range of Q, ω to cover a whole plane of reciprocal space over a wide range of energies. Phased chopper instruments on both reactor and pulsed sources are ideal for this task. 50 counter angles may be usefully employed together with say 100 useful resolution elements along the time-of-flight scan. This gives them significant advantages over any of the crystal analyser instruments. The phased rotor sees the "peak" rather than "mean" flux giving the pulsed source instrument the edge over the reactor instrument.

These comparisons are collected together in table 8.1. The triple axis on the new reactor is pre-eminent for localised (Q, ω) or constant Q scans. The MAX looks very promising on either source for (Q, ω) scans along a defined direction. The pulsed source rotor instrument is pre-eminent for broad (Q, ω) scans.

The group concluded that the challenging experiments in the field of excitations required the ability to focus on particular Q and ω, with flexible resolution and focusing given by the triple axis spectrometer at the steady state source.

9. Crystallography (powder)

Reported by: J.D. Jorgensen (Chairman) Argonne National Laboratory
D.E. Cox Brookhaven National Laboratory
A.W. Hewat Institut Laue-Langevin, France
W.B. Yelon University of Missouri

The use of neutron powder diffraction for both basic and applied research has increased dramatically over the last decade. This renewed interest in powder diffraction is the result of the design and construction of high-resolution, high-intensity powder diffractometers [16,17] and the development of data analysis methods, such as Rietveld structural refinement [18,19], which allow precise structural information to be obtained from powder data. The new high flux sources (i.e., a 10^{16} n cm^{-2} s^{-1} reactor or a 10^{17} n cm^{-2} s^{-1} peak flux pulsed source) will allow powder diffractometer performance to be even further extended and will open some new scientific areas. At these flux levels, the resolution of neutron powder diffractometers is expected to reach $\Delta d/d = 3 \times 10^{-4}$. This is comparable to high resolution X-ray diffractometers including those currently being tested at synchrotron light sources. Additionally, the neutron diffraction method offers the natural advantages of well-defined instrumental line shapes, constant scattering cross sections (no form-factor), penetrating power, and relative freedom from texture and preferred orientation which are often associated with small X-ray samples. Thus, neutron powder diffraction is expected to be the preferred method for many kinds of problems.

Based on current experience and the projected performance of future instruments, neutron powder diffraction is expected to play a major role in four general scientific areas over the next decade:

9.1.1. Structure solution and refinement

Materials which cannot be prepared as single crystals are a growing proportion of all materials studied by neutron crystallography. Examples are catalysts, superconductors, fast ion conductors and materials which crystallize only under special conditions of low temperature, high pressure, sublimation, sputtering, solid state reactions, etc. In some cases, the material may be impossible to prepare as a single crystal; in other cases a single crystal is not what is wanted – the structural properties of the as-formed, "real", material are the subject of investigation.

To date, neutron powder diffraction has been mainly used to refine models of the crystal structure. Current state-of-the-art instrumentation allows reliable refinements for systems up to about 100 structural parameters. However, the eventual goal is not only to refine more complex structures, but to directly solve structures using powder data alone. In both cases, diffractometers of higher resolution are needed.

Presently operating instruments, such as D1A at the ILL [16] or the GPPD at IPNS provide resolution on the order of $\Delta d/d = 2 \times 10^{-3}$. New instruments which will soon begin operation at existing sources, D2B at the ILL and HRPD at SNS, will achieve $\Delta d/d = 5 \times 10^{-4}$, illustrating that substantial gains can be obtained with sophisticated instrument designs on existing sources. The next order of magnitude of neutron flux is expected to allow diffractometers which achieve $\Delta d/d = 3 \times 10^{-4}$ or less, which should extend the number of structural parameters that can be refined from powder data to around 500.

9.1.2. Time-resolved studies

As data rates increase on neutron powder diffractometers, their use for the study of time-dependent phenomena, and the optimization of instruments for that purpose will undoubtedly increase. Important scientific application will include studies of chemical reaction kinetics, intermediate species, rapid phase equilibria, identification of new unstable compounds, in situ

studies of sputtering and chemical vapor deposition, crystallization and grain growth, annealing, precipitation, order–disorder kinetics, diffusion at solid interfaces and hydration–dehydration kinetics. Periodically induced transient phenomena such as magnetic relaxation or response to other external stimuli can also be studied by time-slicing the data collection in phase with the applied field.

