

2.2. SYNCHROTRON RADIATION

to a poor statistical average of grain orientations and a spotty diffraction pattern.

2.2.5.7. Time resolution

The high flux allows powder-diffraction patterns to be measured quickly, opening up the possibilities for time-resolved studies, following the evolution of samples on a timescale, if appropriate, down to milliseconds, *e.g.* to investigate the kinetics and the mechanism of a phase transition caused by a change of the temperature, pressure or other external condition, or a chemical reaction taking place in the sample, such as self-propagating combustion synthesis (Labiche *et al.*, 2007). Many instruments allow great flexibility in the design of experiments to study systems *in situ*, helped by the availability of hard radiation to penetrate through sample environments and reduce the angular range that must be accessed to measure enough diffraction peaks to yield the desired information.

2.2.5.7.1. Using fast detectors

Scanning a detector through the *d*-spacing range of interest necessarily takes a few seconds, so is too slow to measure the fastest processes. Thus, for speed, a multichannel detector system is required that acquires the full diffraction pattern synchronously and that can be read out rapidly, such as *via* a fast PSD or using the energy-dispersive approach. Many different types of detector systems have been exploited for fast powder-diffraction studies using the monochromatic Debye–Scherrer configuration (Section 2.2.4.2), including 1D photodiode arrays (Pennartz *et al.*, 1992; Wong *et al.*, 2006; Palmer *et al.*, 2004), the Mythen curved 1D PSD (Fadenberger *et al.*, 2010), pixel detectors (Yonemura *et al.*, 2006; Terasaki & Komizo, 2011), CCD-based detectors (Malard *et al.*, 2011; Elmer *et al.*, 2007), and medical-imaging detectors (Chupas, Chapman, Jennings *et al.*, 2007; Newton *et al.*, 2010). The former of these last two studies shows that these large detectors working at hard X-ray energies above 60 keV register a wide enough *Q* range in a single cycle to allow PDF analysis to be made, thus allowing the conduct of time-resolved PDF analysis of, for example, catalytic systems composed of evolving nanoparticles. For the latter study, the diffraction measurements were combined with simultaneous monitoring of the reacting system with the acquisition of complementary mass and diffuse reflectance infrared Fourier transform spectra (DRIFTS).

2.2.5.7.2. Using the pulse structure

For investigating very fast, reversible processes, use can be made of the bunch structure of the synchrotron source and the stroboscopic measurement approach. The time for an orbit of an electron circulating in a synchrotron is (circumference/*c*) s. For a synchrotron such as at the ESRF (with a circumference of 844.4 m), this corresponds to 2.82 μ s (*i.e.* a frequency of 355036 Hz). Thus when operating with 16 electron bunches distributed evenly around the ring, there is a burst of X-rays delivered to a beamline every 176 ns, and because of the longitudinal dimension of the electron bunch (\sim 20 mm), each burst lasts \sim 70 ps. Such a pulsed source can be used in pump–probe powder-diffraction experiments, whereby a sample is excited by a short laser pulse (\sim 100 fs duration) then probed by the X-ray beam a chosen delay time later. The scattered X-rays are recorded with a suitable (probably 2D) detector and the process is repeated, with the statistical quality of the diffraction pattern building up over a number of cycles, after which the detector is read out. A high-speed chopper in the X-ray beam can be used to

select the pulse frequency desired for any particular set of measurements. By varying the delay time the evolution of the sample as a function of time after the initial excitation can be investigated. The whole experiment needs fast, accurate electronics to correlate the timing of the firing of the laser, the arrival of the X-ray pulse and the phasing of the chopper.

Examples include the study of 4-(dimethylamino)benzotrile and 4-(diisopropylamino)benzotrile (Davaasambuu *et al.*, 2004; Techert & Zachariasse, 2004), whose fluorescence properties indicate that photoexcitation leads to the formation of an intramolecular charge-transfer state. Powder-diffraction patterns were collected over 10-minute periods at a frequency of 897 Hz at delay times ranging from -150 ps (as a reference before the laser excitation) to $+2500$ ps after excitation. Only about 5% of the molecules are excited by the laser, so the powder-diffraction pattern is from a sample containing both excited and ground-state molecules. Rietveld refinement of the structures from the diffraction patterns gave the fraction of excited molecules as a function of delay time, and the nature of the structural change induced by the photoexcitation. For the isopropyl analogue, an exponential relaxation time of 6.3 (\pm 2.8) ns was observed for the excited molecules (compared to 3.28 ns seen spectroscopically). The main distortion to the molecules was a change in the torsion angle between the diisopropylamino group and the benzene ring, from $13\text{--}14^\circ$ determined from the pre-excitation patterns (14.3° *via* single-crystal analysis) to 10 (\pm 1–2) $^\circ$.

2.2.5.8. Beamline evolution

A beamline at a synchrotron source will certainly evolve in its specifications and capabilities. Users and prospective users should follow updates on a facility's website, or contact the beamline staff, for information concerning possibilities for experiments.

References

- Als-Nielsen, J. & McMorrow, D. (2001). *Elements of Modern X-ray Physics*. New York: Wiley.
- Authier, A. (2006). *Dynamical theory of X-ray diffraction*. *International Tables for Crystallography*, Vol. B, *Reciprocal Space*, 1st online ed., ch. 5.1. Chester: International Union of Crystallography.
- Azároff, L. V. (1955). *Polarization correction for crystal-monochromatized X-radiation*. *Acta Cryst.* **8**, 701–704.
- Balzar, D. & Ledbetter, H. (1993). *Voigt-function modeling in Fourier analysis of size- and strain-broadened X-ray diffraction peaks*. *J. Appl. Cryst.* **26**, 97–103.
- Barnes, P., Jupe, A. C., Colston, S. L., Jacques, S. D., Grant, A., Rathbone, T., Miller, M., Clark, S. M. & Cernik, R. J. (1998). *A new three-angle energy-dispersive diffractometer*. *Nucl. Instrum. Methods Phys. Res. B*, **134**, 310–313.
- Beaumont, J. H. & Hart, M. (1974). *Multiple Bragg reflection monochromators for synchrotron X radiation*. *J. Phys. E Sci. Instrum.* **7**, 823–829.
- Bergamaschi, A., Cervellino, A., Dinapoli, R., Gozzo, F., Henrich, B., Johnson, I., Kraft, P., Mozzanica, A., Schmitt, B. & Shi, X. (2009). *Photon counting microstrip detector for time resolved powder diffraction experiments*. *Nucl. Instrum. Methods Phys. Res. A*, **604**, 136–139.
- Bergamaschi, A., Cervellino, A., Dinapoli, R., Gozzo, F., Henrich, B., Johnson, I., Kraft, P., Mozzanica, A., Schmitt, B. & Shi, X. (2010). *The MYTHEN detector for X-ray powder diffraction experiments at the Swiss Light Source*. *J. Synchrotron Rad.* **17**, 653–668.
- Bilderback, D. H. (1986). *The potential of cryogenic silicon and germanium X-ray monochromators for use with large synchrotron heat loads*. *Nucl. Instrum. Methods Phys. Res. A*, **246**, 434–436.
- Boccaleri, E., Carniato, F., Croce, G., Viterbo, D., van Beek, W., Emerich, H. & Milanese, M. (2007). *In situ simultaneous Raman/high-resolution X-ray powder diffraction study of transformations occurring in materials at non-ambient conditions*. *J. Appl. Cryst.* **40**, 684–693.