Diffraction from Crystalline* Materials

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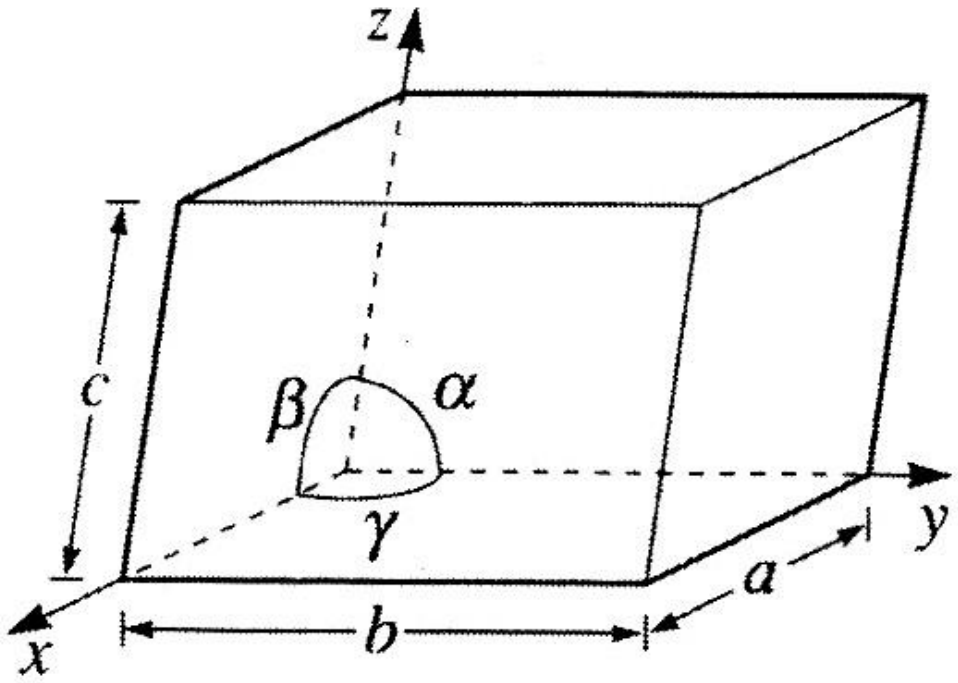
Outline

- Key concepts
- Instrumentation for neutron diffraction

- Extra information 1:Uses of diffraction
- Extra information 2: Structure solution & refinement
- Extra Information 3: Diffraction suites of ILL and ISIS

Key concept 1a: lattice & unit cell



The unit cell has lattice parameters defined by the cell length *a*, *b*, and *c*, and the cell angles α, β, and γ:
γ is angle between *a* and *b*
β is angle between *a* and *c*
α is angle between *b* and *c*

Atomic positions are given as xyz coordinates:
x is fraction of *a* axis
y is fraction of *b* axis
z is fraction of *c* axis

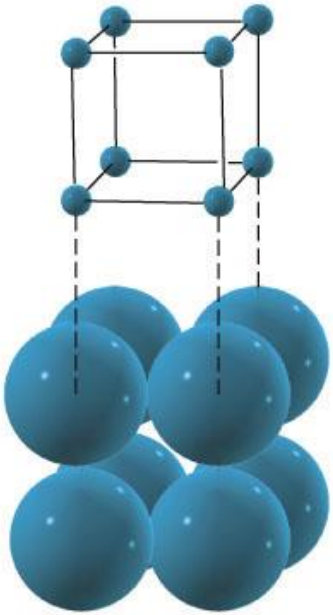
Conventions
- cell parameters are in Å or pm
- Angles are in °

Key concept 1b: crystal systems

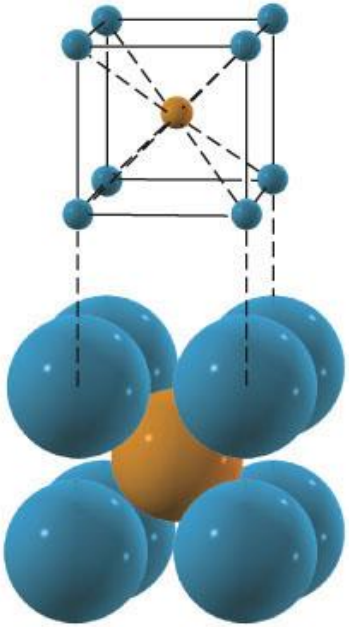
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90°$ $\beta \neq 90°$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°$ $\gamma = 120°$
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$

Key concept 1c: centring

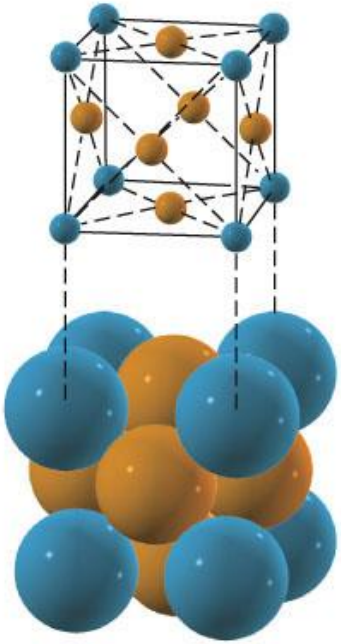
Primitive
P



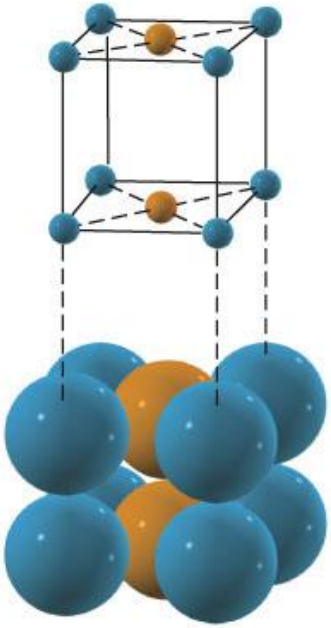
Body centred
I



Face centred
F

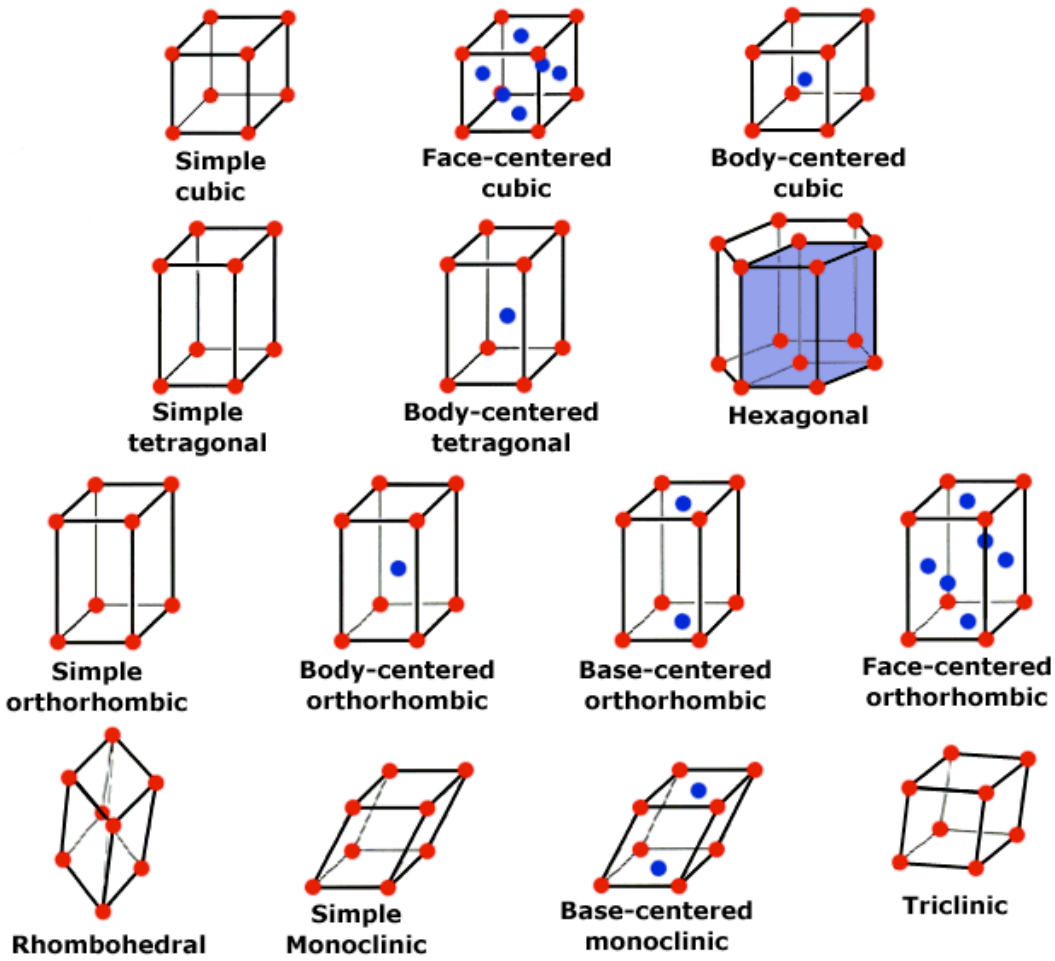


Side centred
C (A/B)



NB: Atom types are identical even though coloured differently

Key concept 1: Summary



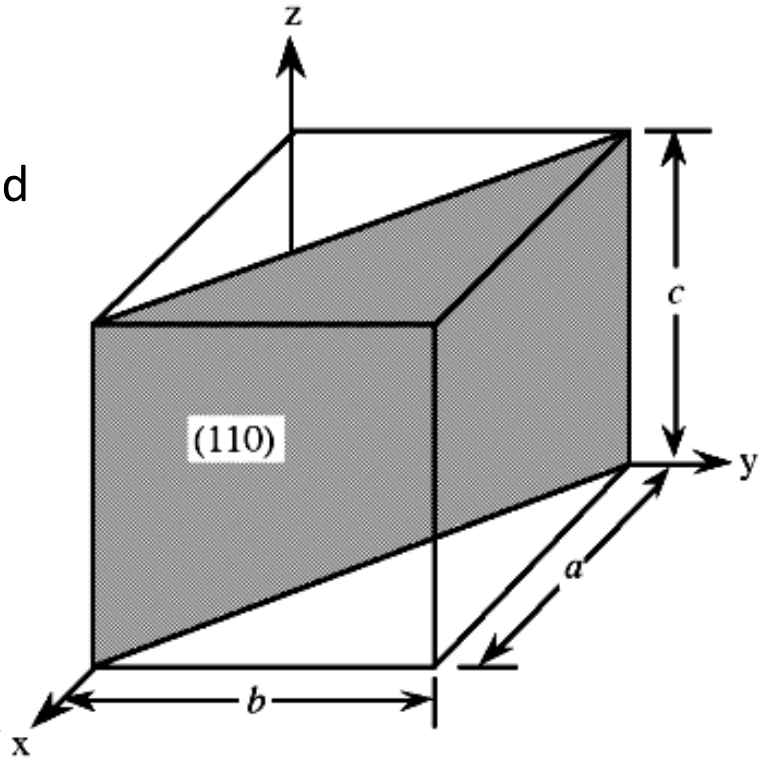
7 crystal classes
14 Bravais Lattice types
230 space groups

Key concept 2: Miller indices / planes

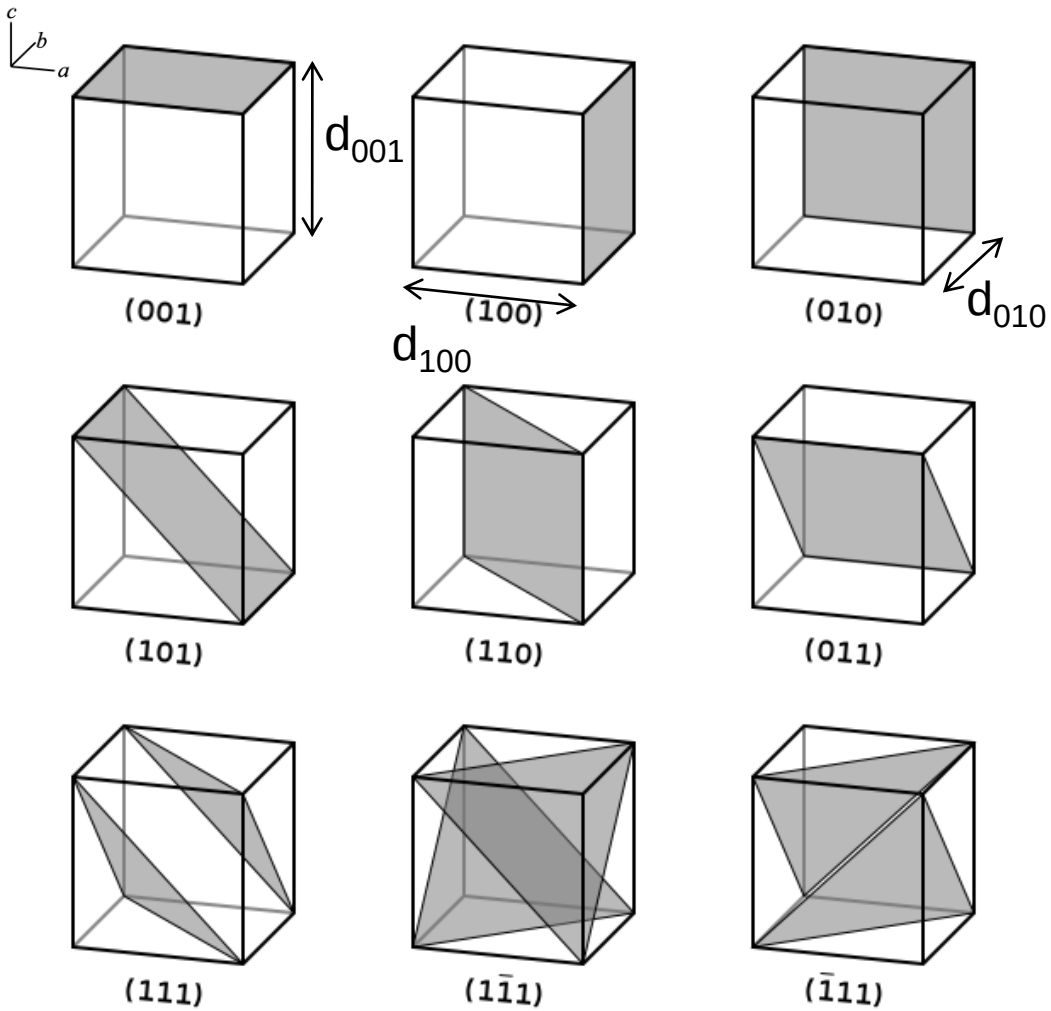
Unit cell planes can be defined by a notation called a Miller index (hkl).

To obtain the Miller indices of a given plane requires the following steps:

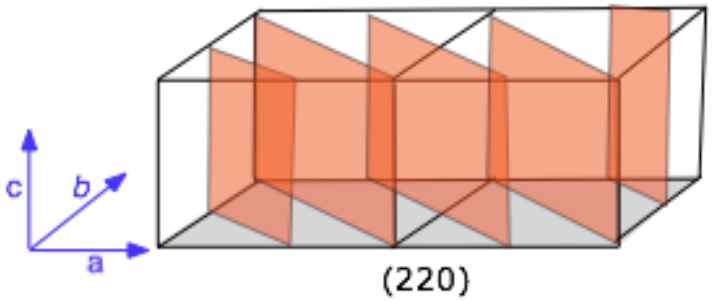
1. The plane in question is placed on a unit cell.
2. Find its intercepts with each of the crystal axes.
3. The reciprocal of the intercepts are taken.
4. Multiply by a scalar to get a ratio of integers.



Key concept 2: Miller indices



The higher the Miller index the less distance there is between equivalent planes, dividing the unit cell into ever smaller slices



For higher symmetry cells interplane distances can be identical

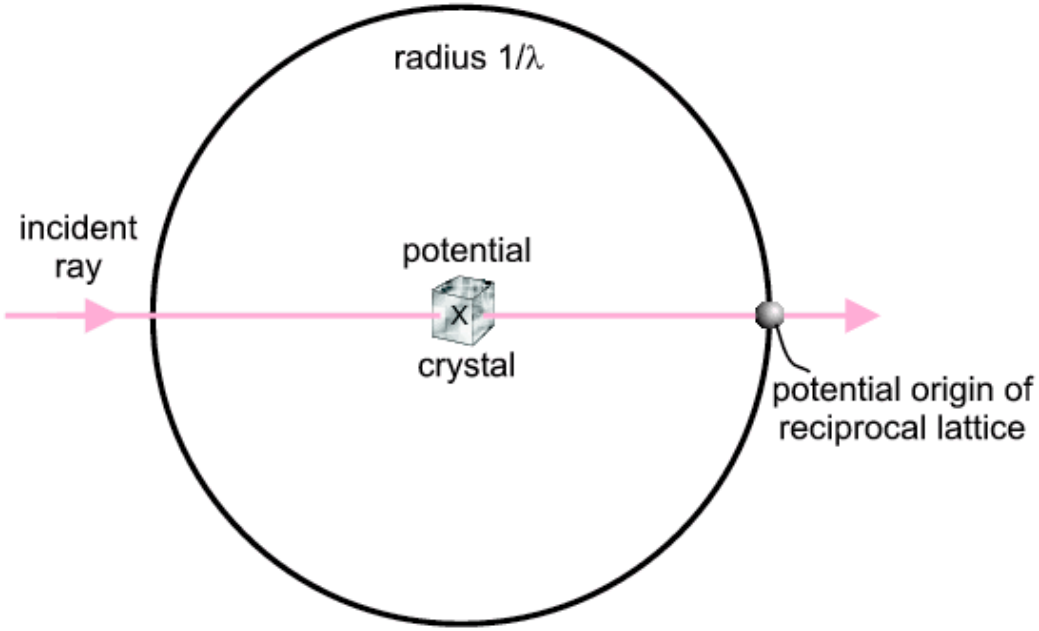
$d_{001} = d_{010} = d_{100}$ for cubic

Key concept 2: Miller planes

d-spacings in different crystal systems

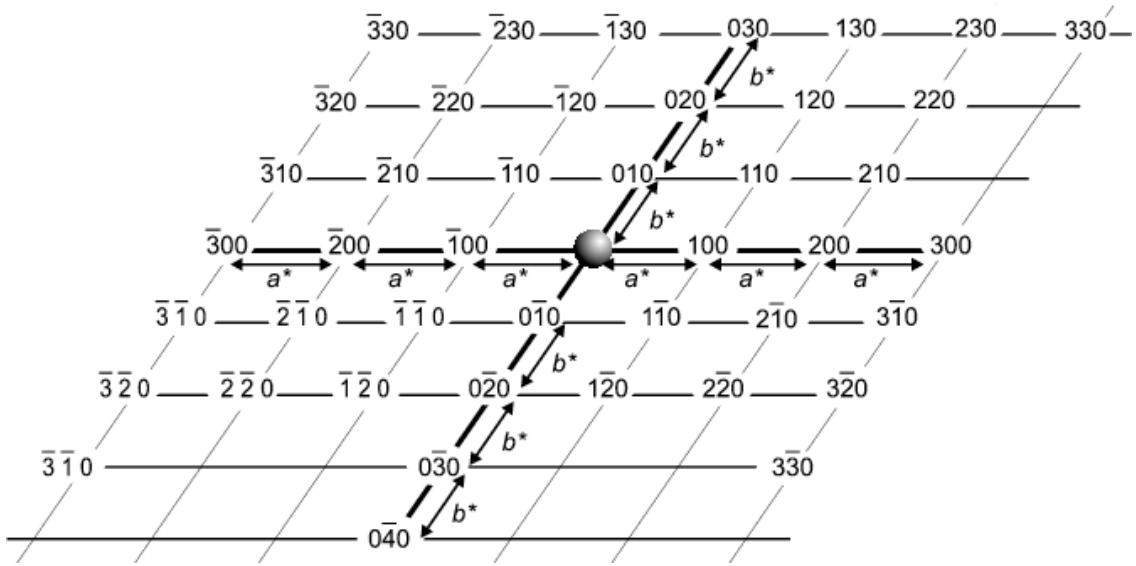
Crystal system	d_{hkl} as a function of Miller indices and lattice parameters
Cubic	$\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2}$
Tetragonal	$\frac{1}{d^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2}$
Orthorhombic	$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$
Hexagonal	$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right) + \frac{l^2}{c^2}$
Monoclinic	$\frac{1}{d^2} = \frac{1}{\sin^2\beta}\left(\frac{h^2}{a^2} + \frac{k^2\sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl\cos\beta}{ac}\right)$

Key concept 3: Ewald sphere



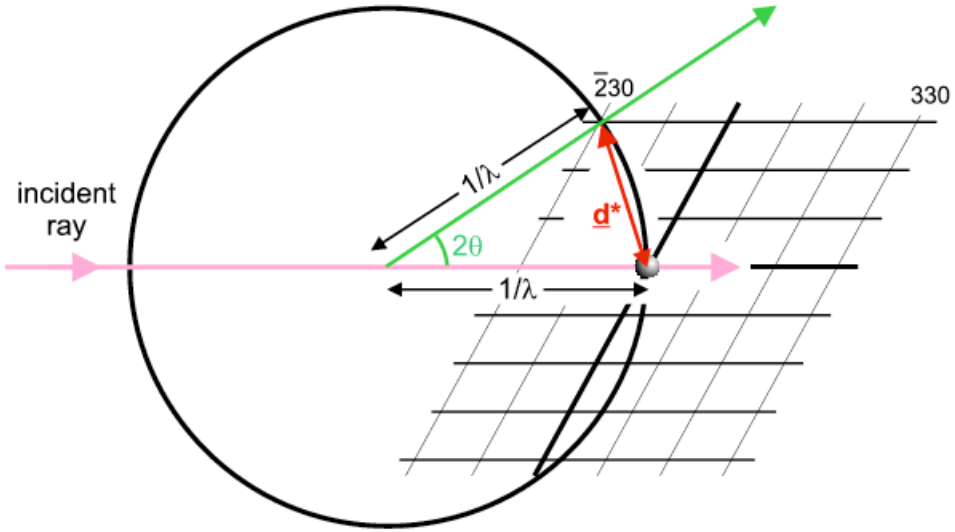
- A sphere of radius 1/λ (2-D projection shown above)
- Diffracted X-rays/neutrons can be along any radius from the centre of the sphere to the circumference

Key concept 4: Reciprocal lattice



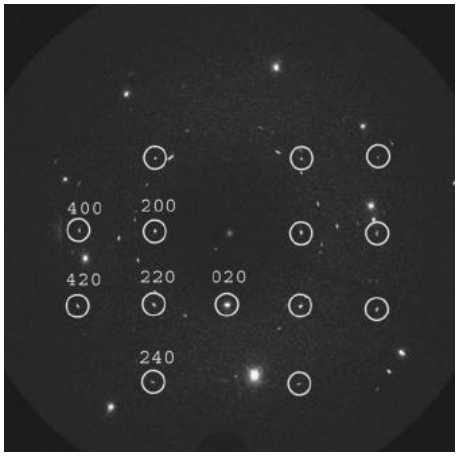
- The reciprocal lattice consists of points which represent diffraction possibilities
- Each point can be labeled with a Miller index
- The units are a*, b* and c* and any point can be reached using the vector equation d* = ha* + kb* + lc*

