Developments in Synchrotron Instrumentation

A. Fitch
Synchrotron Radiation and Powder Diffraction

High intensity, collimation and $\lambda$ tunability

- High angular resolution, i.e. narrow peak widths;
- Rapid data collection / good statistics;
- Highly monochromatic X-rays, or energy dispersive;
- Narrow well defined intrinsic instrumental peak shape;
- Tunable: measure at absorption edges, or well away; optimise for the experiment.
Main technical developments since APD III

- Many new 3\textsuperscript{rd} generation synchrotrons with powder diffractometers
- Analyser stages, multi-analyser stages, and multi-multi-analyser stages
- Mythen curved 1d PSD
- Dedicated insertion device sources (e.g. undulators)
- Hard energy operation
- Large 2d on-line detectors
- Focussing by refractive lenses
- Robotic sample changers
- Self aligning capillary spinners
- Radiation damage
- Beam heating

- + Raman, etc.
- Energy dispersive
- Etc.
Diamond, 3 GeV

Petra, 6 GeV

Australian, 3 GeV

Shanghai, 3 GeV
Accurate data ⇒ use Analyser crystal(s)

Cox, Hastings, Thomlinson, Prewitt, Finger et al.

X16C at NSLS at BNL and CHESS.
XPD diffractometer at LNLS, Brazil
No misalignment aberration

Analyser crystal

Diffractometer axis

Detector

\[ \theta_{an} \]

\[ 2\theta \]
Analyser crystal

↓

narrow peaks (sample limited) and accurate peak positions

Stringently defines a true $2\theta$ angle rather than infers $2\theta$ from the position of a slit or pixel of a PSD.

- Peak positions insensitive to misalignment, transparency, specimen–size/shape/surface effects, etc.;
- widths independent of any $\theta/2\theta$ parafocusing condition;
- supresses fluorescence, Compton, parasitic scatter.
- but **SLOW** (scanning + very selective)
Nine channel multianalyser (MAC) stage

9 detectors

9 Si 111 analyser crystals

Sample

Thanks to J.-L. Hodeau, M. Anne, P. Bordet, A. Prat, CNRS, Grenoble
ID31 powder diffractometer, ESRF
$\Delta \theta \approx 2^\circ \ (\pm 0.1^\circ)$
LaHoSi$_2$O$_7$ (35 keV)

<table>
<thead>
<tr>
<th>$\Delta \theta$</th>
<th>efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.05456833</td>
<td>1.01541956</td>
</tr>
<tr>
<td>5.96777827</td>
<td>1.08103083</td>
</tr>
<tr>
<td>3.98748335</td>
<td>1.11437177</td>
</tr>
<tr>
<td>2.04993441</td>
<td>1.04004295</td>
</tr>
<tr>
<td>0.00000000</td>
<td>0.92708866</td>
</tr>
<tr>
<td>-1.91689474</td>
<td>0.77755602</td>
</tr>
<tr>
<td>-4.03848485</td>
<td>1.02894135</td>
</tr>
<tr>
<td>-5.97433687</td>
<td>1.01258377</td>
</tr>
<tr>
<td>-7.99777260</td>
<td>1.00296507</td>
</tr>
</tbody>
</table>

$\downarrow$

Variation affects hard-energy performance
Standard–Si 111 peak
\( \lambda = 0.395 \, \text{Å} \)
ID31 at ESRF
Beamline 11–BM at APS, 12 analyser crystals with individually adjustable $\theta$ and $\chi$
Beamline I11 at Diamond, 45 analyser crystals
Mythen curved 1d PSD

- Developed at the Swiss Light Source.
- Modular Si–strip photon–counting detector
- 1280 channels, 50µm step, unit ≈4.83°, (≈0.004° strip⁻¹)
- Read out ≈250 µs
- The best 1d PSD for soft and intermediate energies
- Excellent statistical quality in minutes or even seconds
- $10 - 10^2 \times$ faster than MAC

J. Synchr. Rad. 2010, 17, 653
Australian Slide: 17

Alba (Spain) Mythen and MAC detectors
I11 Diamond

Thompson et al., J. Sync. Rad. (2011)
Debye–Scherrer geometry so susceptible to aberrations.

