movement rather than any wobble from tilt misalignment. However, it can still take some time. For systems where the goniometer spinning is controlled by computer software a wireless computer mouse is a very good investment, as it allows the person performing the alignment to stop the spinning capillary without taking their eyes off the sample.

2.10.2. Neutron powder diffraction

2.10.2.1. *Specimen form*

Large penetration depth and sensitivity to lighter elements (especially mobile species such as hydrogen, lithium and oxygen) in the presence of heavier elements make neutron diffraction a powerful and complementary technique to X-ray diffraction for structural studies. Because neutrons are highly penetrating and large sample volumes can be used, sometimes no specimen preparation is needed at all; sintered ceramic pellets, fish otoliths and renal calculi can be placed directly in the beam. However, the most traditional sample holder for standard neutron powder diffraction (Debye–Scherrer geometry) is cylindrical and is usually made of vanadium. If the diffraction instrument has reflection geometry, however, one has to use flat plates. Diffractometers built for the study of engineering materials can accommodate various shapes and forms because they can isolate small volumes within the sample.

2.10.2.2. *Sample size*

Traditionally, a large amount of sample was needed for neutron powder diffraction because of the limited flux available at various neutron sources. However, significant advances have been made in source power and detector technology, making it possible to do standard diffraction experiments with relatively small quantities of samples, both at reactor and spallation sources. There are multiple factors that have to be taken into account to determine how much sample is required. These include source power, detector coverage of the instrument, source-to-sample distance, the scattering power of the sample, beam size, available time and information sought from the measurement. Neutron powder diffraction instruments often have to trade intensity for resolution, and so often a larger quantity of sample is needed for high-resolution instruments. Sample mass can vary from milligrammes to several grammes, so it is always advisable to contact the scientists responsible for the particular instrument to determine the quantity needed for the proposed measurements.

(a)

(b)

Figure 2.10.50
Two examples of sample holders used in neutron powder diffraction. (*a*) A cell made of Inconel used for hydrogen absorption studies in Li$_3$N (Huq *et al.*, 2007). (*b*) Vanadium holders that were specially made for a sample changer built for the Powgen diffractometer located at Oak Ridge National Laboratory.

2.10.2.3. *Specimen containment*

The choice of materials for designing sample holders usually depends on the type of experiments, temperature or pressure conditions, the type of neutron source (constant-wavelength or time-of-flight), the presence or absence of fine radial collimators in the instrument and finally the sample. The scattering of vanadium (σ_{coh} = 0.0184 b) or a TiZr alloy (a null scatterer, because of exact matching of the negative scattering length of titanium and the positive scattering length of zirconium) is almost purely incoherent, making it ideal for sample containment for diffraction measurements. Although the coherent scattering of vanadium is small, in careful work it should not be a surprise to find weak peaks from V (space group $Im\bar{3}m$, a = 3.027 Å) in the powder pattern. Examples of vanadium sample cans are shown in Fig. 2.10.50(*b*). At a reactor source aluminium is even better if low-angle (large *d*-spacing) reflections are of interest, as in the case of many magnetic structural studies, because the aluminium incoherent scattering cross section is three orders of magnitude less than that of vanadium. At elevated temperatures, vanadium easily forms oxides or hydrides in the presence of air or hydrogen, making the cell brittle, so its use is limited to low-temperature studies or in vacuum furnaces. At temperatures higher than 1273 K one often has to use boron nitride caps and molybdenum screws for vanadium sample holders to avoid eutectic formation (an example is shown in Fig. 2.10.51*b*). For

(a)

(b)