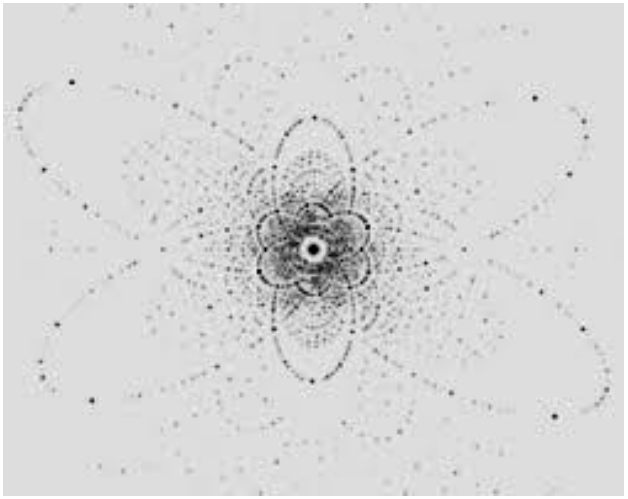
Key concept 5: Bragg diffraction

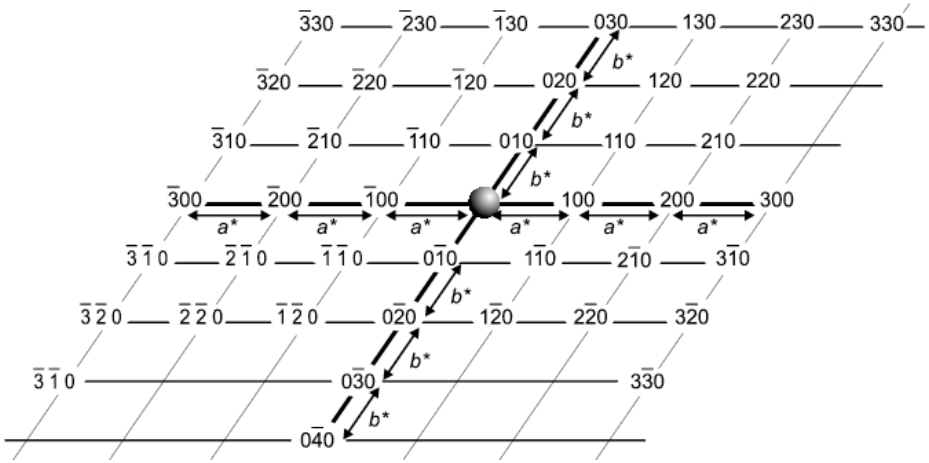


- Diffraction observed when a reciprocal lattice point intersects Ewald sphere
- Crystal rotation brings other lattice points into contact with Ewald sphere
- The vector from origin to lattice point is d* (reciprocal lattice spacing) is red – it is exactly equal to 1/d and its direction is perpendicular to the hkl plane
- The direction of the diffracted ray is indicated in green

Single Crystal Diffraction

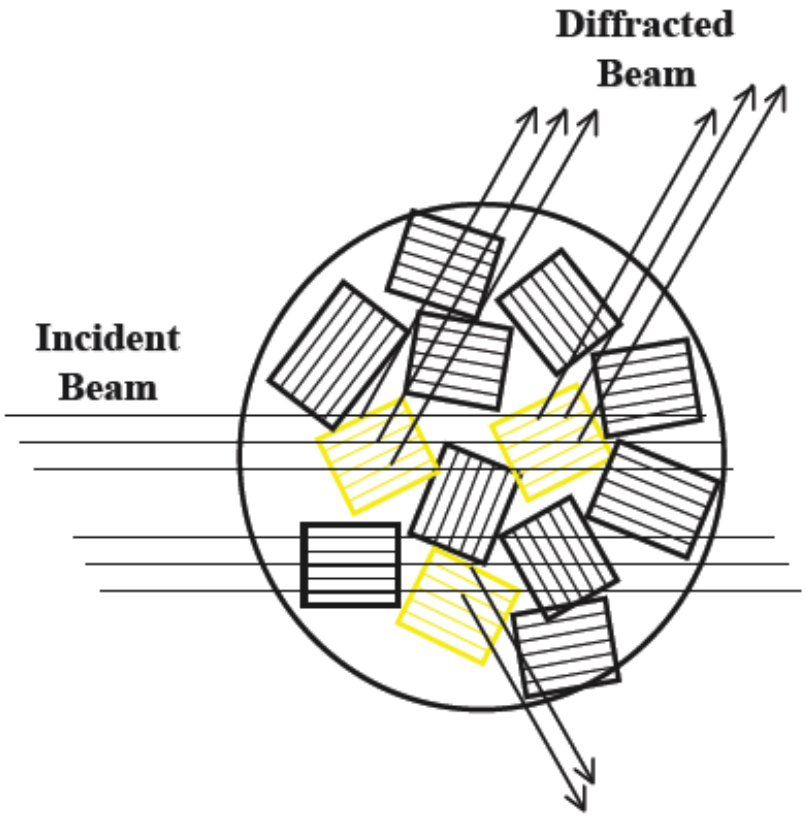




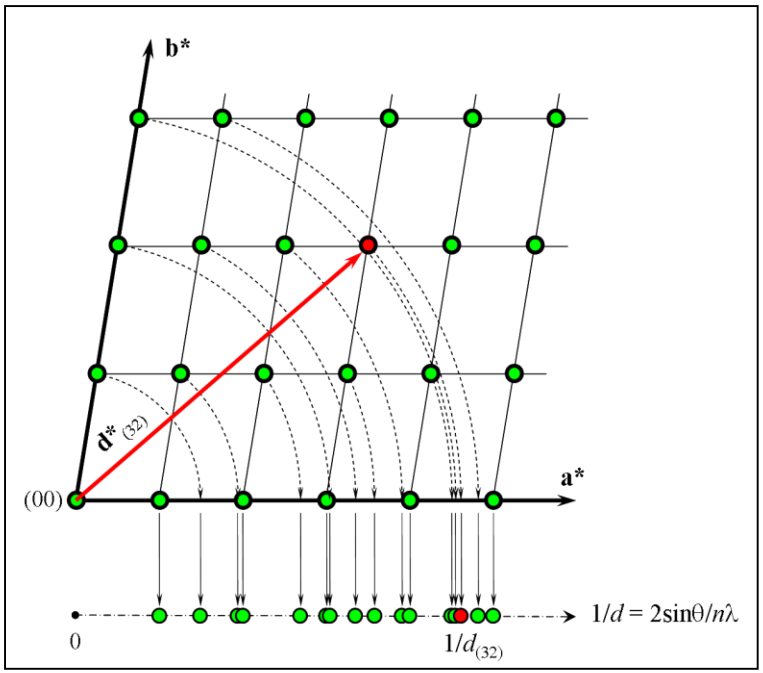


Direct observation of the reciprocal lattice

Powder diffraction

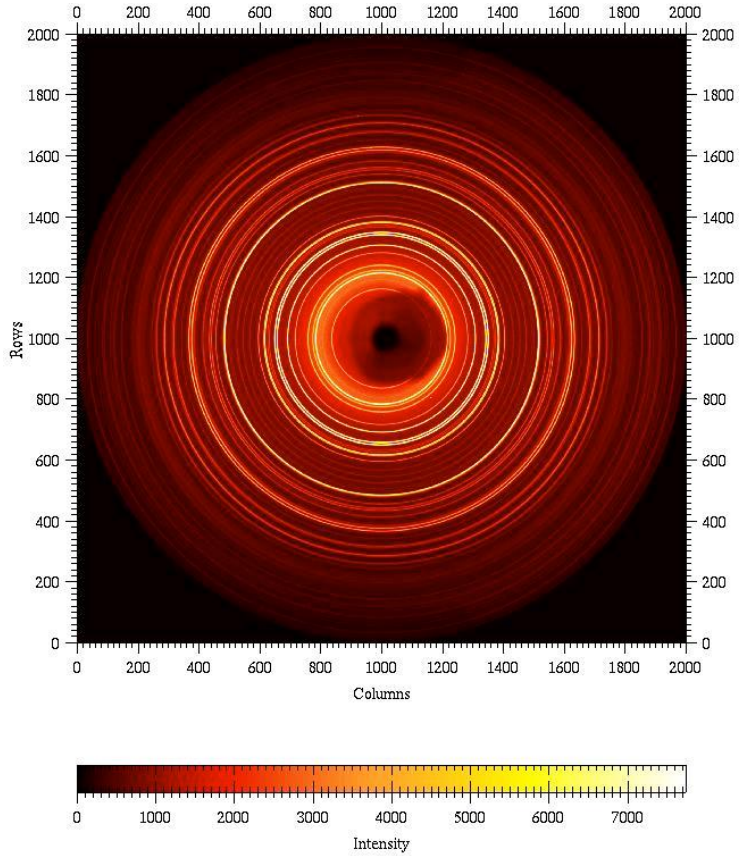


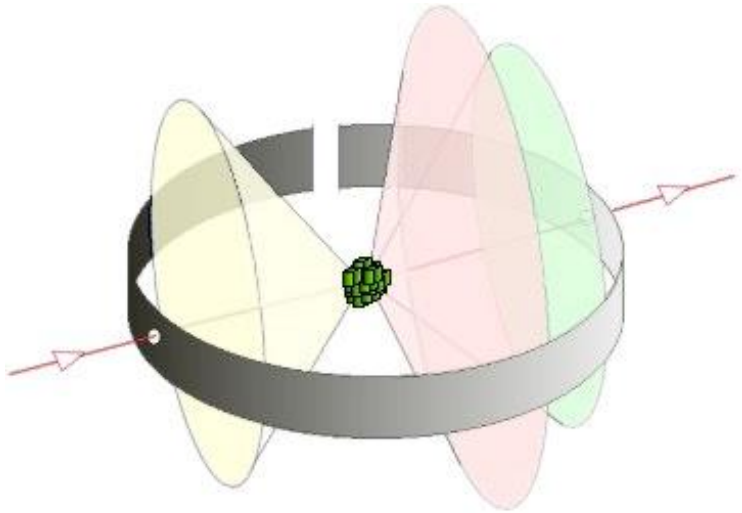
Powder diffraction



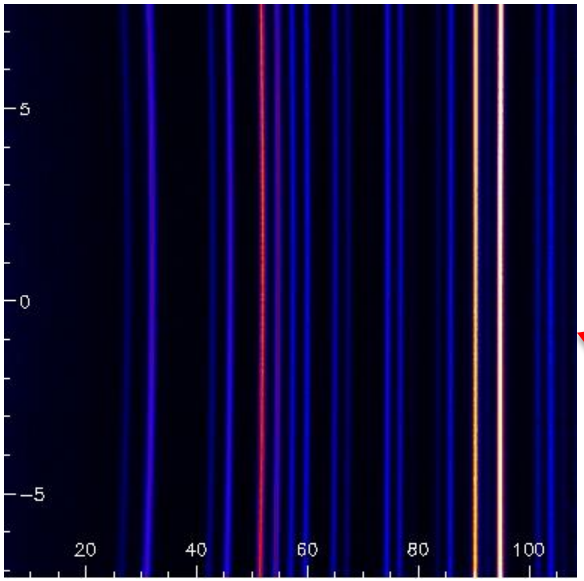
- Many crystallites with random orientation mean that each reciprocal lattice point will occur in every orientation possible, broadening into the surface of a sphere with radius d*
- The intersection of the Ewald sphere and the reciprocal lattice becomes a cone (intersection of 2 spheres)
- The directions of the vectors are lost and only the lengths of the reciprocal lattice vectors are measurable with powder diffractometers
- 3-D information collapsed into 1-D

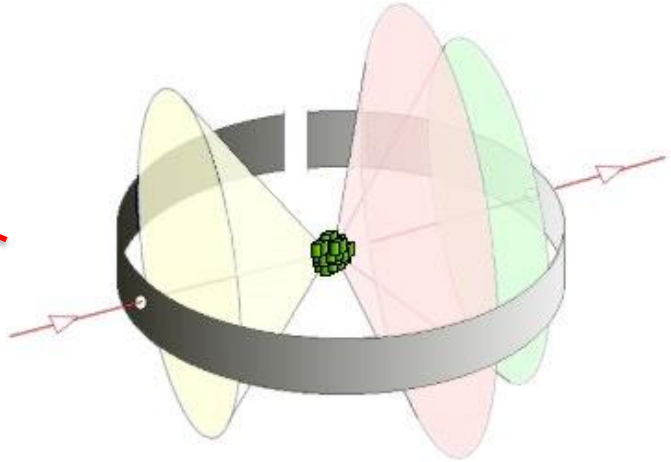
Powder diffraction

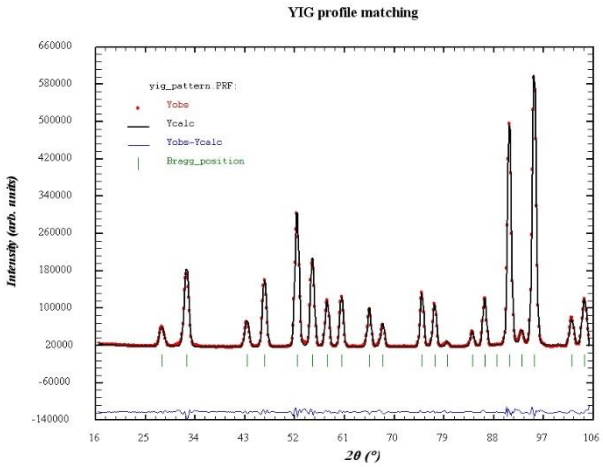




Powder diffraction







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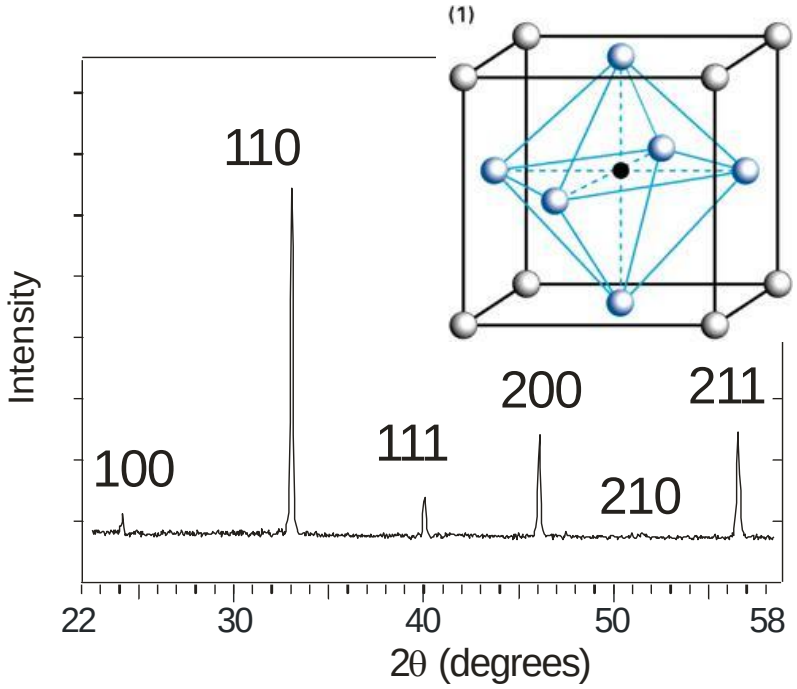
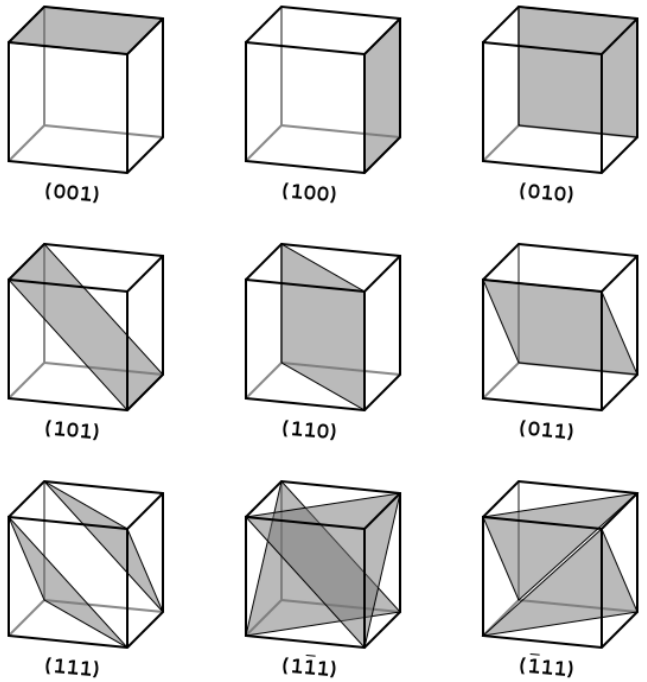
Miller plane equivalence in powder diffraction



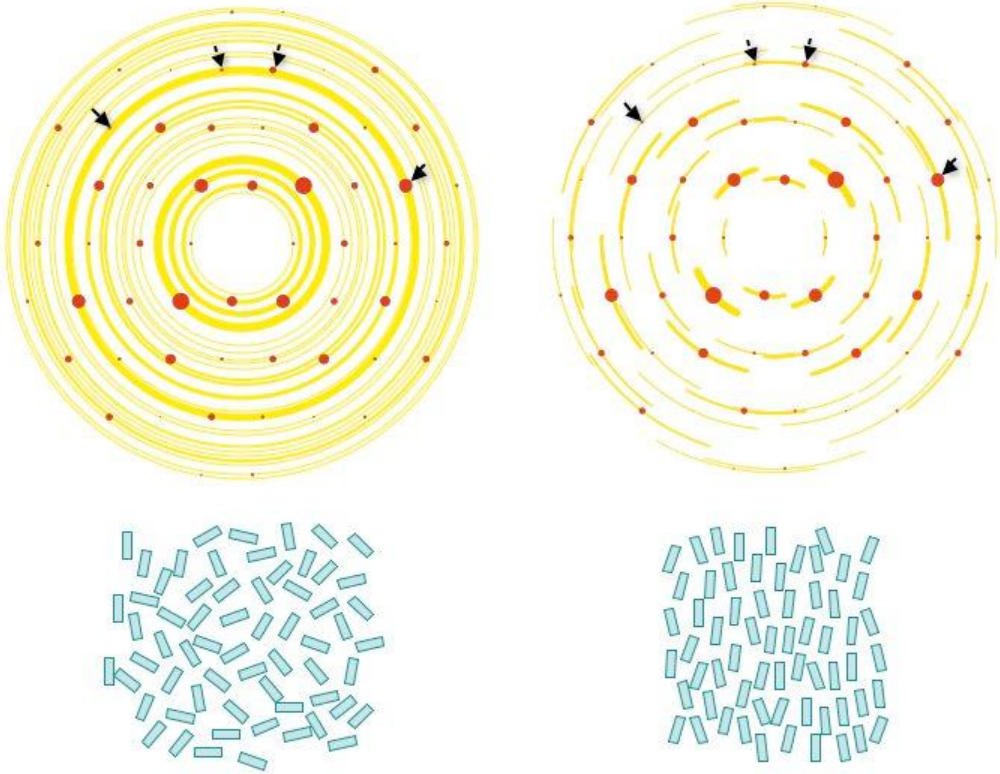


All equivalent planes occur at same scattering angle

All planes separated by the same distance occur at one scattering angle in powder diffraction

e.g. (511) and (333) occur at same 2θ for a cubic material

Not enough crystallites or a non-powder average



When number of crystals is too small, the pattern becomes “grainy” -- diffraction from individual crystals dominate.

- Increase sample size
- Grind the sample to decrease domain size
- Oscillate or rotate the sample
- Use area detection & integrate the entire Debye-Scherrer ring

Intensity and structure factor

$$I_{hkl} \propto |F_{hkl}|^2$$

Measured intensity proportional to F_{hkl}^2 and so we cannot tell whether F_{hkl} is positive or negative – the Phase problem

$$F_{hkl} \propto \Sigma f_i \exp[2\pi i(hx_i + ky_i + lz_i)] \exp(-U_i Q^2/2)$$

f_i is the scattering power (form factor of the ith site i.e. (x_i,y_i,z_i) and incudes fractional occupancy

Contribution of the ith site to the F_{hkl} in question

Atomic displacement of the ith atom site

The phase problem

$$I_{hkl} \propto |F_{hkl}|^2$$

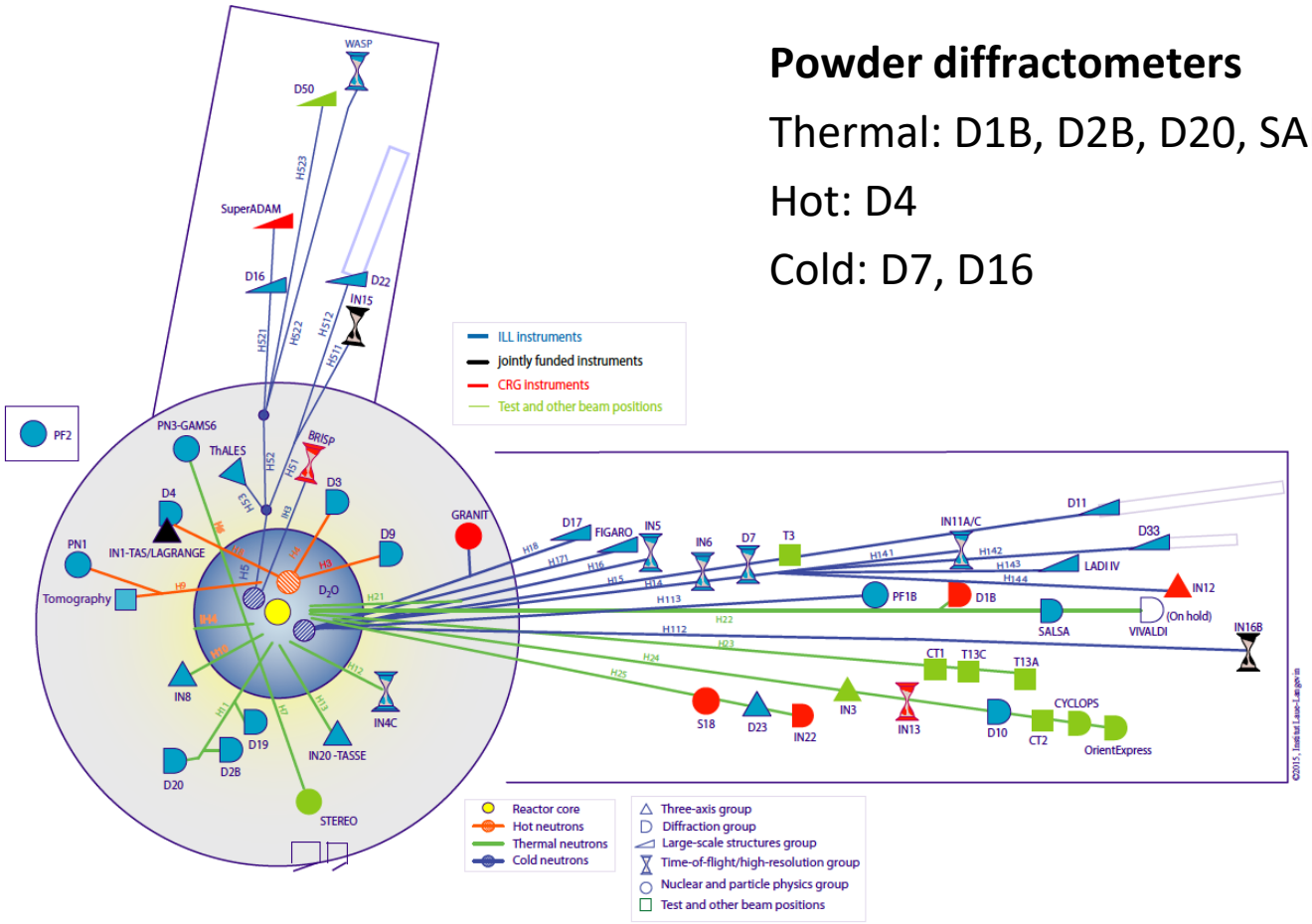
In diffraction we measure the magnitudes and not the phase. The phases contain the bulk of the information. This is why crystallography is hard….