- Beam spatially shifted with respect to the ideal beam path
  \[ \Rightarrow \text{aberration in } 2\theta \]
Ex-vacuum & in-vacuum undulators
ESRF (6 GeV) u35 undulator, 11 mm gap

Undulators have high vertical and horizontal collimation
Damping wiggler for NSLS-II PD beamline (2014)
Hard energy operation

- “Hard energy” $\geq 30$ keV; $\lambda < 0.41$ Å
- Manageable absorption for all capillary samples
- Adjust capillary diameter ($2r$) so that $\mu r < 1.5$
Capillary: scattered intensity vs $\mu r$

Sample volume increases with $\pi r^2$.

Absorption increases with $e^{-2\mu r}$.
Hard energy operation

- Spinning capillary $\Rightarrow$ fewer problems with preferred orientation so accurate intensities
- Capillary perfect for multi-analyser stage
- Reduced radiation damage?
- PDF measurements
- Access useful K edges
- Less far to scan for a $Q$ range
- Obtain full $Q$ range in one shot with large 2d detector and $\geq 60$ keV (e.g. fast-PDF)
- Downside: peaks are at lower angle $\Rightarrow$ more asymmetry (unless using 2d detector)
2D detectors

ESRF designed and constructed Frelon (Fast Readout Low Noise) camera
ID11 ESRF

E = 42 keV
Medical imaging pixel detectors

41× 41 cm²
200 μm pixel
Readout 15 - 30 Hz

GE Healthcare detector (11-ID-B/C)

Perkin-Elmer
(PETRA-III
11-ID-B/C)
Based on amorphous Si + CsI(Tl) scintillator

- Scintillator
  - Absorbs x-rays and converts to light

- Imager Panel
  - Millions of transistors and diodes
  - Turns light into electrical signal

- Motherboard
  - Control & Communication

- Readout Electronics

- Cover & Seal
Rapid (30 Hz) PDF analysis nano-PtO$_2$→Pt

Flat panel detector

P02.1 Petra

multi-analyser
NSLS–II future powder station

3-circle diffractometer
2d flat panel detector
Si-based pixel detectors (structural biology)

Dectris 2M detector
BM01A (SNBL) ESRF

Bending magnet beamline
Study of PbS nanoparticles grown in annealed silicate glass
Kapton + annealed glass

Kapton + raw glass

kapton
<table>
<thead>
<tr>
<th></th>
<th>a (Å) expected</th>
<th>a (Å) fitted</th>
<th>Crystal size (nm) (Lorentzian shape)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>4.9506</td>
<td>4.951( )</td>
<td>39.8</td>
</tr>
<tr>
<td>PbS</td>
<td>5.9315</td>
<td>5.9315 (fixed)</td>
<td>3.2</td>
</tr>
</tbody>
</table>

H.B. Stanley *et al.*
SAXS
Two log-normal sphere distributions
N=.002 R1=21.2 nm  s=.077
N=12.4 R2=1.0 nm  s=0.34
Focussing

- Best resolution with a 1d or 2d PSD is obtained by focussing the beam onto the detector
- Traditionally via a curved metal–coated mirror (set at grazing incidence)
- With an undulator, refractive lenses can be employed because the high horizontal collimation directs much of the beam into the lens’s limited aperture.
Life at the beamline

• Synchrotron experiments are (often) hard work
• Many samples, quick scans, varying sample conditions, long days and longer nights
• Need to minimise human intervention; maximise automation
• To collect accurate data fit for purpose requires keeping on top of things

• 1) Use the 11–BM mail-in service and let an expert–designed system run it
• 2) Robotic sample changers
• 3) Auto aligning capillaries
ID31’s robotic sample changer