Figure 2.10.51
Two sample holders used for high-temperature studies. (*a*) A cell made of quartz with frits at the bottom to allow gas flow through the sample. (*b*) A holder on the right made of vanadium but using a boron nitride top with molybdenum bolt, nuts and washers to avoid melting due to eutectic formation. The fitting on the far left, which is made of stainless steel, is used to attach the boron nitride cap to the stick.
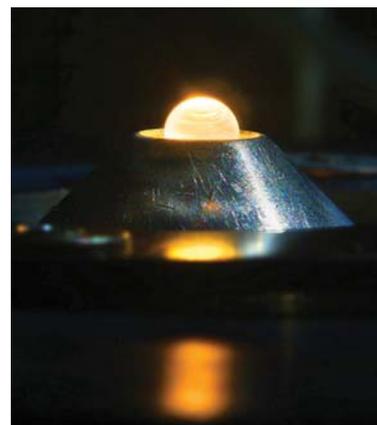
samples that react with vanadium, a thin layer of a noble metal such as gold can be vacuum deposited inside a vanadium can to stop it from reacting with the sample (Turner *et al.*, 1999). If this approach is used, it should be remembered that the melting point of gold is 1337 K, and when it is irradiated by neutrons it becomes activated with a half-life of 2.7 days. For experiments requiring hydrogen pressure at elevated temperature, Inconel (Fig. 2.10.50*a*) is often the material of choice (Bailey *et al.*, 2004). However, in this case for diffraction measurements one has to either exclude the Inconel peaks or make use of radial collimators to reduce the signal from the vessel itself. In spallation sources with large detector area coverage one can also do an experiment where only detectors at a scattering angle of 90° are used. For gas-absorption experiments at low temperatures, however, vanadium is still the material of choice. For pressure measurement in anvil-type cells, TiZr is used for the gasket.

For opposed-anvil pressure experiments the anvil materials can be either cubic tungsten carbide or boron nitride. The latter is preferred as boron is highly absorbing and does not contribute anvil reflections to the sample measurement, so therefore effectively works as an incident-beam collimator. The use of tungsten carbide is reserved for techniques where a 'through-gasket' approach is required, such as furnace measurements with a graphite heater where the use of a null scattering alloy as a gasket material is not possible. A recent development in high-pressure neutron scattering is the use of sintered diamond anvils, also called PCDs (from polycrystalline diamond). They allow the accessible pressure range to be doubled at the cost of adding very strong diamond reflections to the pattern.

However, for gas pressure cells aluminium is often used, as it can withstand higher pressure and Al absorbs neutrons only weakly as the absorption cross section of aluminium, σ_{abs} = 0.231 b for a wavelength of 1.8 Å, is small. For high-temperature gas-flow experiments fused silica ('quartz') glass is generally used for sample containment. These holders can also have glass frits attached at one or both ends for easy flow of gas through the sample, as shown in Fig. 2.10.51(*a*).

Figure 2.10.52
Aerodynamic levitation system to suspend melts at temperatures to 2773 K and beyond for neutron diffraction measurements.

A few very high intensity instruments are now able to carry out powder diffraction from milligramme quantities of sample. For these measurements vanadium cans produce too much background, as there is more vanadium in the beam than the sample. The use of thin-walled silica/glass or Kapton capillaries maybe more appropriate in those circumstances.

It is also important to remember that an exchange medium is used for low-temperature (heat transfer) and pressure (pressure transfer) measurements. Helium gas is generally used as a low-temperature exchange medium. Typically, cans are sealed with a flange and lid that supports an indium (or other soft metal) gasket. If the sample is air sensitive and has to be loaded in a glove box, one should try to use a helium-filled glove box. Argon- or nitrogen-filled glove boxes are more common but the freezing temperatures of argon and nitrogen are 84 K and 77 K, respectively. They will no longer work as exchange gases below these temperatures and, because of their rather large neutron-scattering lengths, new diffraction peaks will emerge at or below these temperatures. Similarly one should ensure that a pressure medium will remain hydrostatic for the pressure range for which it is being considered (Varga *et al.*, 2003).

It is also worth noting that cooling powder samples below 1 K relies entirely on thermal conduction through the walls of the sample holder and to the specimen itself. If great care is not taken, the specimen temperature may be far higher than that reported by a thermometer attached to the sample holder. At a minimum, the holder lid should be made from copper, as it is expected that the superconducting transitions in aluminium and vanadium would cause the walls of the sample holder to become thermally insulating and greatly reduce their ability to cool the sample. Of course, properly sealing the loose powder under an atmosphere of ^{4}He is equally important. It is essential that the indium seal be installed correctly, as ^{4}He undergoes a transition to a superfluid at 2.17 K and has effectively zero viscosity, and can easily escape from a poorly sealed can.