…but not impossible. We can recover phase information from:

- Related or isostructural materials
- Knowledge of atom positions (heavy atoms from X-rays)
- Known motifs (molecules)
- Brute force

Instrumentation for neutron diffraction

Diffraction at a continous source: ILL



Powder diffractometers

Thermal: D1B, D2B, D20, SALSA

Hot: D4

Cold: D7, D16

Single crystal diffractometers

Thermal: D19, D10, CYCLOPS, VIVALDI, D23, OrientExpress

Hot: D3, D9

Cold: LADI-III, D7

Half of instrument suite are diffractometers

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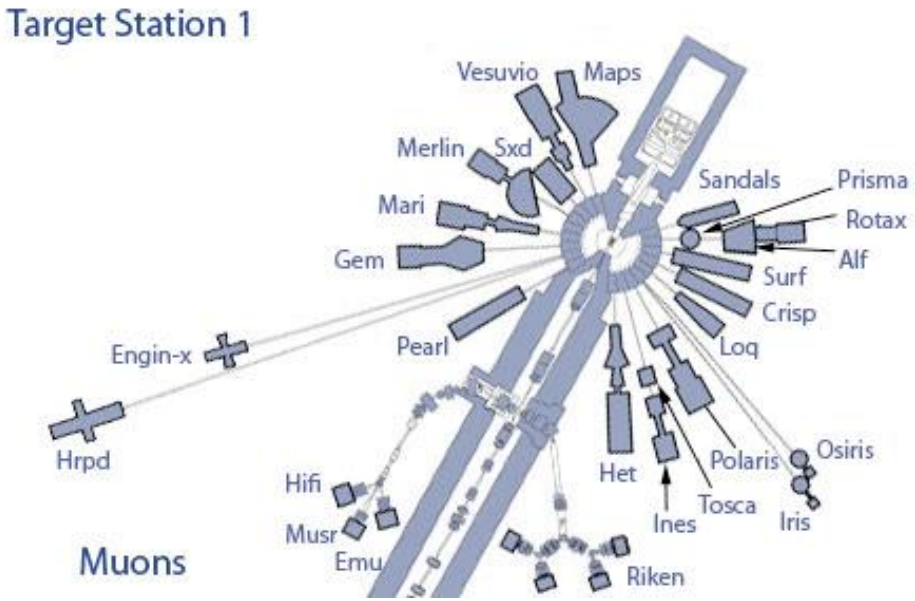
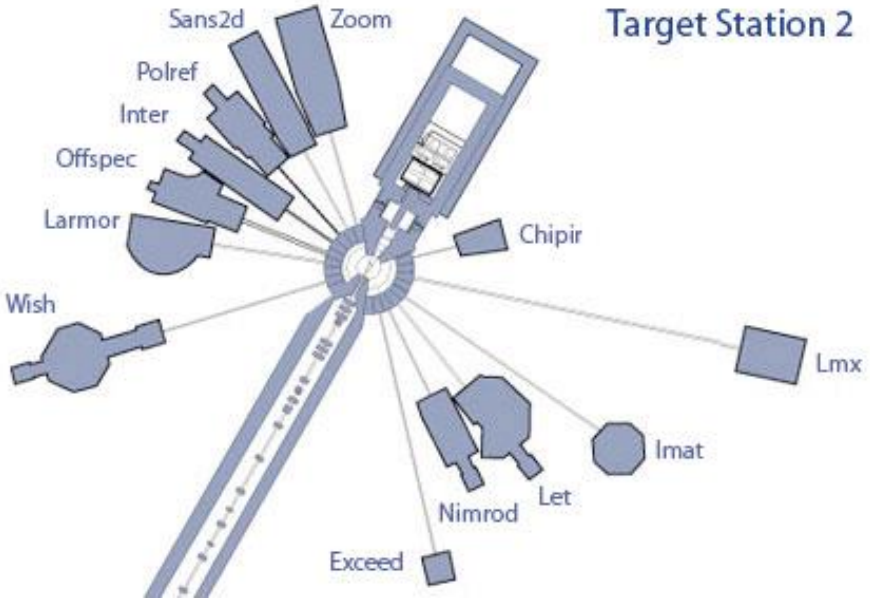
Diffraction at a pulsed source: ISIS





HRPD	WISH
ENGIN-X	IMAT
GEM	(LMX)
SXD	(EXCEED)
INES	SANDALS
PEARL	NIMROD
POLARIS	OSIRIS

Almost half of the instrument suite are diffractometers or carry significant diffraction capability

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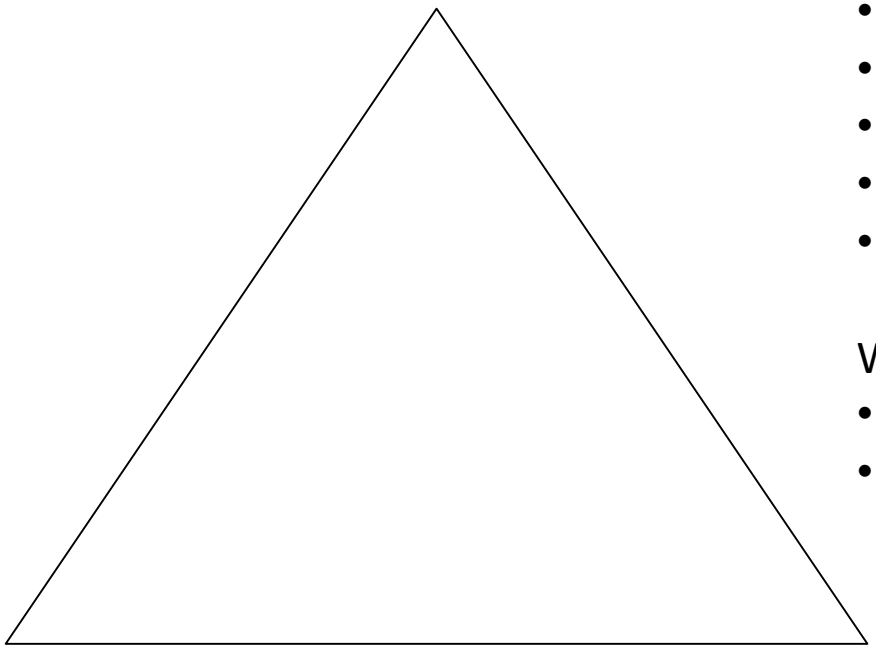
Why so many diffractometers?



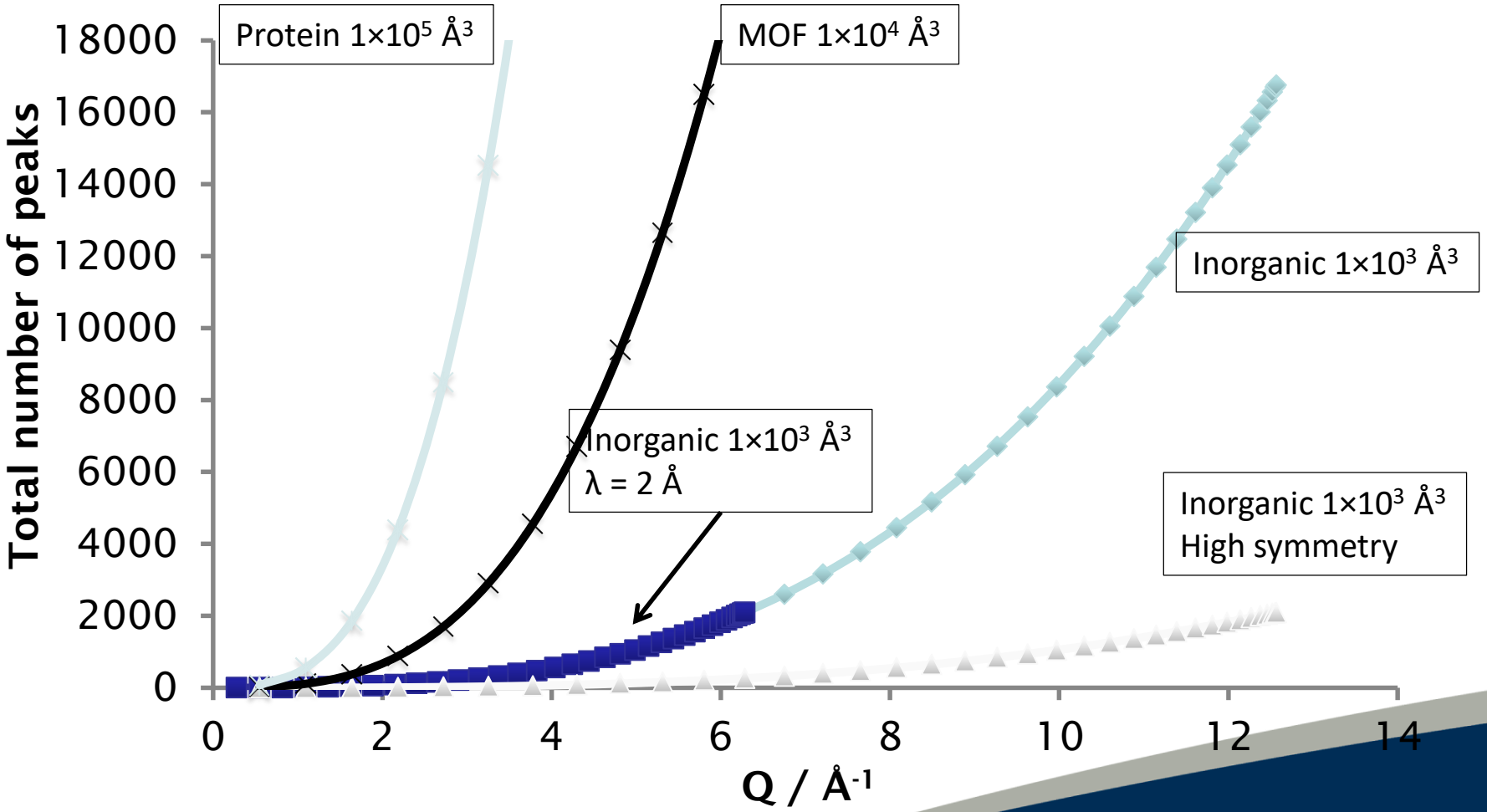
But also:

- Unit cell volume
- Sample environment restrictions
- Need for *in situ* capability
- Sample size
- Sample state
- Etc…

Which come from:

- Science case requirements
- Available budget!

Number of possible reflections



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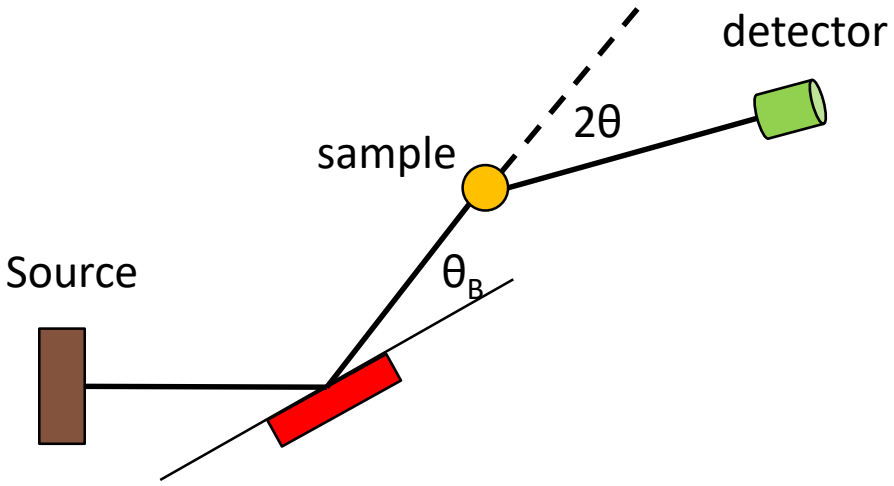
Types of diffractometer

$$\lambda = 2d\sin\theta$$

- Monochromatic (CW)
  - Fix wavelength and scan detector angle
  - Multiple 2θ required to cover Q(d) spacing range
  - Q(d) spacing limit $4\pi/\lambda$ ($2\pi/d$)
  - Instrumental count rate factors: Source power, monochromator reflectivity, detector coverage and efficiency, etc
- TOF
  - Fix detector angle and scan wavelength
  - Single 2θ covers range of Q(d) space
  - Q(d range) determined by λ_{max}, λ_{min} and θ
  - Instrumental count rate factors: Source power, moderator performance, beam transport efficiency, detector coverage and efficiency, etc

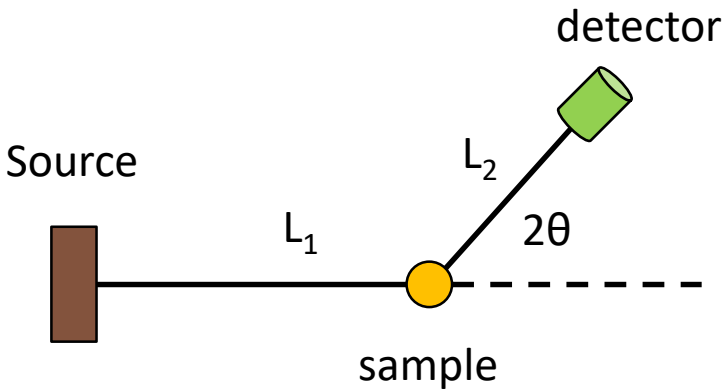
Instrument layouts

CW



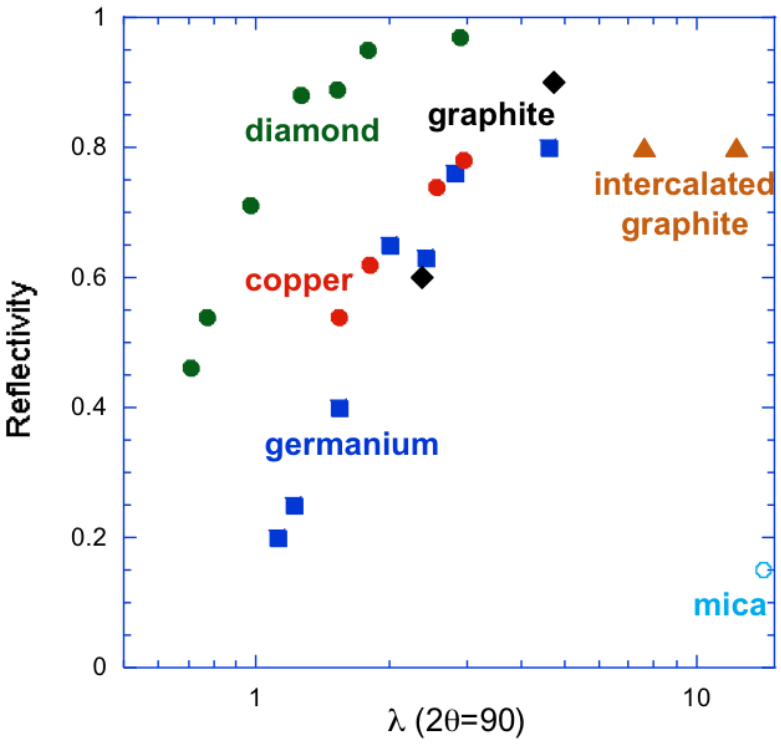
$$\lambda = \frac{2d_c \sin\theta_B}{n}$$

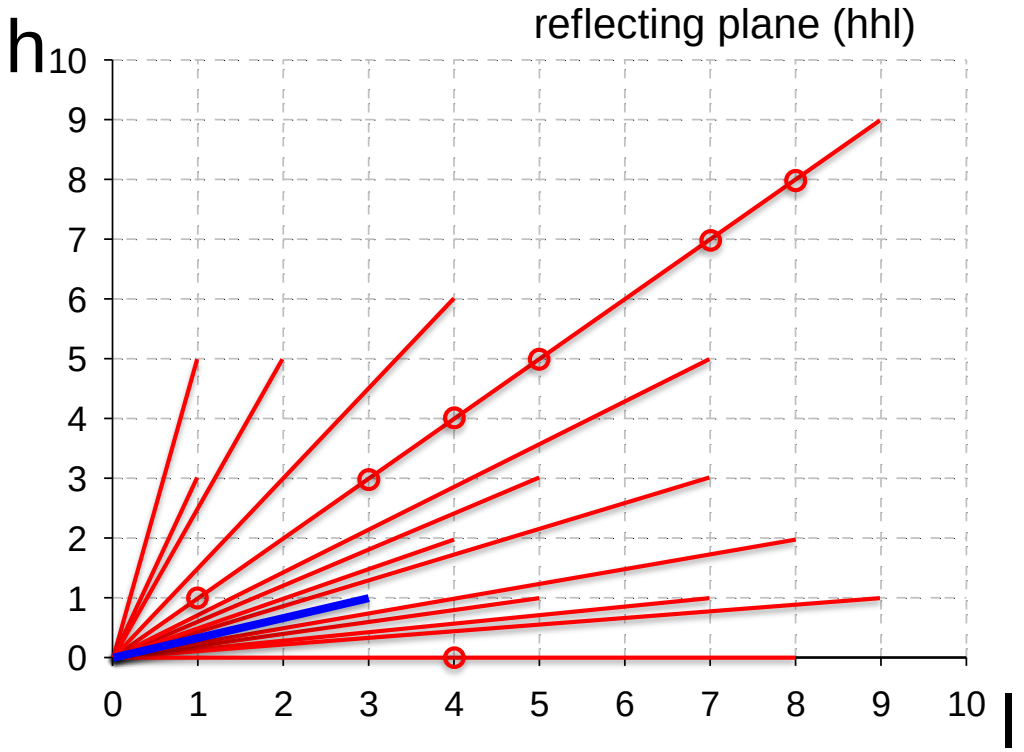
TOF



$$\lambda = \frac{3956}{v} = \frac{3956\,(t-t_0)}{L_1+L_2}$$

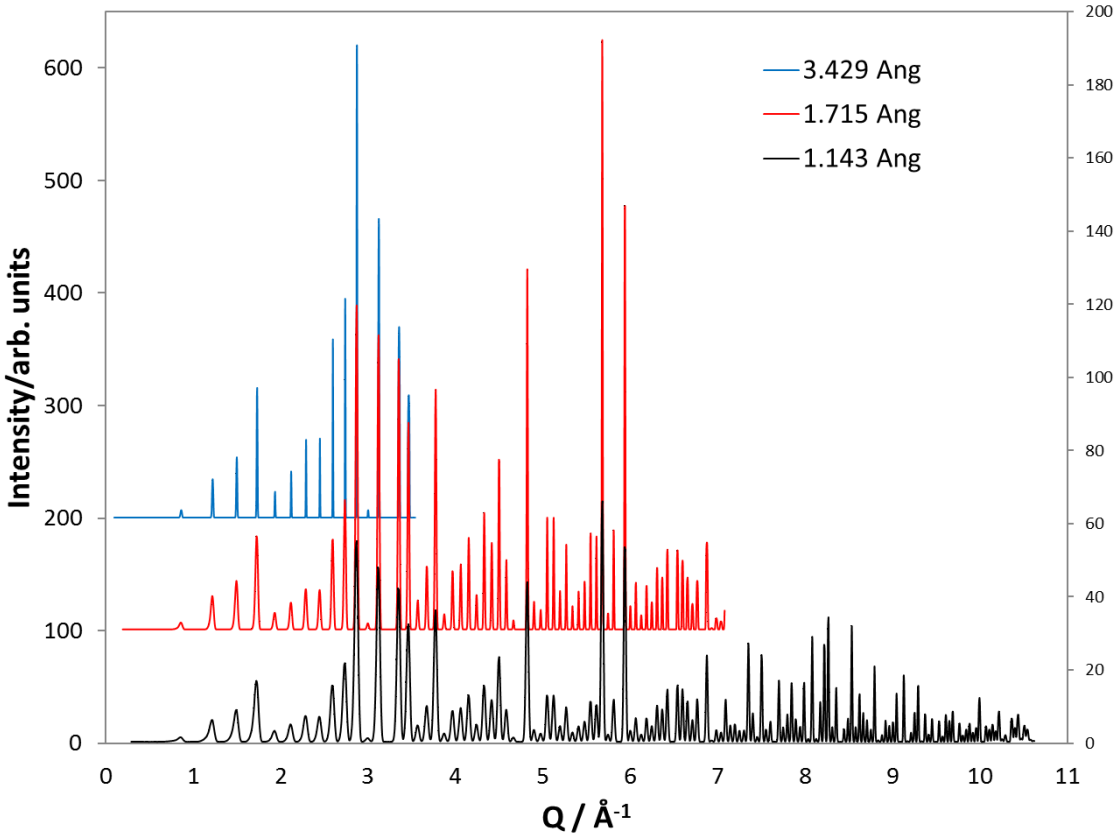
Monochromator materials





Choose material and plane to access necessary Q-range
Reflectivity falls as wavelength decreases