Only a small number of presently-operating instruments are optimized for time-resolved measurements. The area detector diffractometer, D1B, at the ILL can collect complete data in 1–10 min at about 1% resolution in favorable cases and has been used to study chemical reactions, phase transformation kinetics and crystallization processes. A new ILL area detector diffractometer, D20, with a factor of 50 increase in the flux on the sample and twice the detector area will soon be operational, achieving a data rate increase of two orders of magnitude. Future instruments at the SNS and higher flux sources will further increase data rates by an additional one to two orders of magnitude reducing data collection times to 10^{-1}–10^{-2} s for instrumental resolutions around 1%.

9.1.3. Small samples

In addition to time-resolved studies, the future high-data rate instruments will find wide application for the study of small samples or samples in environments where the sample volume accessible to neutrons is small. With future instruments, it should be possible to perform high resolution diffraction measurements on samples as small as 1 mg. This will make possible the study of samples which can be produced only in small quantities by techniques such as chemical vapor deposition or sputtering. Compounds which contain exotic or very expensive elements (e.g., transuranics) or particular isotopes which are available in very limited quantities will also become possible to study. Very small samples can also be used to overcome the problems of doing diffraction studies of compounds containing elements with high neutron absorption cross sections (e.g., Gd, Dy, Cd, Eu).

Special sample environments sometimes impose a severe restriction on the volume of sample accessible to the incident and scattered neutron beams. For example, in the area of high pressure diffraction, the sample volume decreases markedly upon going to higher pressure regimes, the present experimental extreme being pressures in the Mbar range for samples of dimensions 100 μm or less in diamond anvil cells. Higher neutron flux will make possible neutron diffraction in multiple anvil (cubic) presses, to about 100 kbar, for effective sample volumes of about 0.01 cm^3 and possibly even opposed anvil designs, similar to diamond anvil cells, at pressures to a few hundred kbar.

9.1.4. Applied materials science – mechanical properties

The neutron has significant advantages as a probe of the mechanical/metallurgical properties of many systems because of its high penetrating power compared to X-rays. Recent applications have concentrated on measurements of texture and residual or applied stress. These measurements require both high resolution and high intensity. High resolution is required to extract the needed information from small shifts in Bragg peak positions and shapes. High intensity is required to allow focusing the probe on a localized region of a bulk sample. With future instrumentation it should be possible to reduce the probed volume to about 1 mm^3 while maintaining sufficiently high resolution for a precise determination of the strain tensor.

9.2. Steady state vs. pulsed sources

Sufficient experience has been gained at existing sources to make some meaningful comparisons between powder diffraction instruments on steady state and pulsed sources and to quantitatively project the performance of future instruments. A valuable figure of merit for comparing instruments is the product of the flux at the sample position, the maximum sample volume (allowed by resolution and focusing restrictions) and the total detector solid angle at a given resolution. In making this comparison it must be noted that the resolution of a constant wavelength diffractometer is a function of the scattering angle, 2θ, while the pulsed source time-of-flight instruments typically have almost constant resolution at a given, fixed scattering angle. This distinction will become less meaningful as future TOF instruments are designed to optimally exploit multiple scattering angles for collecting complete data. Additionally, some present TOF designs do not effectively use all of the time-averaged neutron flux incident on the sample, the short wavelengths neutrons often provide no useful data. Again, future moderator designs and the use of guide tubes will result in instruments which use essentially all of the flux on the sample.

Taking these factors into consideration, future pulsed source and steady state powder diffraction instruments are expected to be nominally equivalent for most experimental applications, e.g., general structure solution and refinement, where high resolution is needed, and time-resolved and small sample experiments, where high data rate instruments are needed. The time-of-flight technique offers a clear advantage where a fixed scattering angle must be used, such as for highly restricted sample environments and also may offer some advantage for refinement of structures where the data can be extended to high-Q, thus taking advantage of the large short-wavelength neutron flux available at the pulsed sources.