Levitation methods (*e.g.* gas flow, acoustic, electrostatic) as shown in Fig. 2.10.52 offer a containerless method, which eliminates altogether sample–container reaction problems and diffraction or additional background scattering from a sample container (Weber *et al.*, 2014). Levitated samples are typically used in conjunction with laser heating to achieve high temperatures, *in situ* melting of samples and prevention of heterogeneous nucleation.
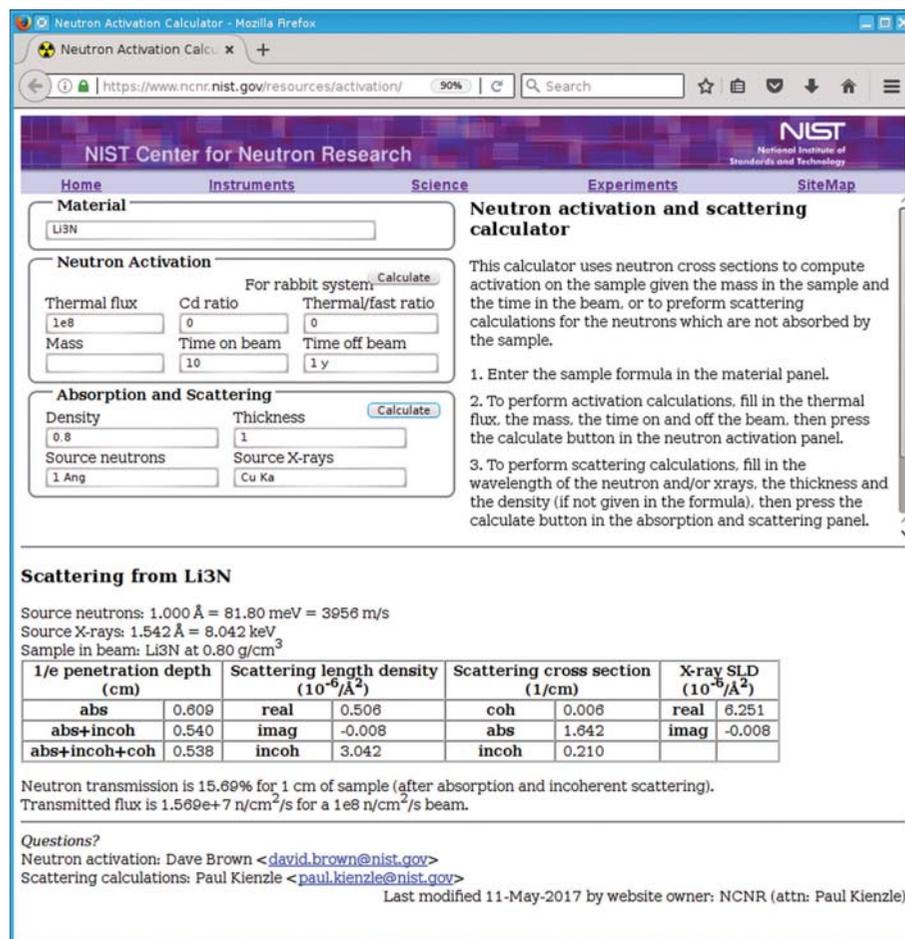
Figure 2.10.53
Calculation of the penetration of neutrons into Li_3N using the online tool at https://www.ncnr.nist.gov/resources/activation/.

2.10.2.4. *Isotopes, absorption and activation*

There are usually multiple sizes of vanadium cans available, the most common sizes being 6, 8 and 10 mm diameter. The choice of can depends on the quantity of sample available and the nature of the elements. Some elements such as cadmium, gadolinium and boron have extremely large absorption for neutrons and may not be feasible for measurements. Some elements have high absorption for the naturally occurring isotope mixes, but by choosing an alternative isotope one can often reduce or eliminate the absorption problem completely. For example, natural lithium is mostly ^7Li and has an absorption cross section of 70.5 b. However, pure ^7Li has an absorption cross section of 0.0454 b. The difference is due to the small amount of highly absorbing ^6Li (absorption cross section = 940 b) present in naturally occurring lithium. With commercially sourced lithium salts it is not always safe to assume a natural abundance of lithium isotopes. ^6Li is used in the production of tritium and, depending on their history, commercial lithium salts may be deficient in ^6Li. Given the significantly different scattering lengths of ^6Li and ^7Li, this can have serious consequences for a structure refinement, so it may be necessary to perform an isotopic analysis to verify the ^6Li:^7Li ratio. The various neutron scattering cross sections are available on the NIST website http://www.ncnr.nist.gov/resources/n-lengths/ and in Table 4.4.4.1 in *International Tables for Crystallography* Volume C (2006). If the sample contains any element with a large absorption and is not isotopically substituted, it is prudent to calculate by how much the neutrons will penetrate the sample. Tools are available at the NIST website http://www.ncnr.nist.gov/resources/activation/ to carry out this calculation. The input information is the composition of the compound, the density (generally a 50% packing fraction and hence $\frac{1}{2}$ of the calculated density is a good approximation for planning purposes) and the wavelength of the neutrons used. Fig. 2.10.53 shows a calculation for Li_3N. Natural lithium has a quite large absorption, but in this case 1 Å neutrons will penetrate through 5 mm and so the use of a 6-mm diameter can is appropriate.