Q range with monochromators



Shorter wavelengths access higher Q but have lower reflectivity

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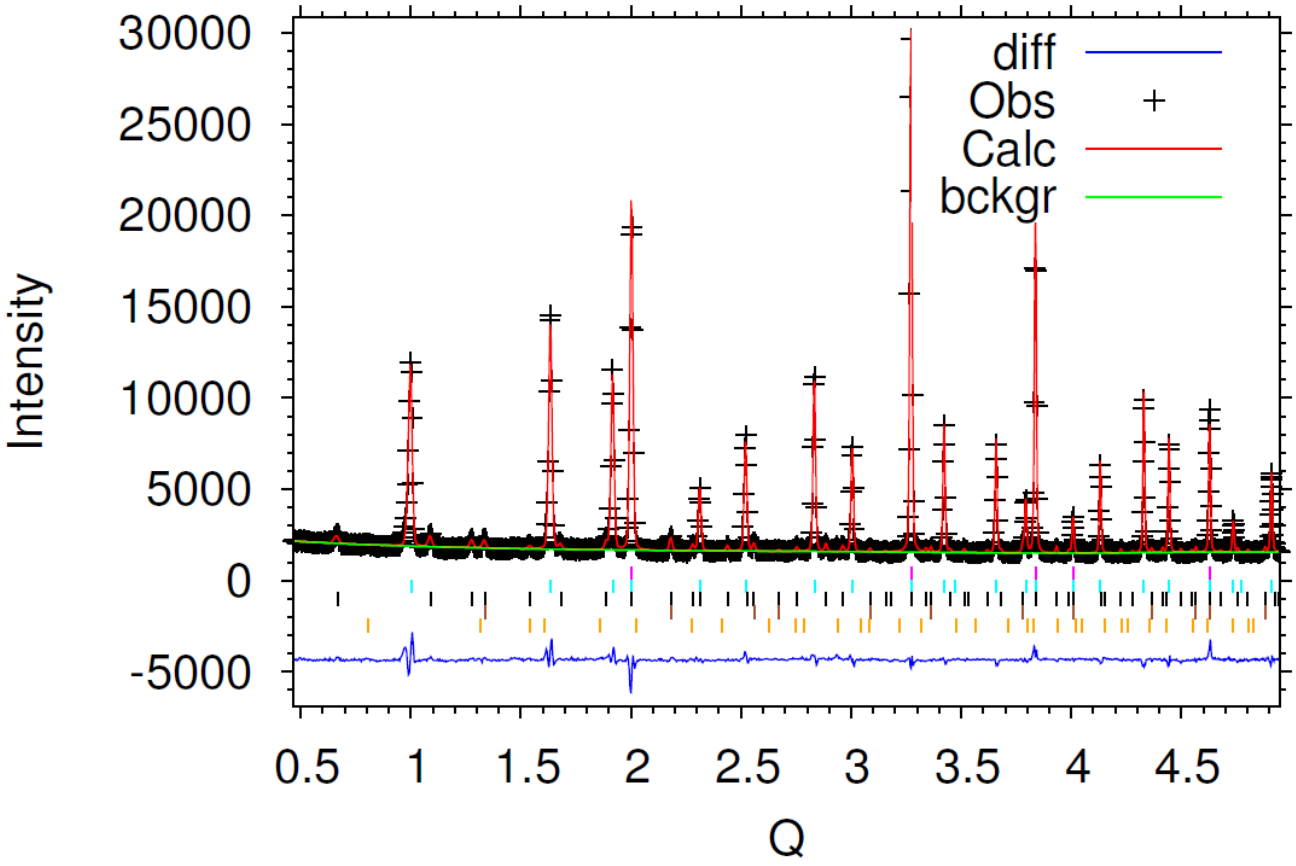
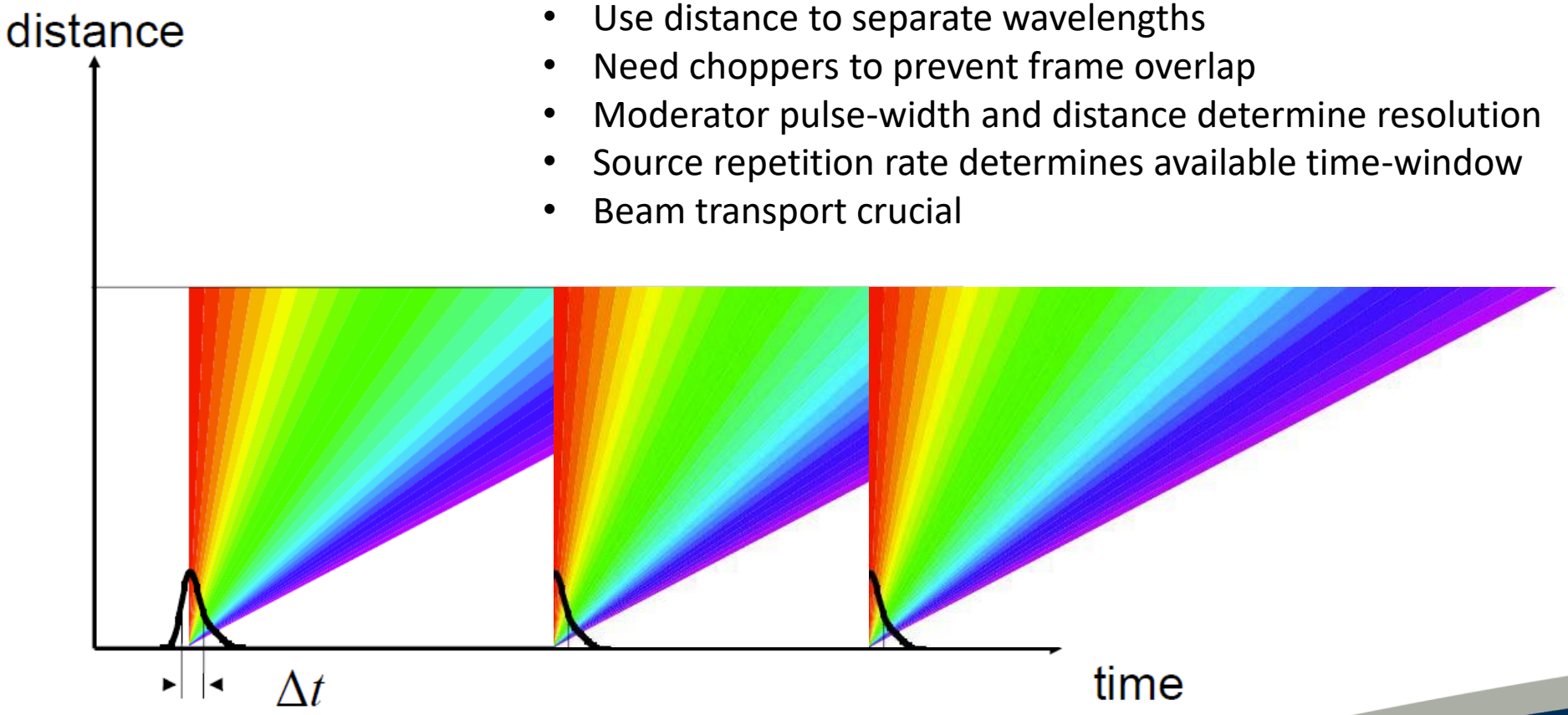
Higher reflection order contamination



High reflection order contamination complicates analysis with CW data

TOF method



- Use distance to separate wavelengths
- Need choppers to prevent frame overlap
- Moderator pulse-width and distance determine resolution
- Source repetition rate determines available time-window
- Beam transport crucial

CW or TOF: Q-range summary

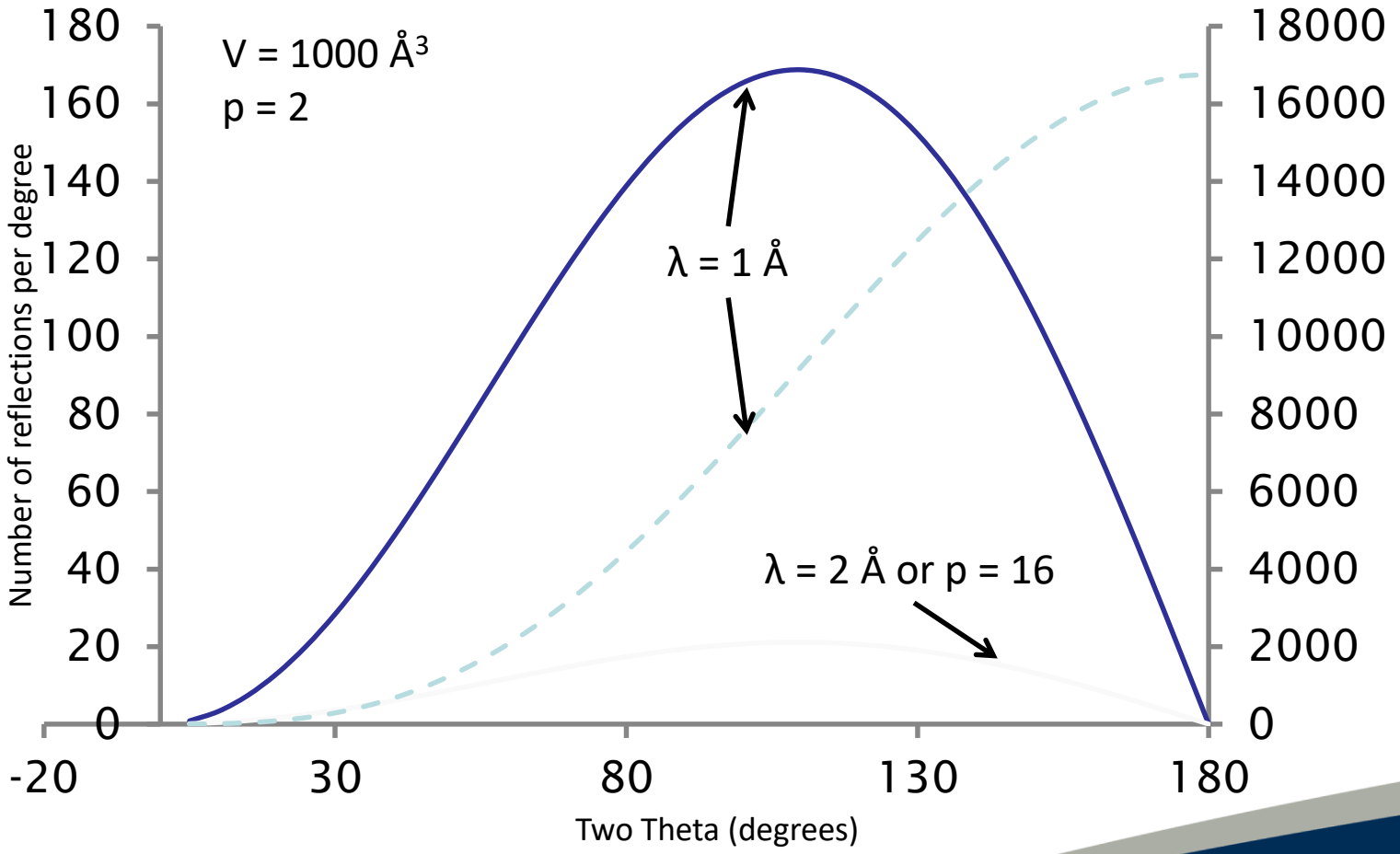
For CW:

- For monochromatic instruments the Q_{max} is $4\pi/\lambda$ i.e. when $\sin\theta = 1$, $\theta = 90°$, $2\theta = 180°$
- If a high Q_{max} is required a shorter wavelength must be used.
- Shorter wavelengths are produced by higher order hkl planes
- Reflectivity is lower for shorter wavelengths
- Realistic Q_{max} of around 25 $Å^{-1}$

For TOF:

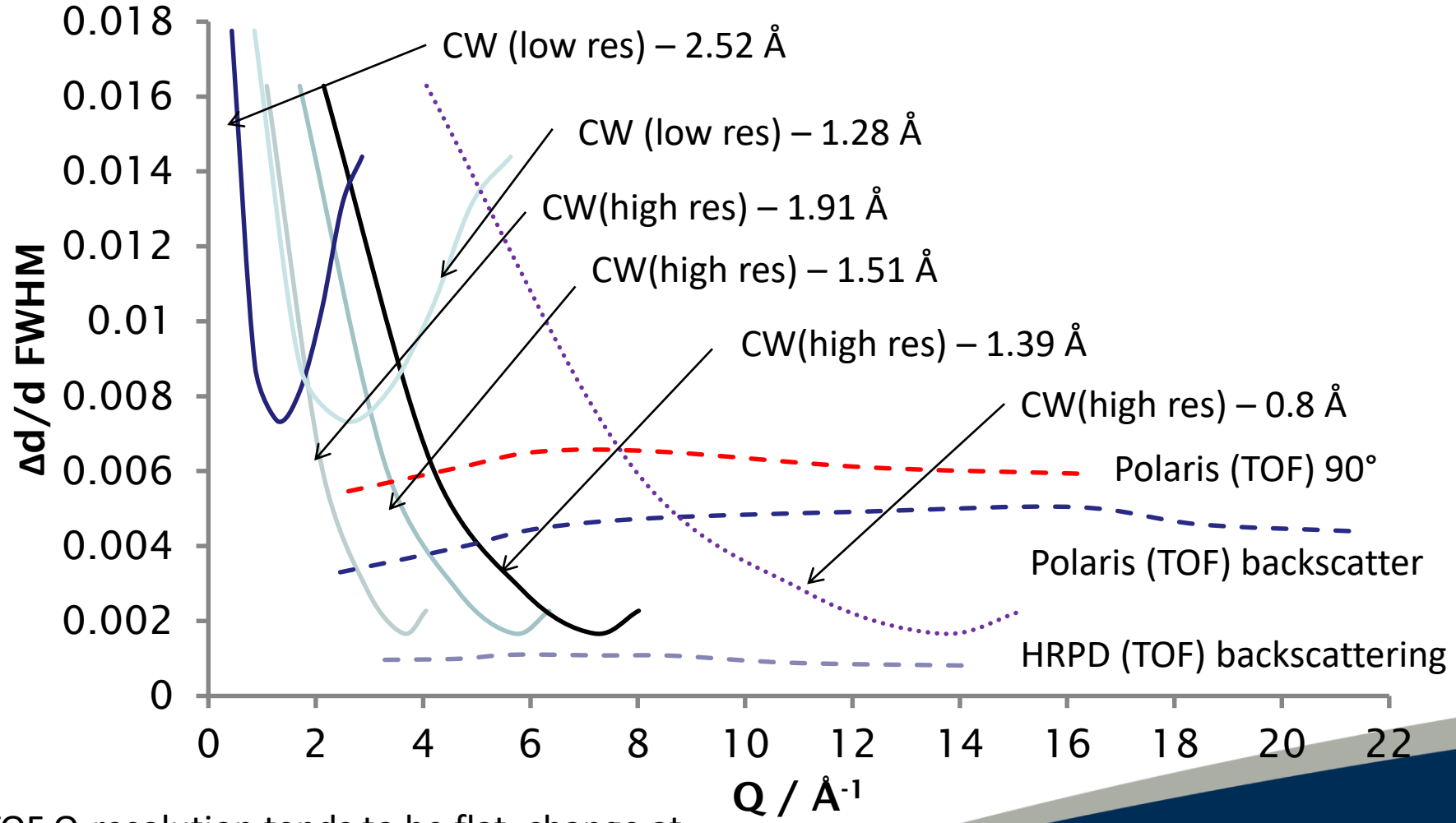
- Q_{max} depends on λ_{min} and detector θ.
- λ_{min} can be much lower than for the CW case allowing $Q_{max} > 100$ $Å^{-1}$
- λ_{min} determined by the moderator, transport characteristics of the guide and which frame the instrument is working in

Reflection density for CW



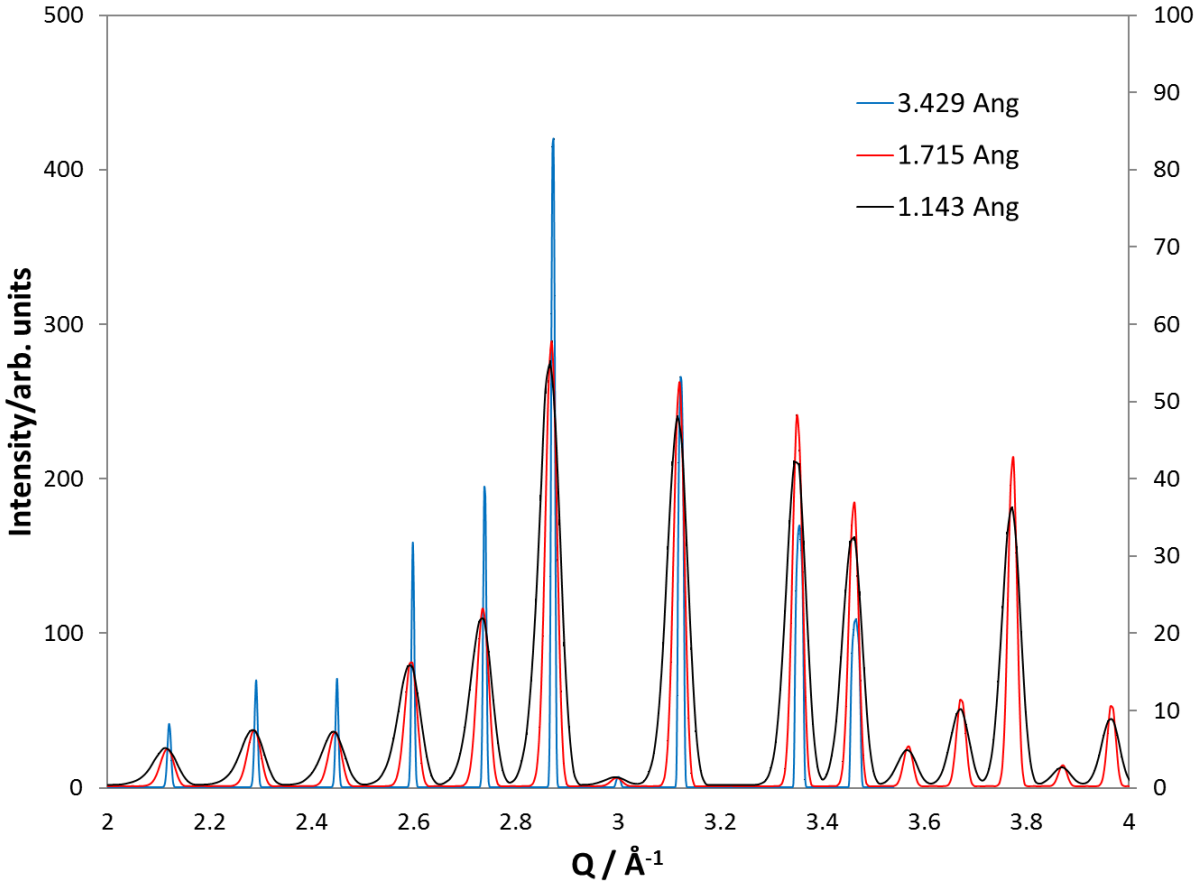
CW instruments designed to have best resolution at highest peak density

Resolution functions CW v TOF



TOF Q-resolution tends to be flat, change at high Q caused by moderator residence time

CW Q resolution example



Choose wavelength to match Q resolution required by science in a given Q range

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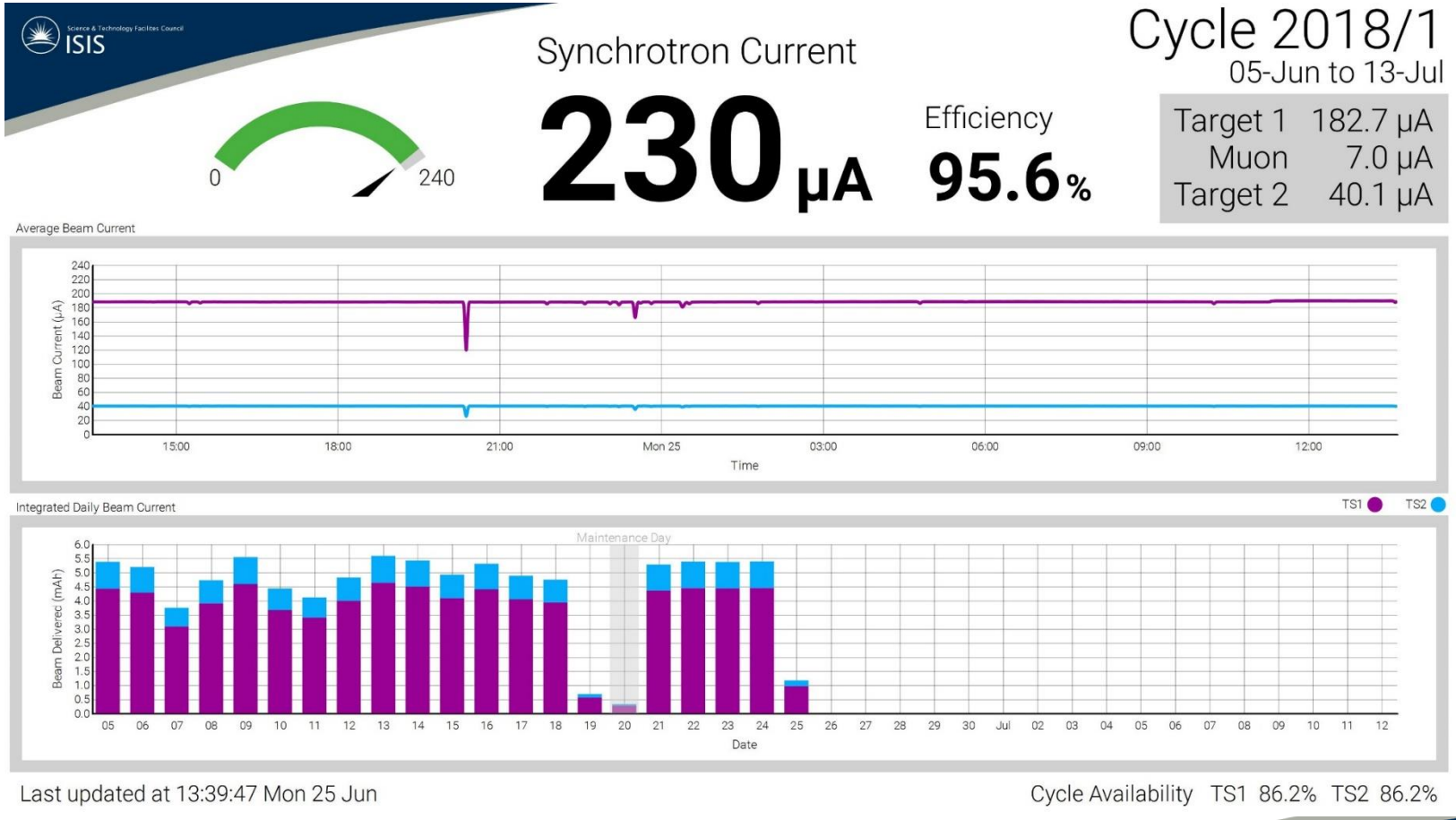
CW or TOF: Q resolution

- CW:
  - Simple, symmetric peakshape function
  - Best resolution where diffraction peak density is highest in scattering angle
  - Different wavelength can be used to give Q resolution where required
  - Different takeoff angle can be used to change resolution function and wavelength
  - Instrument can be high Q resolution but with very limited Q range

- TOF:
  - Complex asymmetric peakshape related to moderator characteristics
  - Instrument length and moderator give wavelength band and overall resolution
  - Q resolution almost constant for a given detector bank so increasing peak density with Q can be an issue
  - Q resolution improved by moving to higher scattering angle detector bank
  - Q range determined by scattering angle of detector bank