Robots also at 11–BM; Swiss Light Source; I11
45 capillaries filled and ready to run
Auto capillary spinner alignment

Precision hole to fit capillary

Good enough for analyser crystal

Video-controlled goniometer head at Australian synchrotron; excellent alignment essential for Mythen or other PSD.
I11: Automatic capillary filler; “48 capillaries in 30 mins”

Radiation damage

- High photon densities (ID31 has $\approx 1.5 \times 10^{12} \text{ mm}^{-2} \text{ s}^{-1}$) at 31 keV
- Even greater flux at softer energies where absorption is also higher
- Loss of peak intensity, peak broadening, and anisotropic shifts in positions
- Really complicates things
Radiation Damage
(certain organics, proteins, organometallics)
Automatic sample translation between scans to expose fresh sample to the beam.

[Image of a sample translation mechanism with a 10 mm measurement]
Anisotropic peak shifts can use useful

- because they change the degree of overlap between reflections increasing the overall information content, (c.f. anisotropic thermal expansion, Shankland et al. 1997)

- Exploited by Margiolaki et al., e.g. in solving and refining SH3 domain of protein “Ponsin”
Ponsin: variation of lattice parameters with exposure

Degree of “completeness” with increasing number of datasets
The crystal structure has the space group $P 2_1 2_1 2_1$ with the following lattice parameters:

- $a = 24.7066(4)$ Å
- $b = 36.4304(6)$ Å
- $c = 72.1058(10)$ Å
Beam heating

- This can be a problem at low temperature

- Consider a 31 keV beam with $10^{12}$ photons mm$^{-2}$ s$^{-1}$
- $\mu$ for Si = 0.31 mm$^{-1}$ (so normally we’d ignore it)
- A 1$\mu$m$^3$ cube intercepts $10^6$ photons and absorbs 310 s$^{-1}$
- Absorbed power = $1.54 \times 10^{-12}$ W
- Mass of Si cube = $2.33 \times 10^{-15}$ kg
- Specific heat capacities: 300 K = 704.6 J kg$^{-1}$ K$^{-1}$
  10 K = 0.3 J kg$^{-1}$ K$^{-1}$
- Heating rate: 300 K = 0.9 K s$^{-1}$
  10 K = 2200 K s$^{-1}$
• Obviously absurd prediction!
• Some energy is lost by re-emission (20%)
• and by the gas surrounding the grains transporting heat to the capillary walls.

**PROBLEM**

• Seal your capillary under air, N$_2$, Ar, etc, these solidify below $\approx 50$ K leaving a vacuum in the capillary.
• On ID31 we have seen diffraction patterns from sealed capillaries behave wholly unpredictably at low temperatures; weird peak shifts; broadening, irreproducible behaviour.

**SOLUTION**

• Seal capillaries under He, or leave unsealed to allow entry of He exchange gas in the cryostat
ID31 is moving in late 2013 to ID22

- Reduced horizontal divergence ⇒ more photons on the sample
- In-vacuum undulator ⇒ more flux at 30 – 40 keV; increase upper energy range from 63 keV (now) to 80 keV (90 keV ??)
  - improved data for absorbing samples, PDF analysis, studies at lanthanide K edges (e.g. for lanthanide glasses), strain mapping, etc.
  - penetration into steels (as well as Ti and Al), dense ceramics, etc.
New high resolution powder diffractometer

Strain diffractometer

2d detector
Summary

• Explosion of new facilities and beamlines, offering high resolution and accuracy via multianalyser stages;
• very fast acquisition / excellent statistics via Mythen or 2d detectors;
• Some of the latest machines offer both capabilities.
• Experiments are done with intermediate or hard energies ($\lambda \leq 1$ Å, $\lambda \leq 0.41$ Å) exploiting insertion device sources where possible.
• Watch out for radiation damage, and beam heating at low T.
• Don’t forget it’s only powder X–ray diffraction data (so don’t over–interpret in the analysis).