However, if the penetration depth $1/e$ is 1–2 mm, one has to reconsider the choice of sample holder. For a high-intensity beamline capillaries can be considered. The other option is to use an annular holder made using co-axial, thin-walled vanadium or aluminium cylinders, or flat-plate mounts based on aluminium foils where the total depth of the sample is approximately the calculated $1/e$. Perhaps the best way to maximize the transmission and improve the signal-to-noise ratio is to use silicon flat-wafer sample holders. When loading a can it is also important to record the weight and height of the sample in the can so that the absorption correction for the sample can be calculated. Alternatively, the neutron transmission through the sample can be measured using a pinhole mask and a detector downstream from the sample.

One of the other factors to keep in mind for neutron sample preparation is that hydrogen is a very special element in terms of its interaction with neutrons. Hydrogen has a very large incoherent scattering cross section (σ_{inc}) of 80.26 b, while its coherent cross section (σ_{coh}) is 1.758 b. In comparison, for deuterium $\sigma_{inc} = 2.05$ b and $\sigma_{coh} = 5.59$ b. If the scattering nuclei contain a mixture of isotopes or have a non-zero nuclear spin, the neutron scat-

tering length consists of a coherent component, which is the average over all spins, and an incoherent part, which gives the deviation from this average value. In other words, coherent scattering describes interference between waves produced by the scattering of a single neutron from all the neutrons in the nuclei of the sample. On the other hand, incoherent scattering involves correlations between the position of an atom j at time zero and the position of the same atom at time t, and so the scattered waves from different nuclei no longer interfere. Thus incoherent scattering provides an excellent tool for studying processes involving atomic diffusion, but produces large backgrounds for diffraction experiments. Based on the available flux at the instrument of choice and the atom% hydrogen present in the sample, complete or partial deuteration of the sample may be necessary.

When illuminated by a neutron beam, some nuclei are converted into other radioactive nuclei (activated). Thus it may not be possible to return the specimen to the home laboratory, but it may have to be treated as radioactive waste. A sample-activation calculator is also available at http://www.ncnr.nist.gov/resources/activation/.

2.10.3. Conclusions

Powder diffraction as a technique encompasses a wide range of possible experimental setups. Diverse though they are, specimen-preparation methods are a key component in obtaining the best possible data for the best possible analysis. Many issues are common whether X-rays or neutrons are the probe of choice (*e.g.* particle statistics, preferred orientation), but neutrons do pose some unique issues such as sample activation and isotope-dependent scattering behaviour. Given that X-ray and neutron diffraction are frequently used in a joint analysis, some forethought may be required if the desired situation of the same sample being used for both is to be achieved.

For the common laboratory setups a recurring theme should be apparent through this overview – specimens should ideally have crystallite sizes of the order of a few µm. If this is the case, then many of the issues mentioned (particle statistics, preferred orientation, extinction) will either disappear or be significantly reduced. The same is true for microabsorption, except in this case it is particle as opposed to crystallite sizes that are the issue. Grinding or milling can easily reduce crystallite size to this range, but the milling action should be chosen so as to avoid damaging the crystal structure of the sample or possibly amorphizing it completely.

Ideally, the in-house laboratory should have the flexibility to tailor the experiment to the sample, using transmission or reflection geometry depending on the nature of the sample. Unfortunately, in many instances this is not possible. 'Coping strategies' for non-ideal samples such as diluting samples in capillaries or using very thin organic specimens on flat plates are available, but their limitations and compromises should be understood by the person receiving the data.

In many instances, the experimental configuration at a central facility, such as a synchrotron or neutron source, can be customized for a particular experiment. However, the need for high throughput for rapid-access mail-in services may dictate a more standardized setup.

In summary, specimen preparation is the foundation upon which powder diffraction measurements are built. Good specimen preparation will not guarantee excellent data, but poor preparation can pretty much guarantee poor data.

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