Pulsed source availability



A very good day in terms of beam
All experiment types possible

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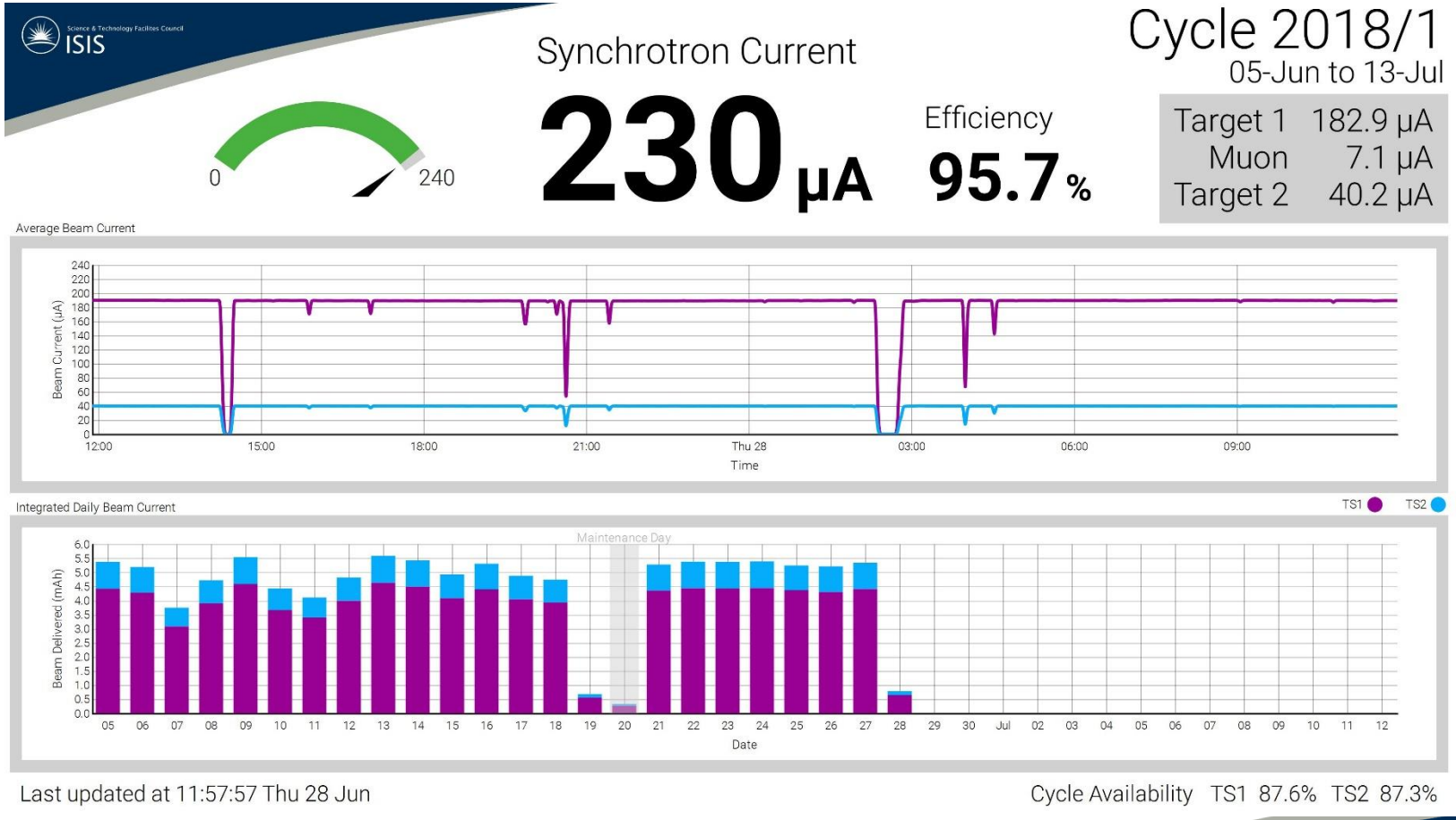
Pulsed source availability



A good day in terms of beam – still possible issues with *in situ* and time resolved experiments

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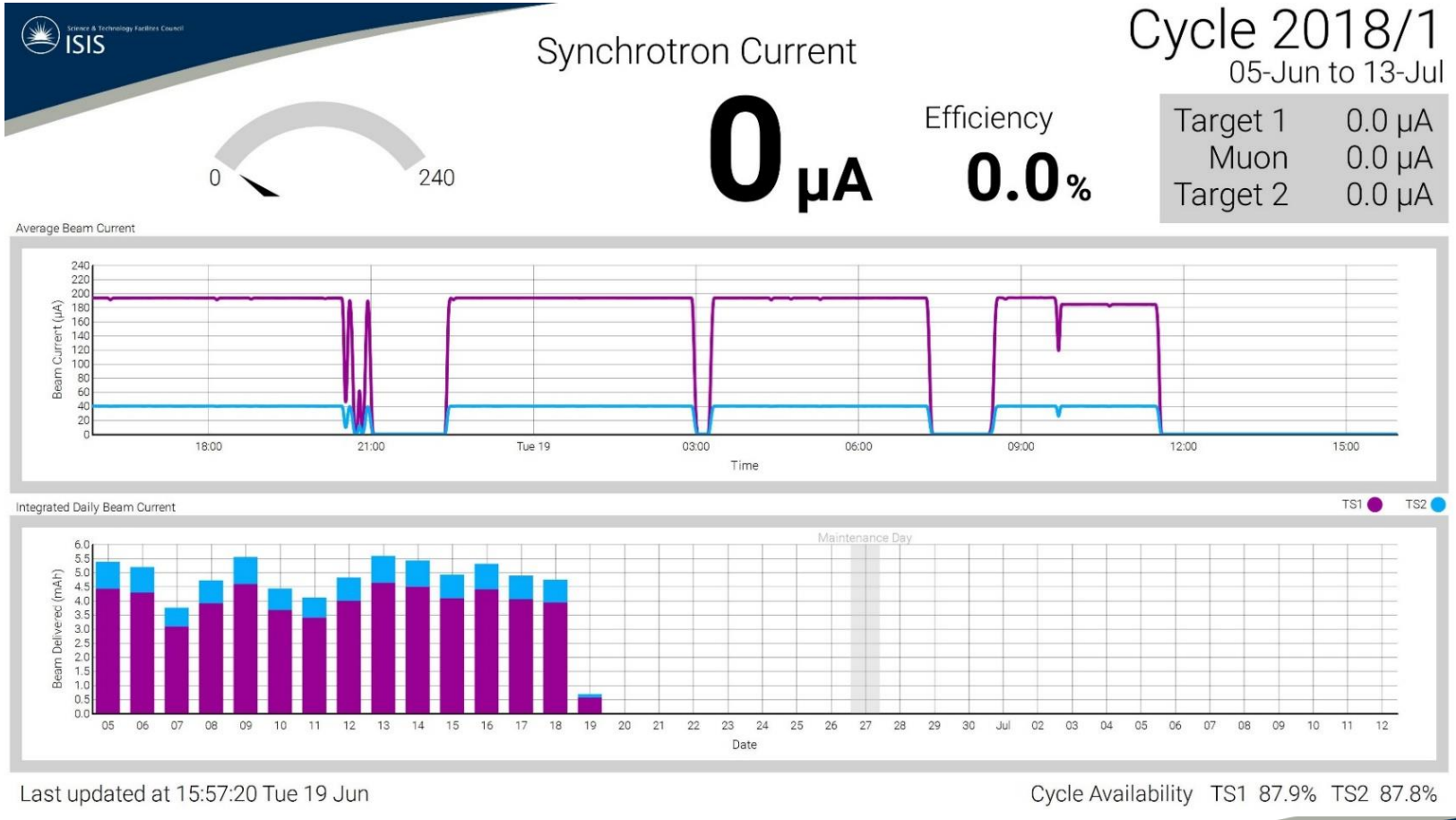
Pulsed source availability



A bad day – any time resolved experiment is compromised

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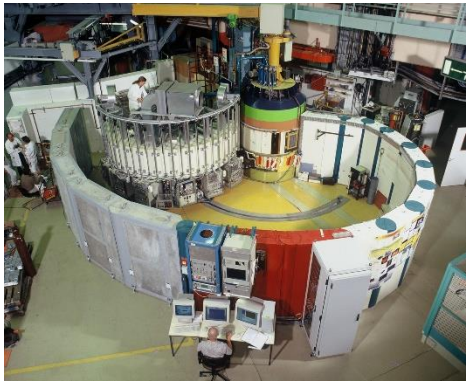
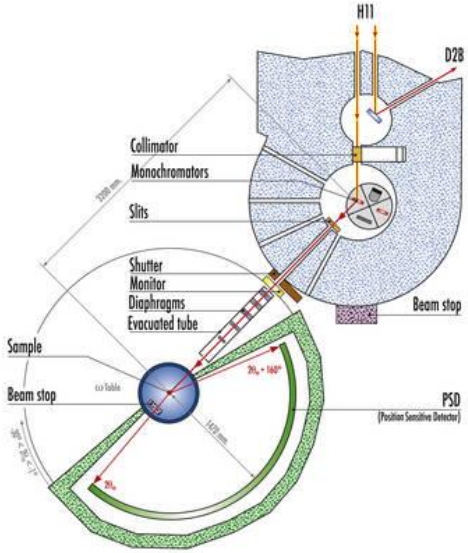
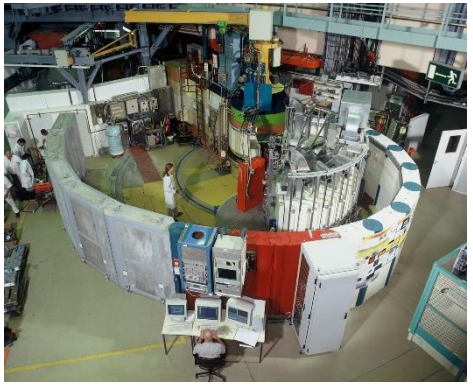
CW, variable resolution, thermal powder diffractometer: D20

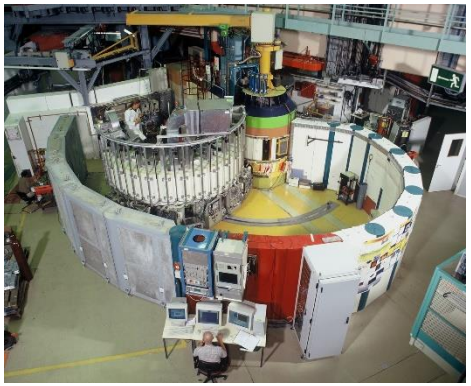


120°



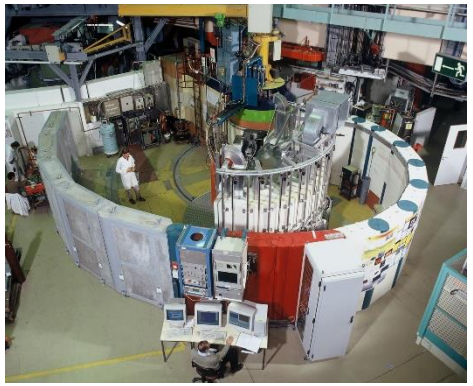


28°



90°

65°



42°

Photos courtesy T. Hansen ILL

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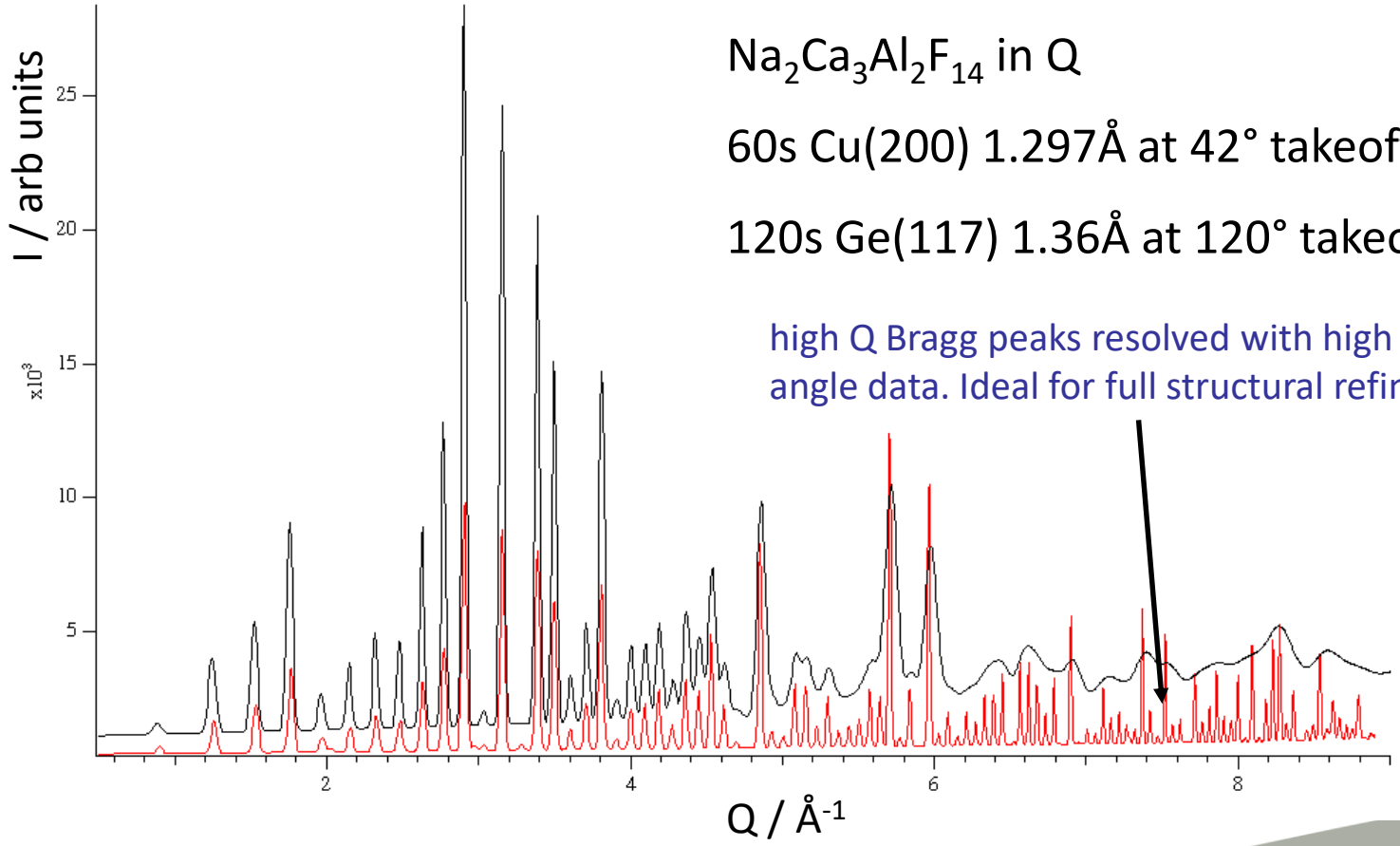
Low θ_B v high θ_B: Q resolution v count-rate



$Na_2Ca_3Al_2F_{14}$ in Q

60s Cu(200) 1.297Å at 42° takeoff (black)

120s Ge(117) 1.36Å at 120° takeoff (red)

high Q Bragg peaks resolved with high take off angle data. Ideal for full structural refinement

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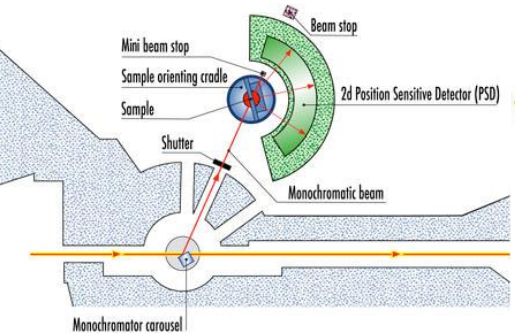
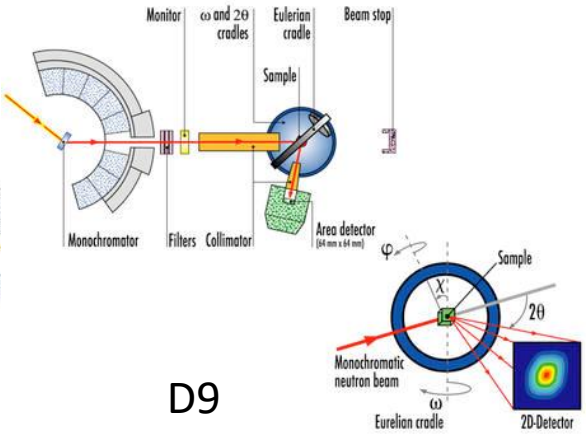
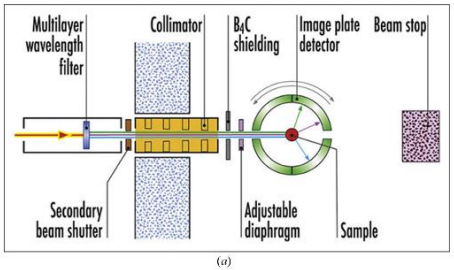
CW single crystal diffraction

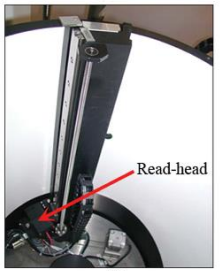


D19

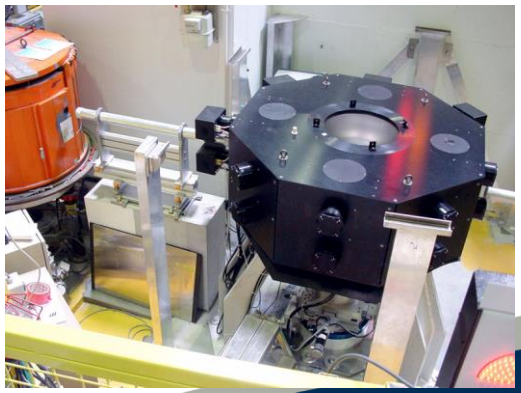


D9





LADI-III



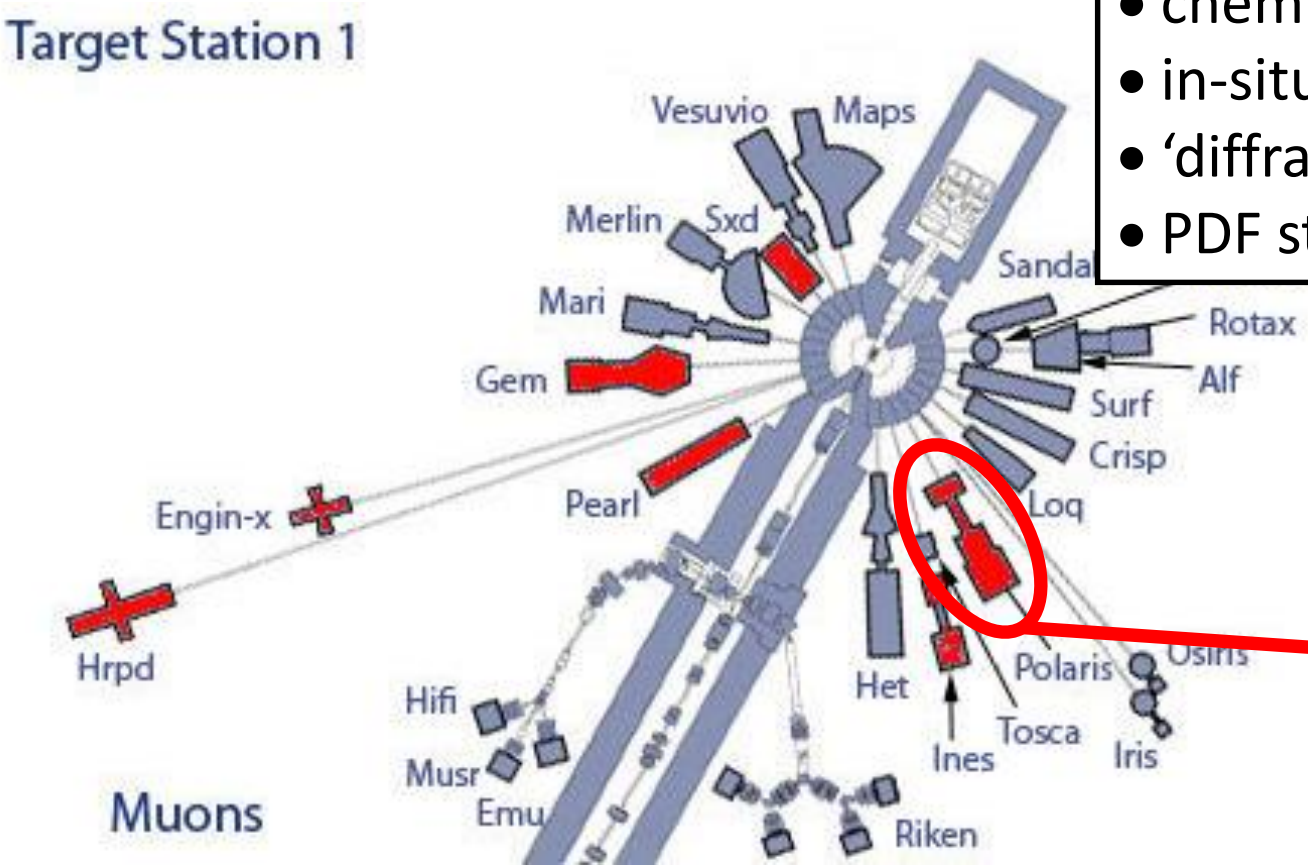
CYCLOPS

- Monochromatic and Laue type instruments are represented
- Q-range of interest and unit cell volume determine whether hot, thermal or cold neutron spectrum required for both instrument types

http://www.ill.eu/instruments-support/instruments-groups/

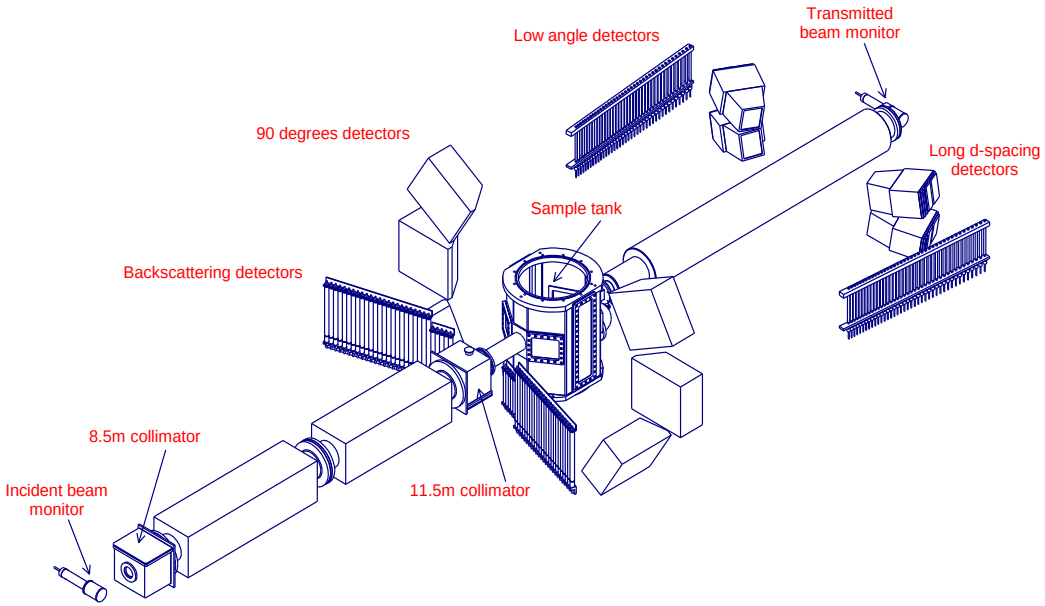
TOF: high intensity powder diffraction

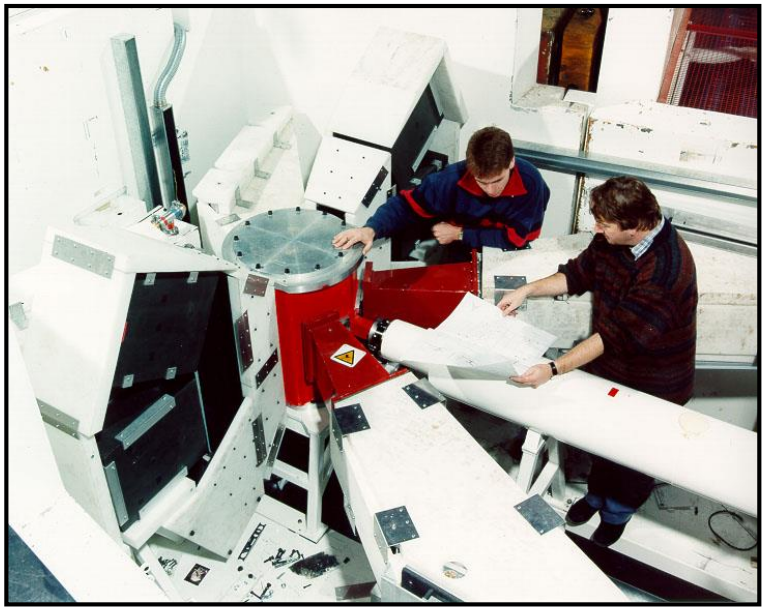
- chemical crystallography
- in-situ studies
- ‘diffraction plus’
- PDF studies



Polaris

Polaris: old configuration





Compare with GEM:

- Higher sample flux
- Wider bandwidth
- Lower resolution
- Hotter spectrum
- Lower detector coverage

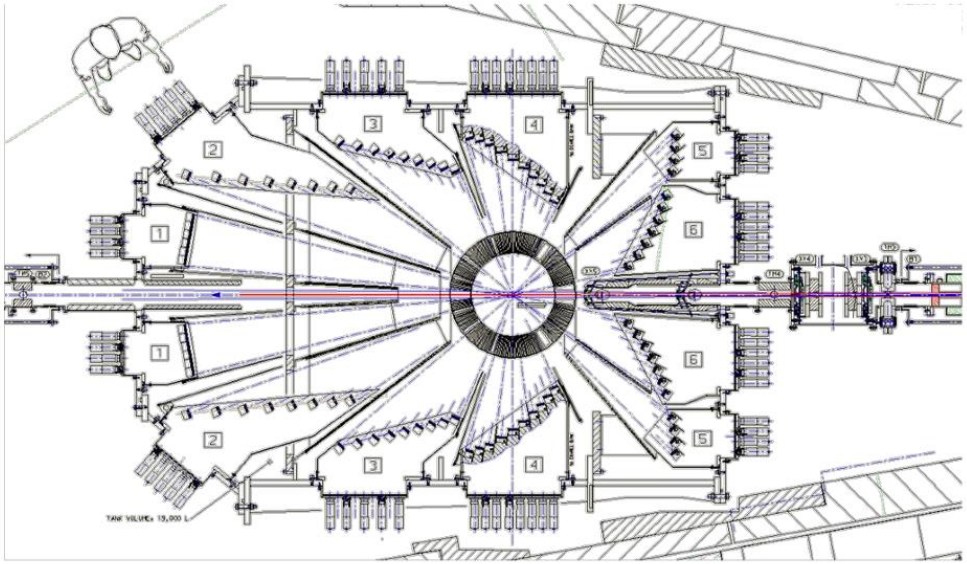
http://www.isis.stfc.ac.uk/instruments/polaris/polaris4643.html

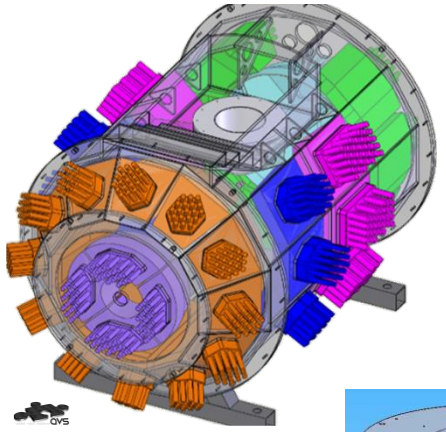
Polaris: old configuration

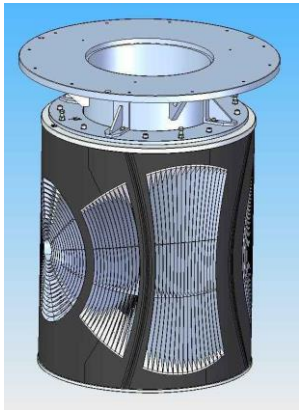
bank position (label)	low angle (A)	low angle (B)	backscattering (C)	90 degrees (E)
detector type	^{3}He	ZnS	^{3}He	ZnS
no. of elements	2 x 40 = 80	4 x 20 = 80	2 x 29 = 58	6 x 36 = 216
L_2 (m)	1.72 - 2.65	~2.2	0.65 - 1.35	~0.80
2θ range	28°< 2θ < 42°	13°< 2θ < 15°	130°< 2θ < 160°	83°< 2θ < 97°
Ω (ster)	0.046	0.009	0.29	0.48
Δd/d	~1x10^{-2}	~3x10^{-2}	~5x10^{-3}	~7x10^{-3}
d-range (Å)	0.5 - 8.3	0.5 - 21.6	0.2 - 3.2	0.2 - 4.0
Q-range (Å^{-1})	0.75 - 12.6	0.3 - 12.6	2.0 - 31.4	1.5 - 31.4

- Good workhorse instrument for powder diffraction
- High Q accessible for disordered materials investigation using the PDF method
- Some in situ capability but limited by count-rate
- Compatible with a wide range of restricted geometry sample environment

Polaris upgrade







- Increase primary flight path to 14 m
- Optimise each detector bank to give constant resolution
- Increase detector coverage
- Design a collimator to reduce background and parasitic scattering

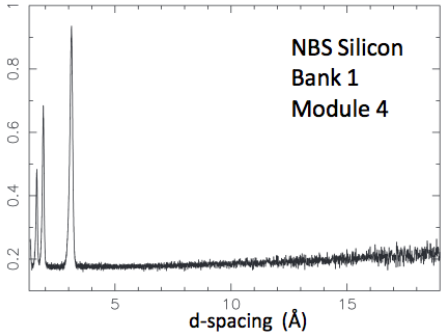
http://www.isis.stfc.ac.uk/instruments/polaris/polaris-upgrade-poster11575.pdf

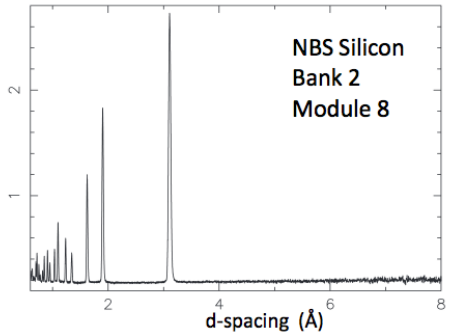
Polaris upgrade

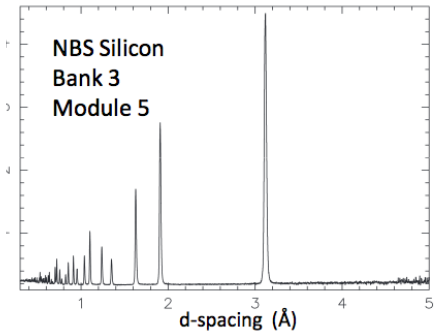
http://www.isis.stfc.ac.uk/instruments/polaris/polaris4643.html

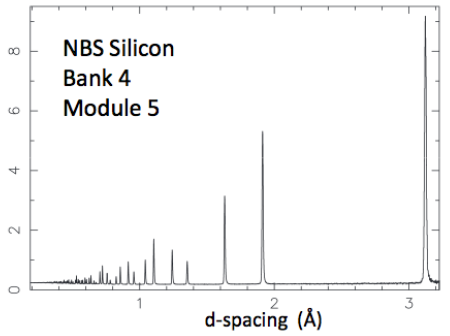
Current Polaris

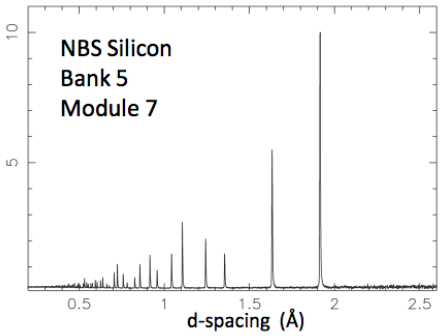
http://www.isis.stfc.ac.uk/instruments/polaris/polaris-upgrade---first-diffraction-pattern12763.pdf

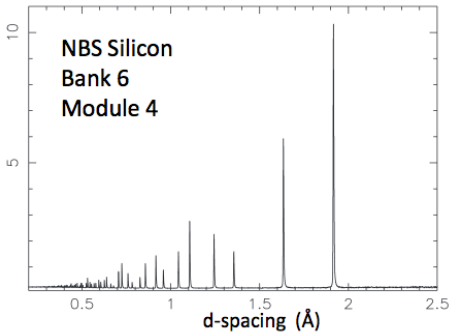


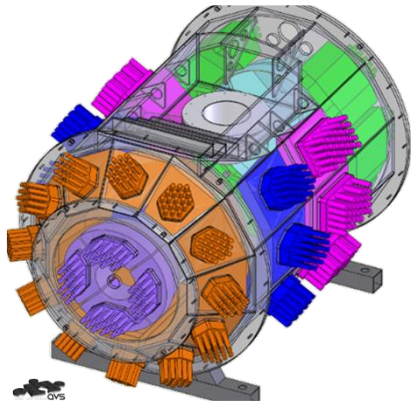












Bank 1 – cyan
Bank 2 – green
Bank 3 – pink
Bank 4 – blue
Bank 5 – orange
Bank 6 - purple

- Increased count rate ×3 at high scattering angle to >20 for low angle banks
- Resolution improvement e.g. bank 5 and 6 of 3×10^{-3} cf. 5×10^{-3}
- Improvement in data at high Q

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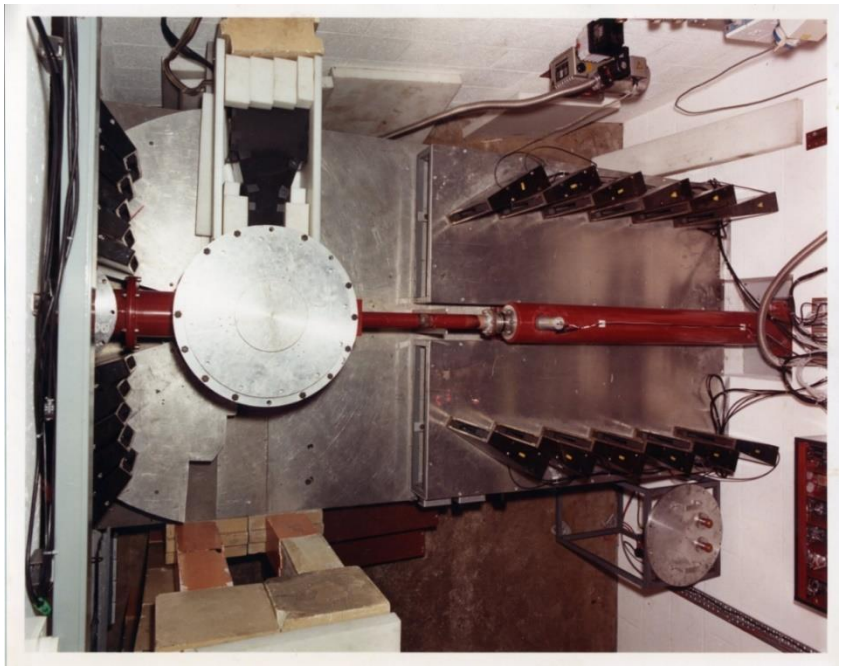
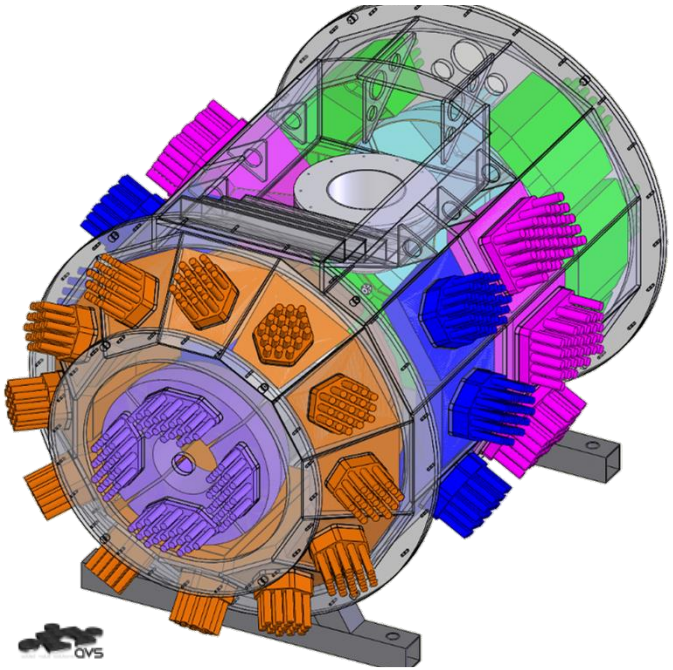
Polaris 1995 v 2013

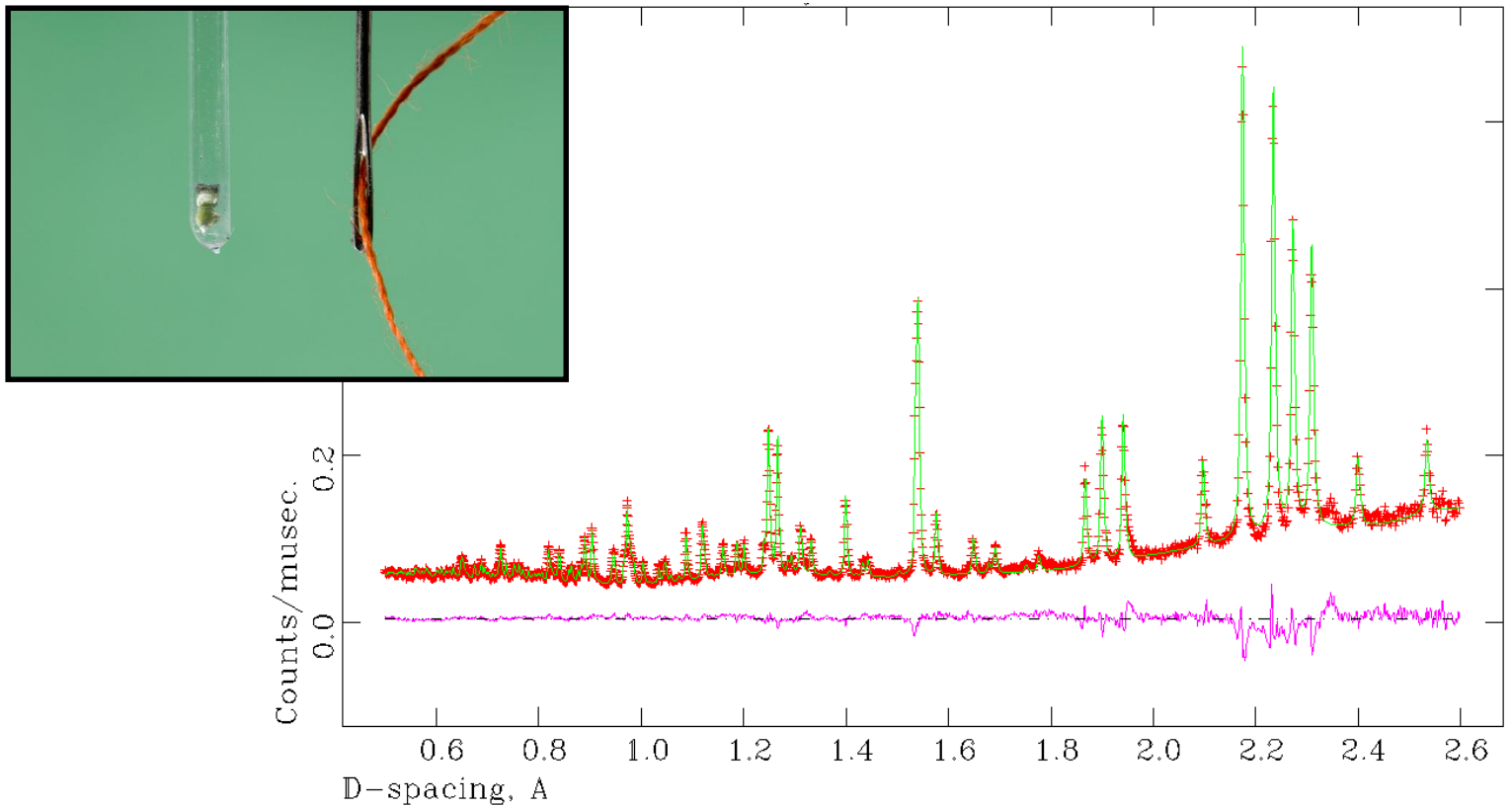




- 1995 500 mg 24+ hrs
- 2013 500 mg 15-20 minutes with increased Q-range

Contemporary instruments NOVA and iMateria (J-PARC), POWGEN-3 (SNS)

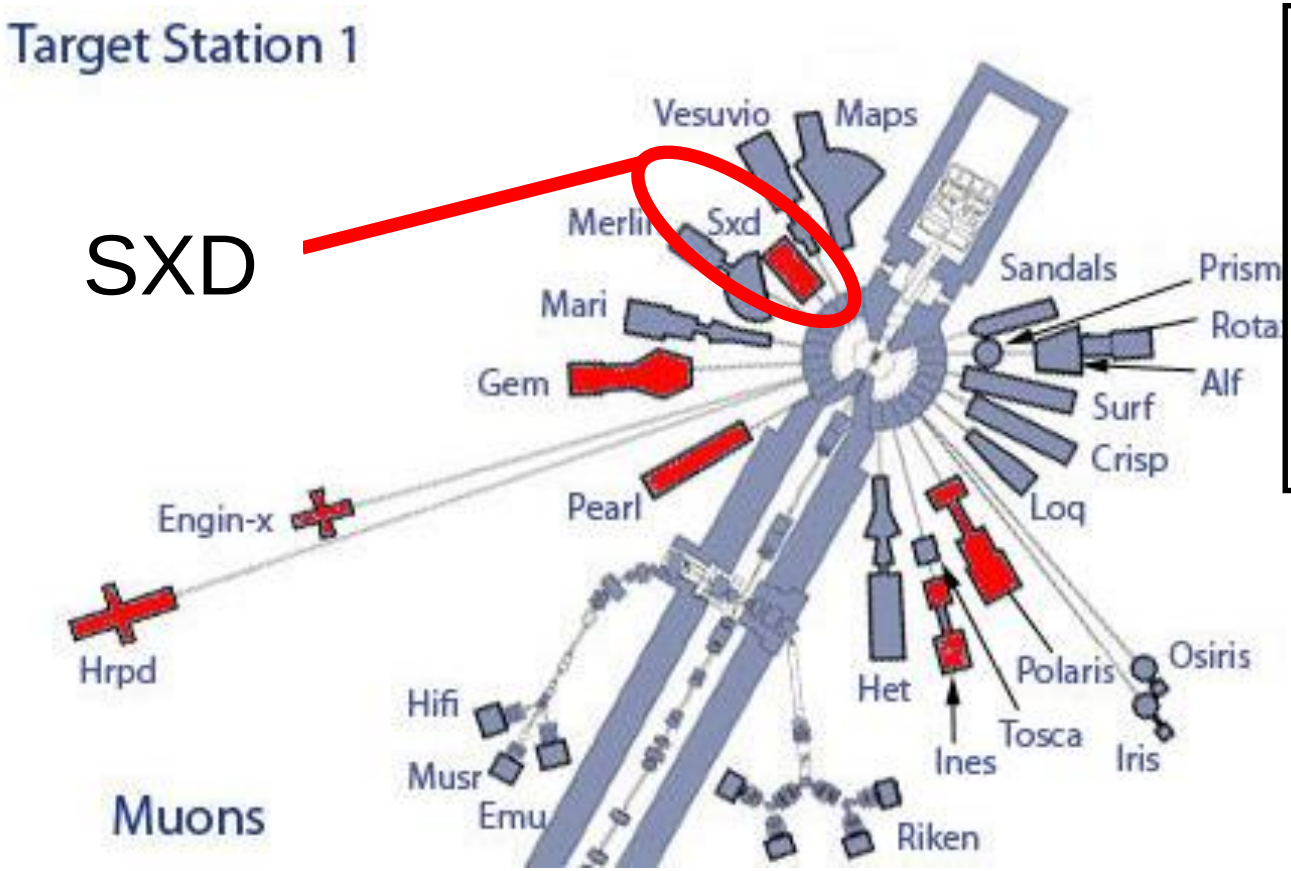
Polaris: pushing boundaries in sample size



~1mm^3 sample of $NaNiF_3$ phase prepared at high *p* + high T

Lindsay-Scott *et al*, J. Appl. Cryst., **47**, 1939 (2014)

SXD: single crystal diffraction



- chemical crystallography
- Q space mapping
- incommensurate structures
- high pressure

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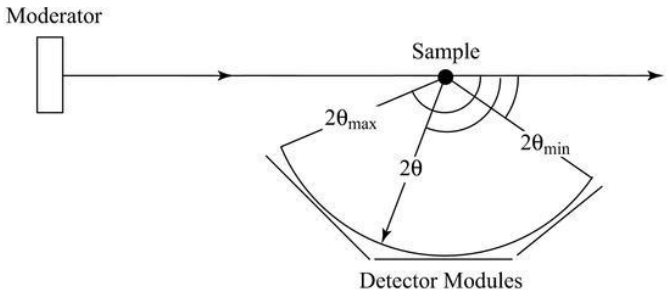
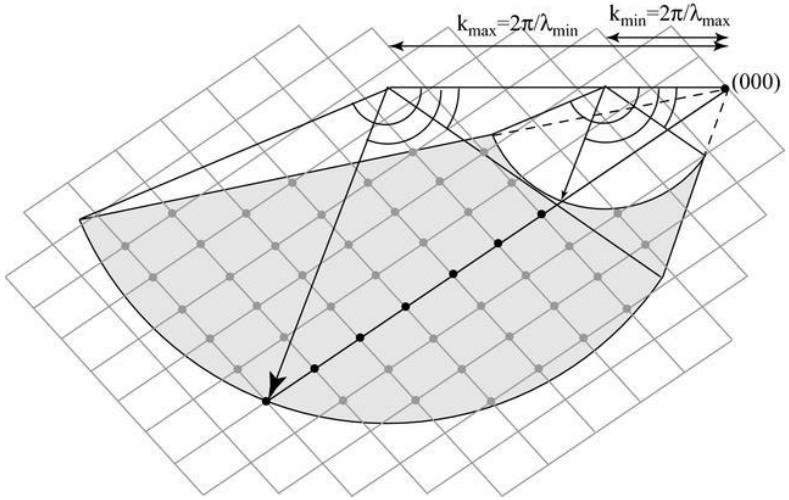
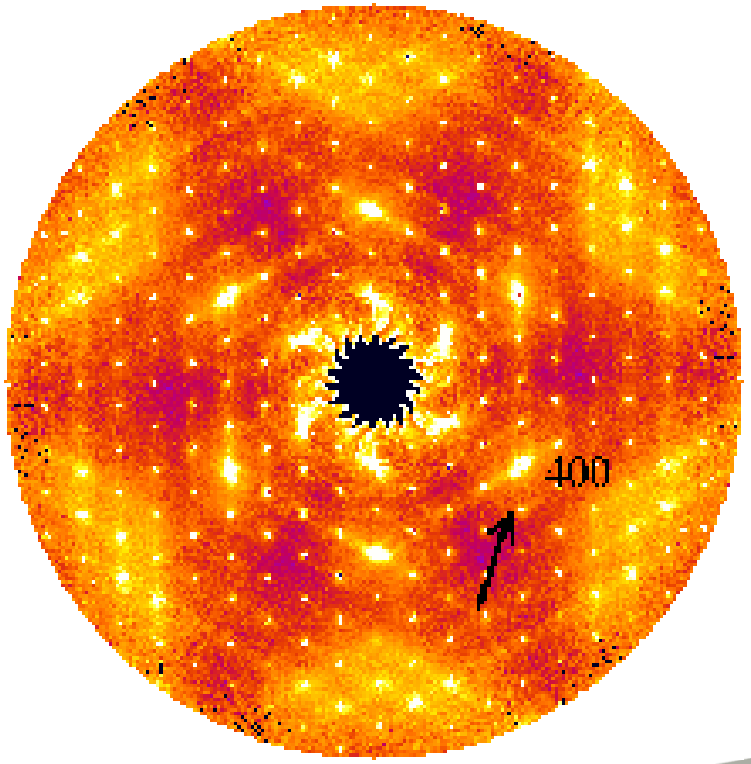
TOF Laue method

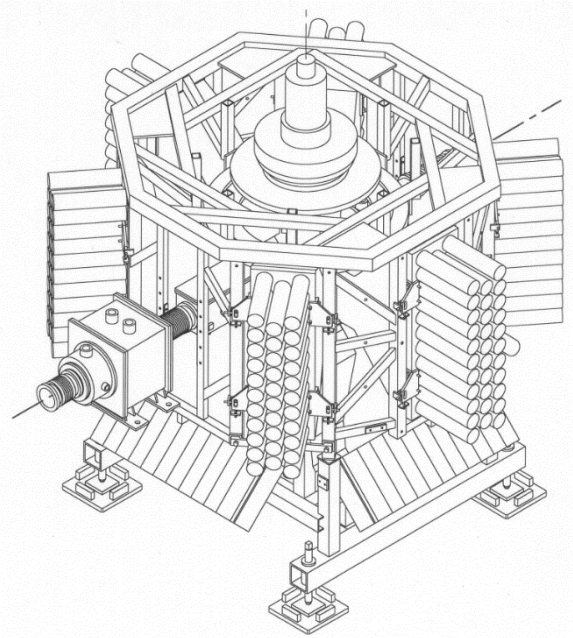
SXD uses the ‘time-of-flight Laue’ method to scan a large volume of reciprocal space at each crystal orientation.





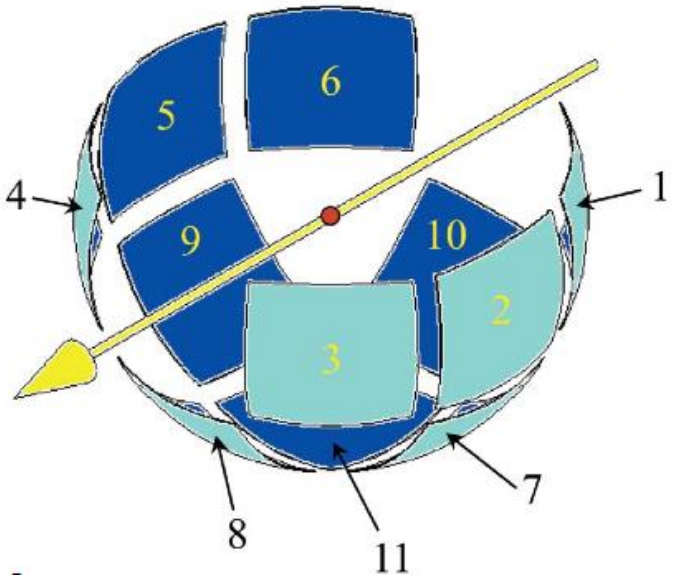


SXD: single crystal diffraction



SXD: single crystal diffraction

- H_2O moderator poisoned at 2 cm
- 0.2 – 10 Å wavelength band
- Primary flight path 8.3 m
- Beam size < 15 mm
- Eleven 192 × 192 mm^2 detectors (3 × 3 mm^2 resolution)



Unlike an image plate set-up the detectors are continuously read-out as a function of TOF allowing spatial overlap to be resolved in the TOF channel while minimising background

Keen *et al.* J. Appl. Cryst. (2006), **39**, 714-722) http://www.isis.stfc.ac.uk/instruments/sxd/sxd4813.html

Contemporary instruments: Topaz (SNS), Senju (J-Parc), Mandi (SNS)

Summary: Diffraction instruments

- Reactors build CW instruments*
  - Low peak brilliance, high time-average brilliance
  - Variable reflectivity from monochromators limit low λ use
  - High Q not easily reached
  - Match moderator and monochromator take-off angle to Q range and resolution
  - Beam always on

*Except when significantly restricted geometry constraints from science case necessitate use of TOF

- Pulsed sources build TOF instruments#
  - High peak brilliance, low time-averaged brilliance
  - Require efficient beam transport
  - High Q possible
  - Increase instrument length to improve resolution at expense of bandwidth
  - Variable Q range and resolution from detector angles
  - Beam availability can compromise science

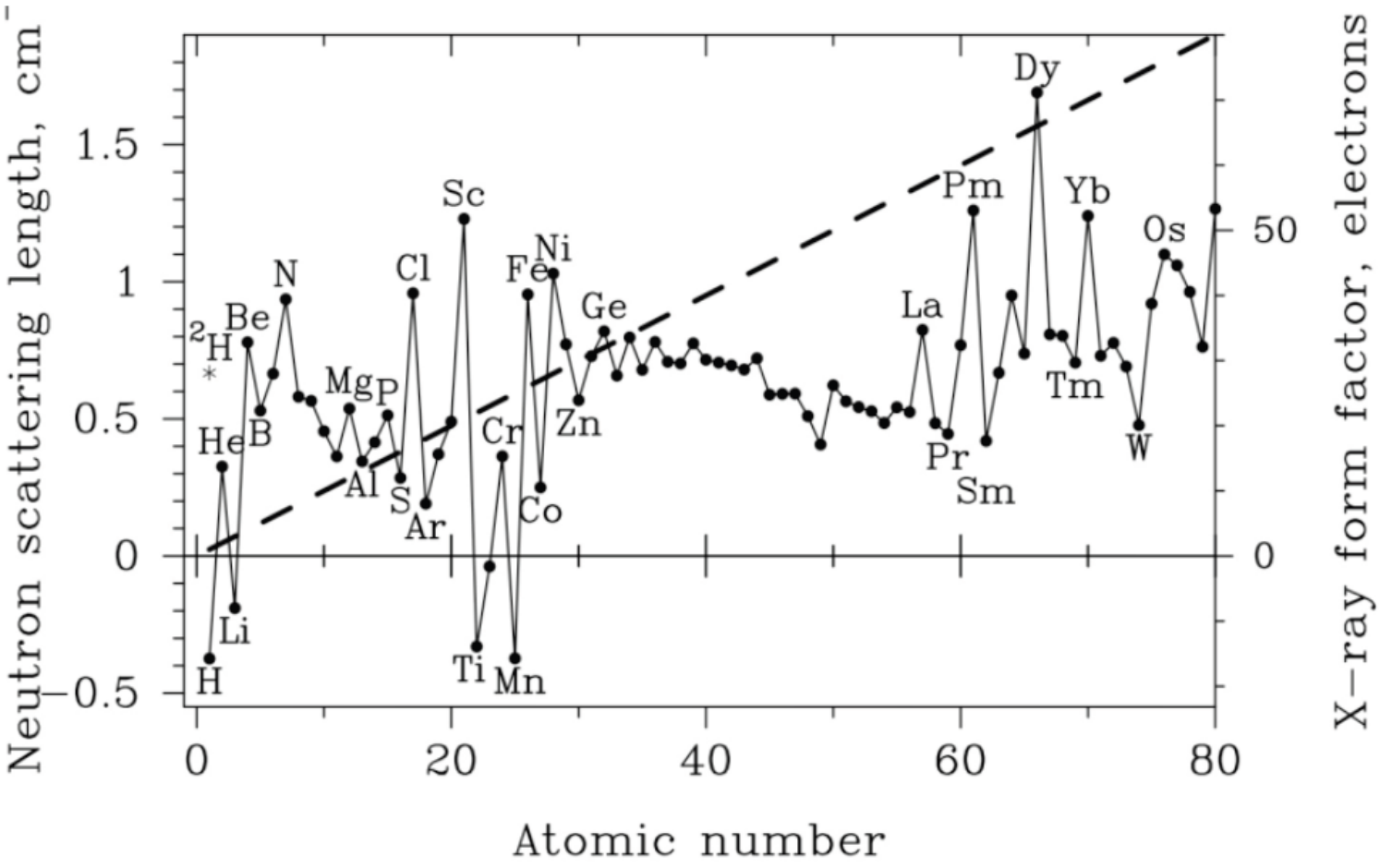
#Remains to be seen for long pulse sources

Extra Information 1: Uses of diffraction

Uses of diffraction

- Check purity of a sample
- Identify known phases
- Identify new phases
- Collect data for structural analysis
- Follow phase transitions
- Construct phase diagrams (T, P, B, etc)
- Study chemical processes *in situ*
- Monitor particle sizes
- Analyse residual stress within materials
- Process control
- Etc…

X-ray vs neutron scattering power



https://www.ncnr.nist.gov/resources/n-lengths/

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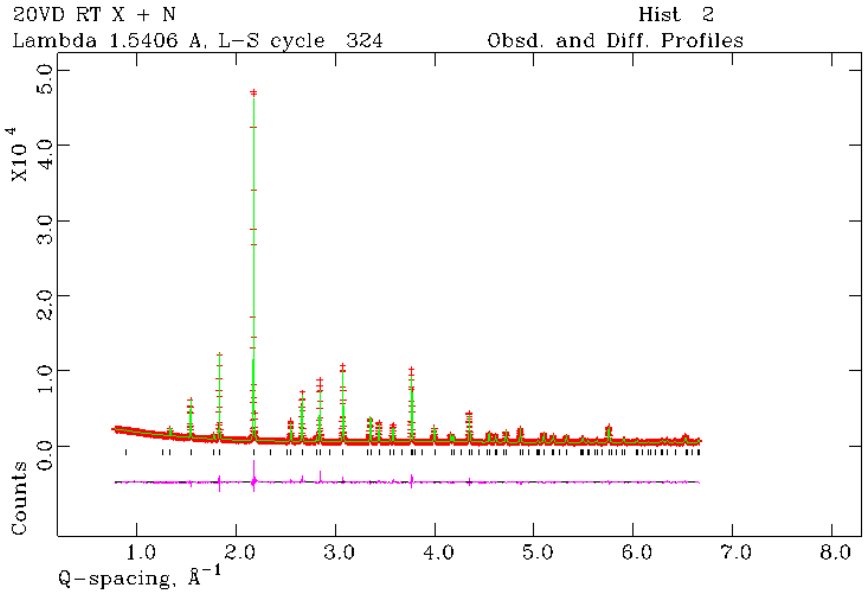
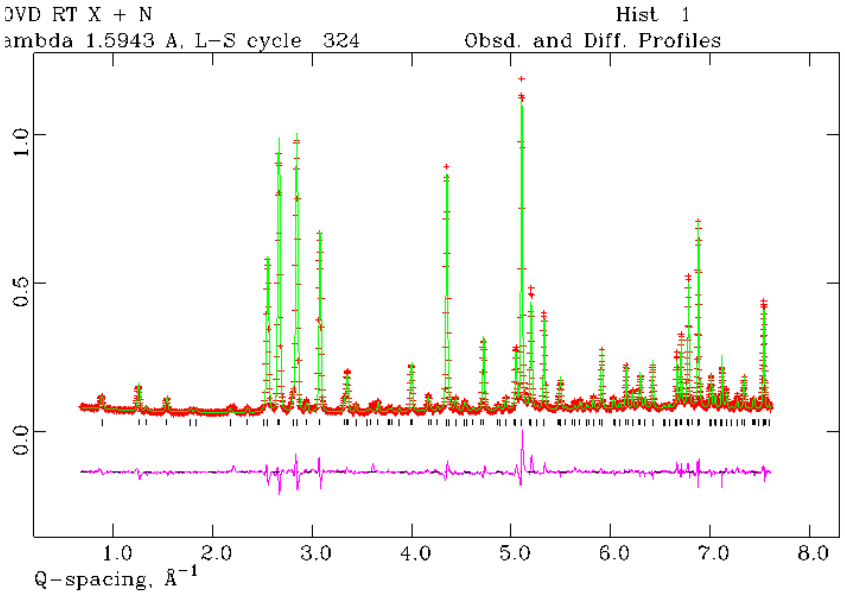
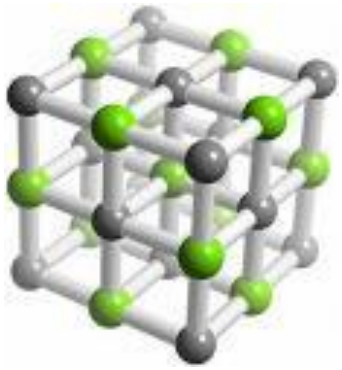
Complementarity of neutrons and X-rays





Note peak intensity differences – complementary information
Main peak in X-ray data (left) almost zero intensity in neutron pattern (right)
Scattering to higher Q in neutron data (form factor)

Neighbouring Element Discrimination



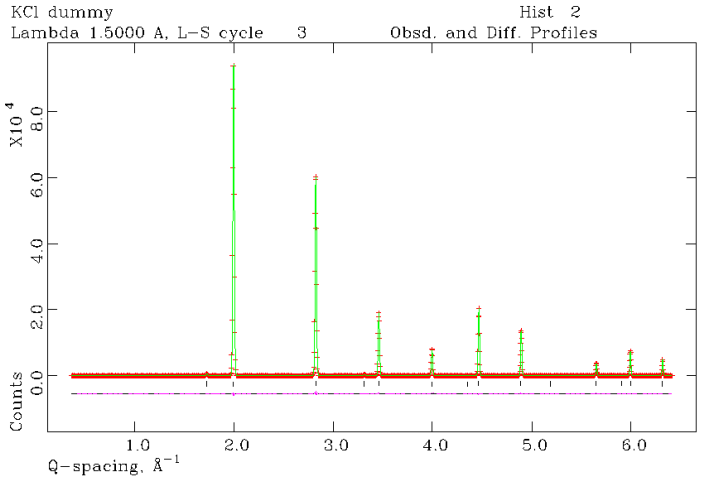
KCl

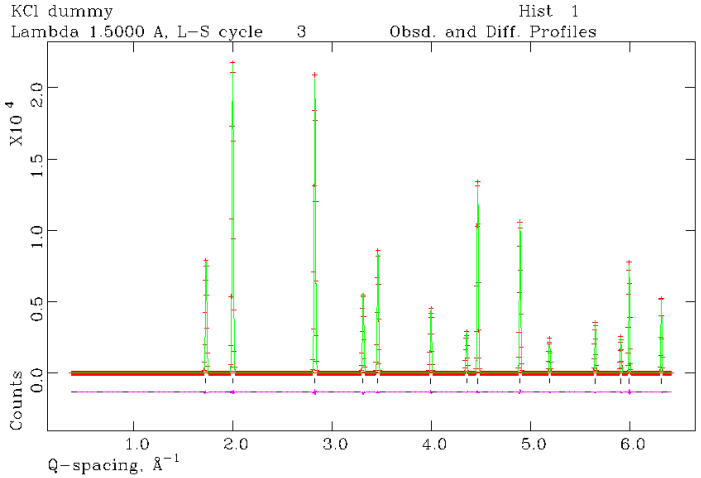
Fm-3m *a* = 6.29 Å

K z = 19

Cl z = 17

But $K^+ = Cl^- = 18\ e^-$

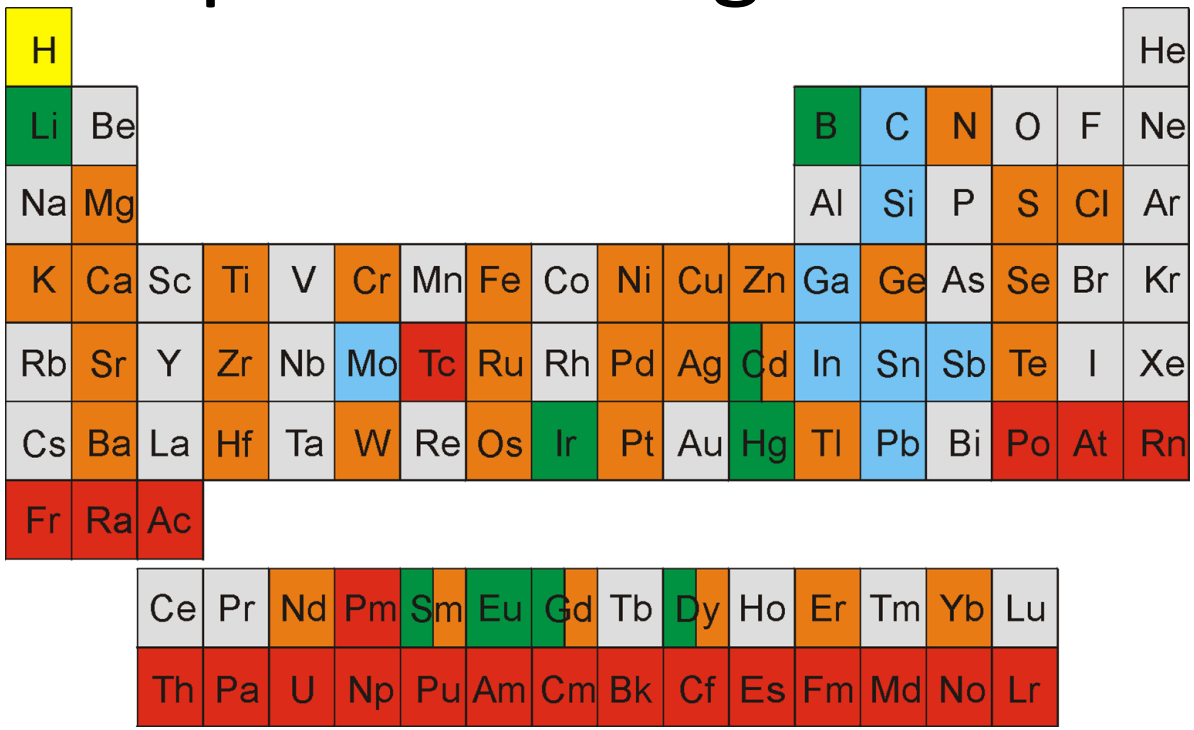




Without care KCl indexes from X-ray data on a cell that is ½ that from neutron data as elements are identical to X-rays as both have 18 e^-

The non-linear relationship of neutron scattering length between neighbouring elements is crucial

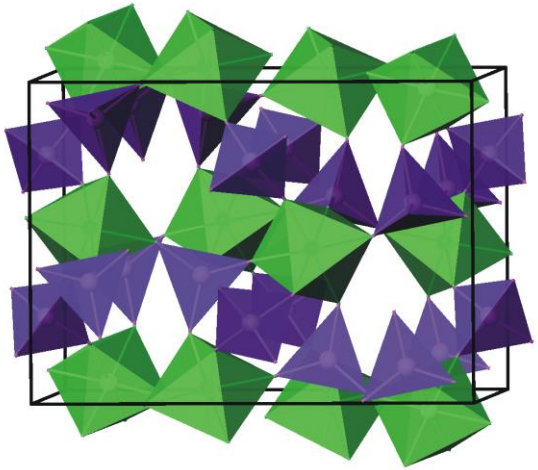
Isotope scattering contrast



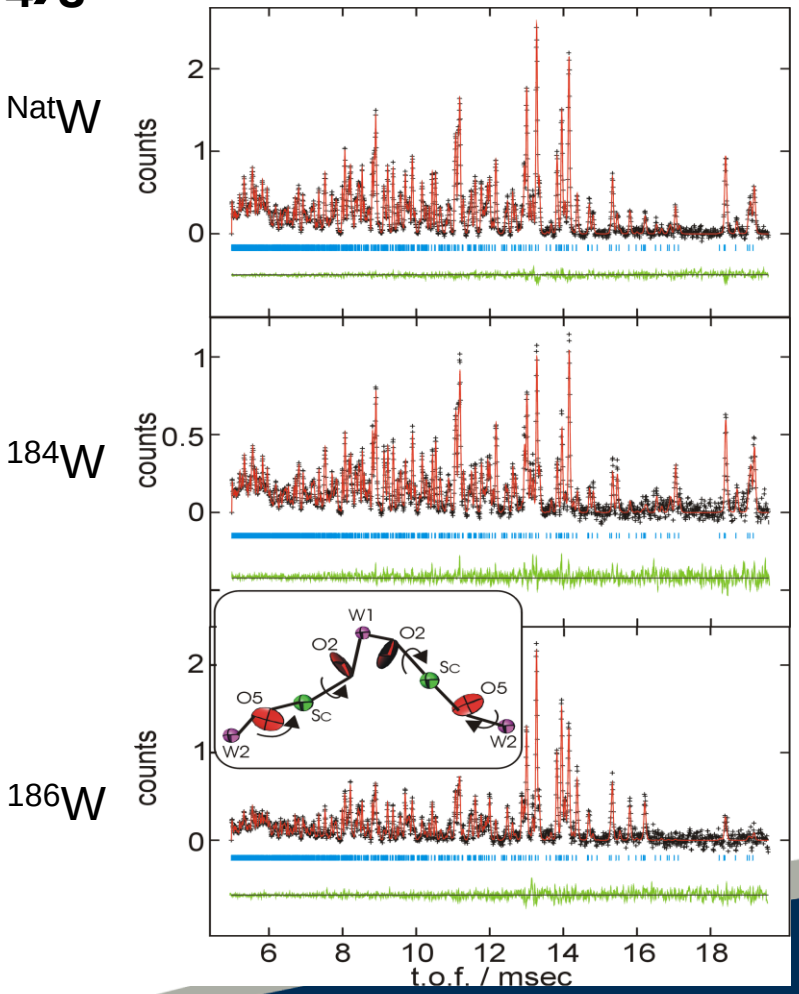
- > 20% scattering length contrast isotopes
- 5-20% scattering length contrast isotopes
- Non-absorbing isotopes available
- Non-incoherent scattering isotope available
- Mono-isotopic elements
- Radioactive elements

Isotopes have different scattering properties for neutrons

Example: Origin of Negative thermal expansion in $Sc_2(WO_4)_3$



- Resolved co-operative atomic displacements
- First example using PND
- 10 years later same experiment possible without ISND on upgraded instrument HRPD



M.T. Weller, P.F. Henry, C.C. Wilson. *J. Phys. Chem. B* 2000, **105(51)**, 12224-12229

Science & Technology Facilities Council
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Single crystal or powder?

Depends on the scientific problem:

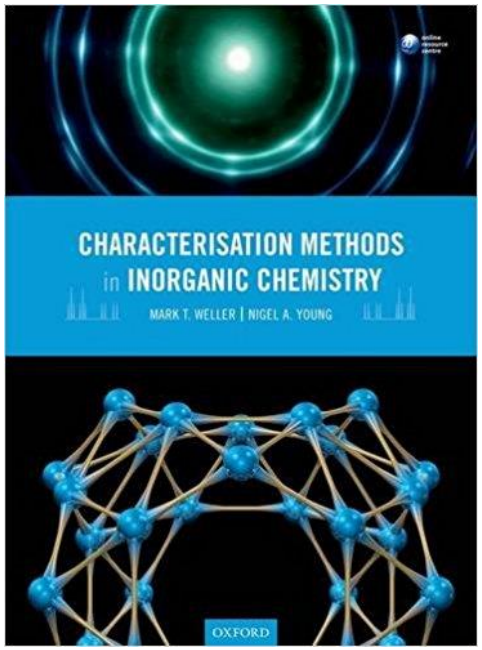
- Unambiguous structure determination – single crystal
  - Beware extinction and absorption issues
- In situ studies – powders
  - Generally the only practical option
- Fast measurements – powders
  - Larger samples
- High background materials (such as incoherent scattering) – single crystal
  - BUT is possible with powder
- Multi-component systems investigations – powder
- Structural phase transitions – powder
  - Crystals tend to shatter
- Real systems – powders
- Very small samples – single crystal
  - Can become difficult to get a powder average

CW or TOF?

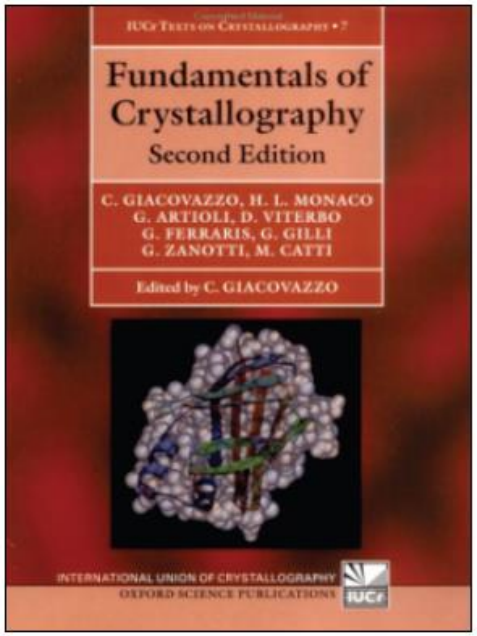
Depends on the scientific problem:

- Structure refinement – either but TOF preferred as complexity increases
- *In situ*, time resolved studies – CW
- Parametric studies – either but CW probably faster for T, P, B mapping
- Fast measurements – either (flux for CW, detector coverage for TOF)
- Small samples – either (lowest background instrument)
- PDF studies – TOF to access high Q
- Magnetic structures – CW preferred but TOF catching up
- Polarised neutron work – traditionally CW but TOF developing
- Hydrogenous materials – CW still preferred but TOF developing
- Large unit cells – either source type, but use Laue methods (quasi-TOF)
- High pressure – TOF offers wider Q range, CW higher flux
- Engineering applications – either, pick depending on Q range
- Texture – either but requires specialized instrument

Summary: further reading



Weller & Young
Chapter 2



Giacovazzo *et al.*
Chapter 1

Pecharsky & Zavalij
Chapters 1-9

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Extra Information 2
(Structure solution & refinement)

Intensity and structure factor

$$I_{hkl} \propto |F_{hkl}|^2$$

Measured intensity proportional to F_{hkl}^2 and so we cannot tell whether F_{hkl} is positive or negative – the Phase problem

$$F_{hkl} \propto \Sigma f_i \exp[2\pi i(hx_i + ky_i + lz_i)] \exp(-U_i Q^2/2)$$

f_i is the scattering power (form factor of the ith site i.e. (x_i,y_i,z_i) and incudes fractional occupancy

Contribution of the ith site to the F_{hkl} in question

Atomic displacement of the ith atom site

The phase problem

$$I_{hkl} \propto |F_{hkl}|^2$$

In diffraction we measure the magnitudes and not the phase. The phases contain the bulk of the information. This is why crystallography is hard….

…but not impossible. We can recover phase information from:

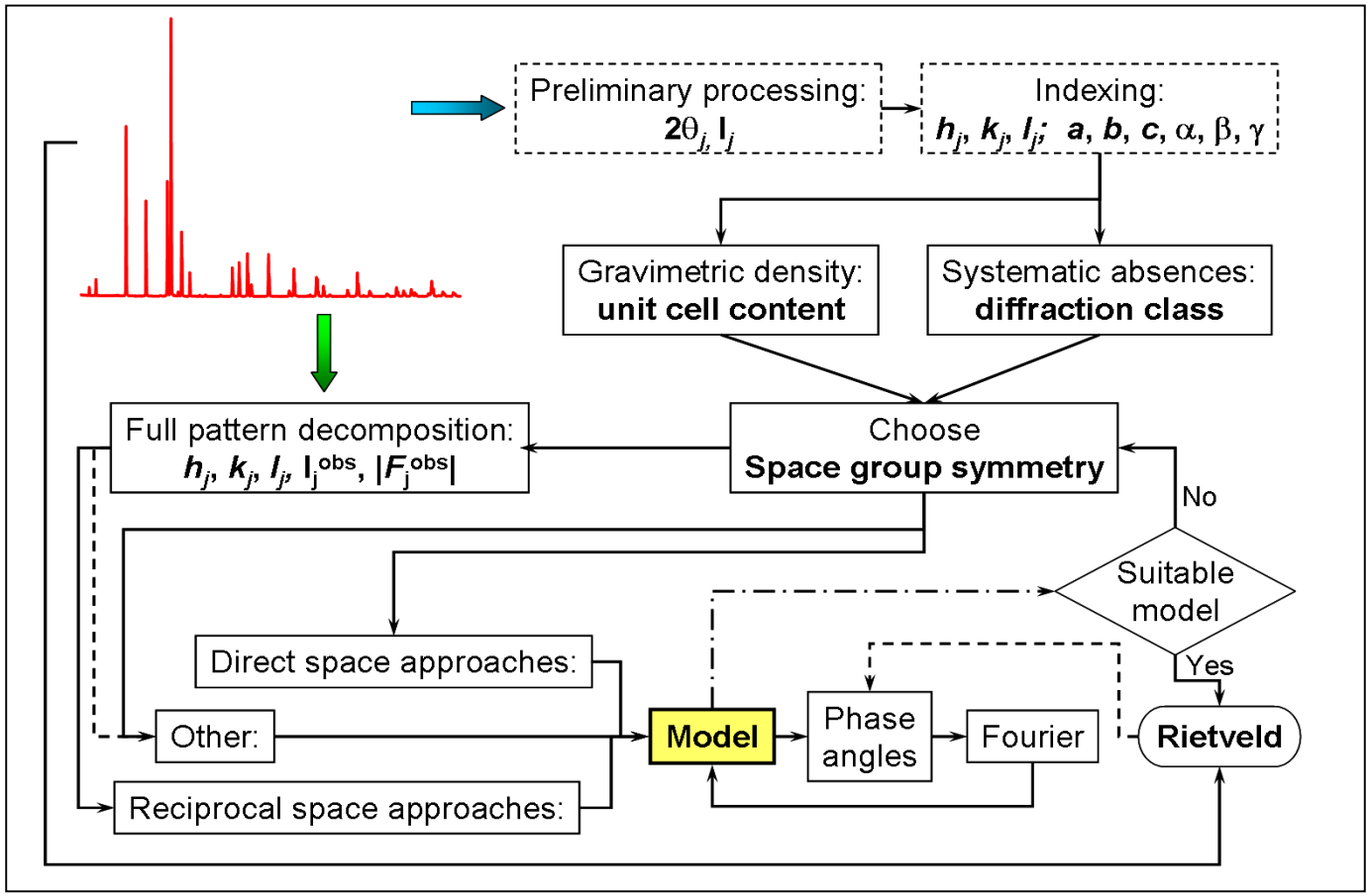
- Related or isostructural materials
- Knowledge of atom positions (heavy atoms from X-rays)
- Known motifs (molecules)
- Brute force

Other factors contributing to measured intensity

$$I_K = S M_K L_K |F_K|^2 P_K A_K E_K$$

- S is an arbitrary scale factor
  - used to adjust the relative contribution of individual phases to the overall diffraction pattern
- M is the multiplicity of the reflection
  - accounts for the fact that some observed diffraction peaks are actually the product of multiple equivalent planes diffracting at the same position 2θ (for example, (001) (100) (010) etc in cubic)
  - automatically calculated based on the crystal structure
- L is the Lorentz polarization factor
- P is the modification of intensity due to preferred orientation
- A is the absorption correction
- E is the extinction correction
- F is the structure factor, which is the amplitude of the scattering due to the crystal structure

Process for structure solution



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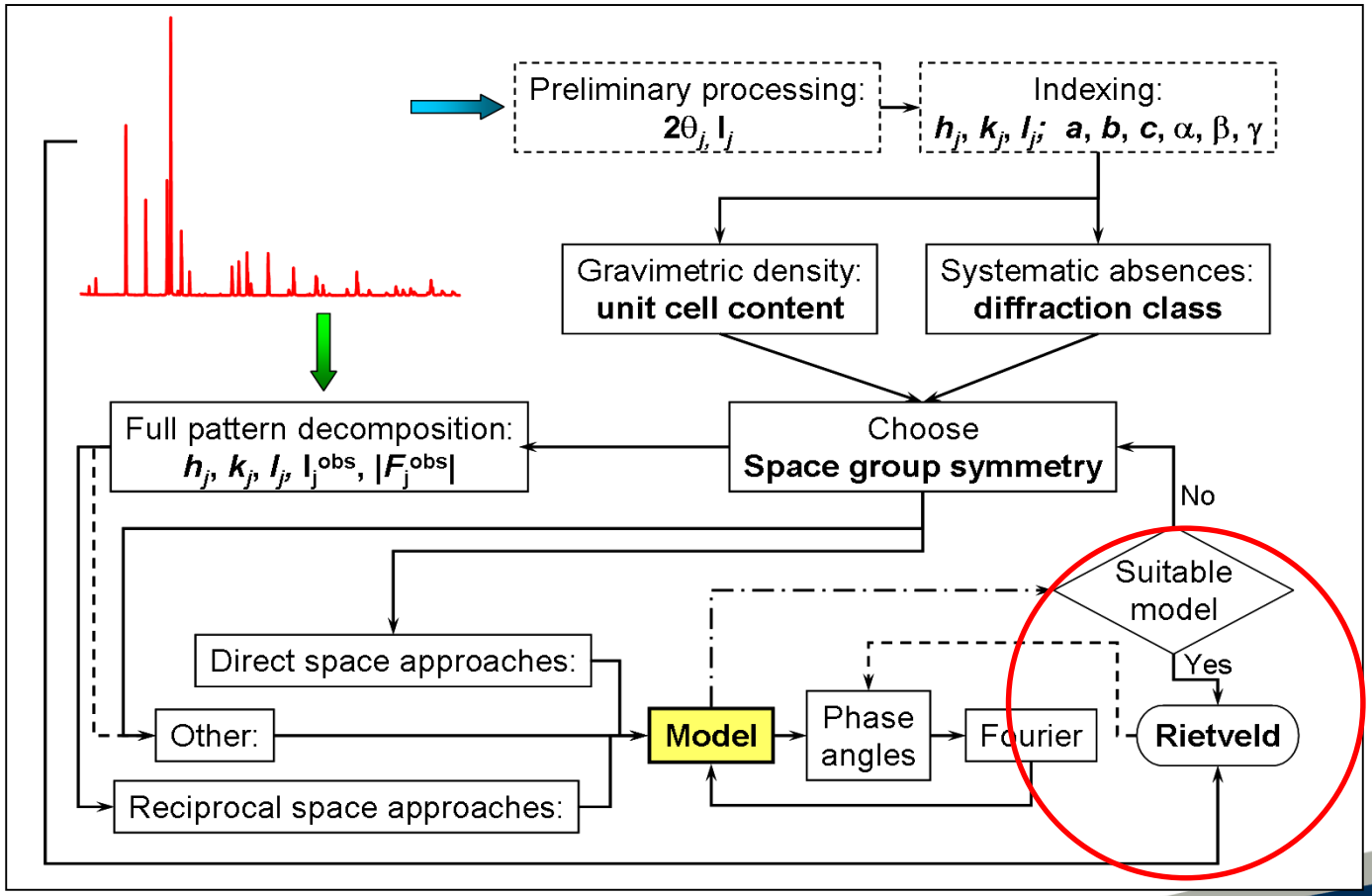
Structure refinement



Structure solution/refinement

To unambiguously solve a structure the ratio of resolved and observed unique Bragg reflections to crystallographically independent atoms should be at least 10.

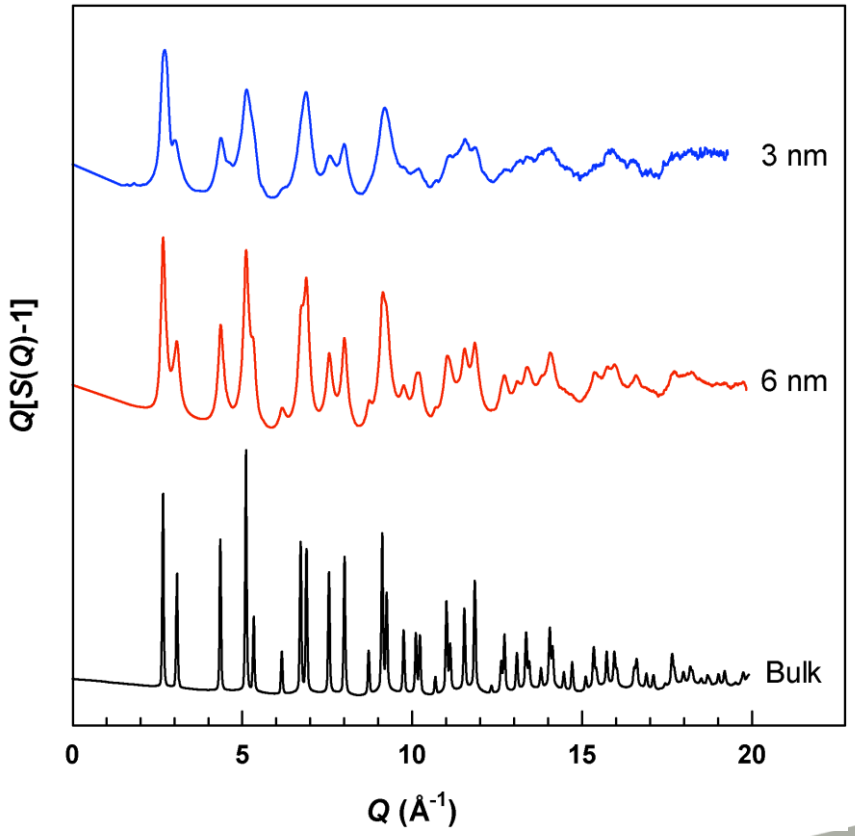
Crystal / powder sample requirements:

- Diffract out to beyond Q_{max} of the instrument
- Be of adequate particle size
- Preferably not contain any local ordering

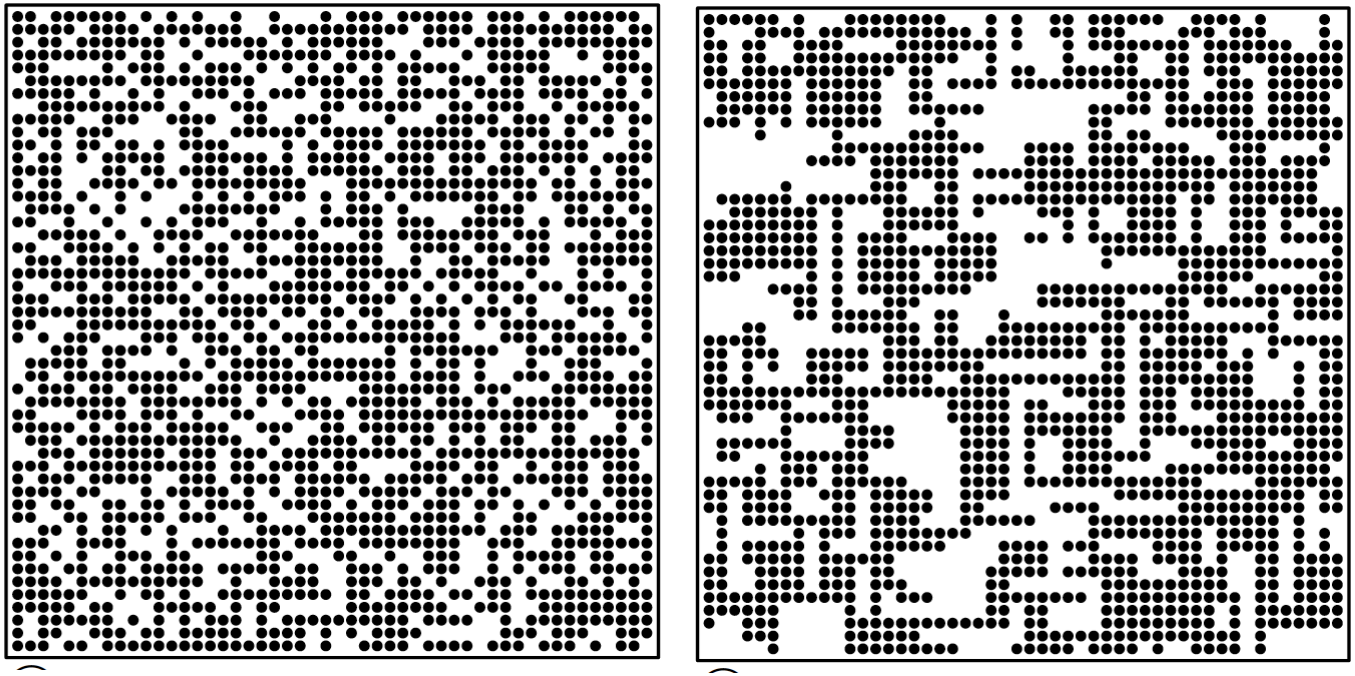
Instrument requirements:

- Access a Q_{max} such that ratio of accessible Bragg reflections to crystallographically independent atoms is met
- Have a Q-resolution to resolve these Bragg reflections
- Be able to accurately measure the Bragg reflection intensity above the background

Particle size effect

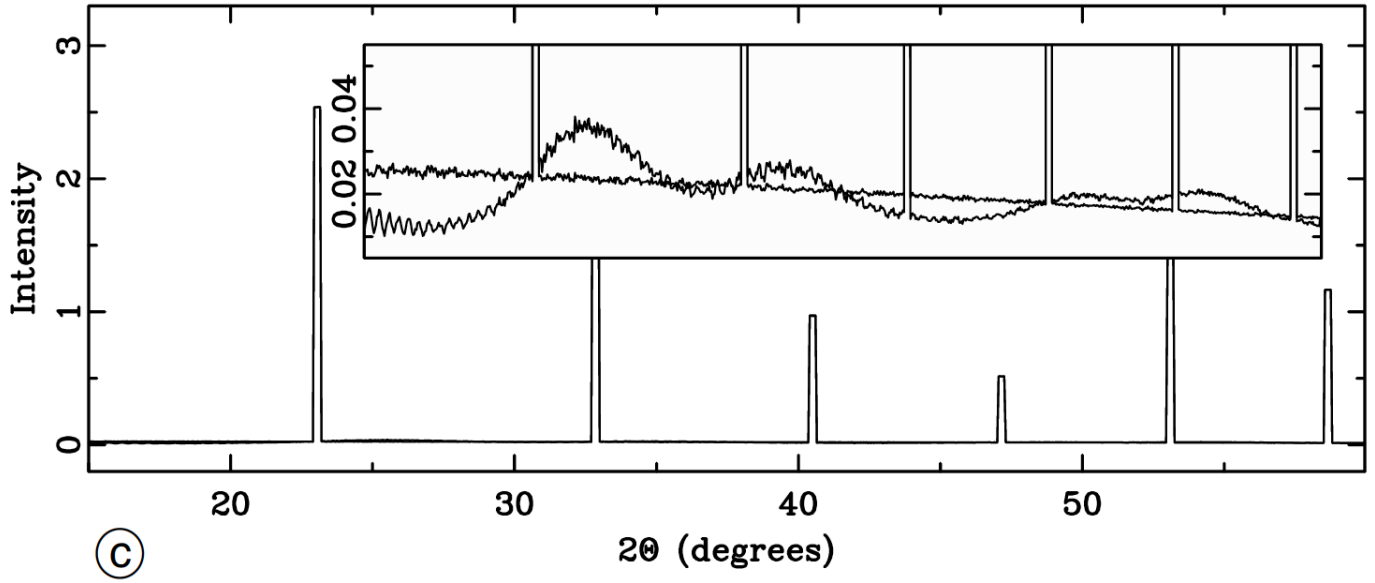


Local Order



(reproduced from Proffen *et al.* (2003). *Z. Kristallogr.* **218**, 132-143)

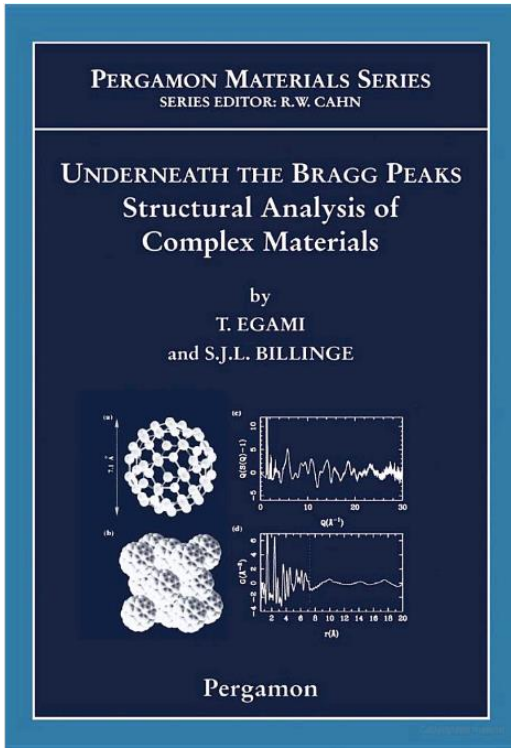
Local order



Diffuse scattering contributions appear between the Bragg reflections. This is ignored by the standard crystallographic approach, which only yields the long range average structure.

(reproduced from Proffen *et al.* (2003). *Z. Kristallogr.* **218**, 132-143)

Pair distribution function (PDF) analysis



The PDF is obtained from the powder diffraction data via a sine Fourier transform of the normalized scattering intensity $S(Q)$:

$$G(r) = 4\pi r[\rho(r) - \rho_0]$$
$$= \frac{2}{\pi}\int_0^\infty Q[S(Q) - 1]\sin(Qr)\,\mathrm{d}Q\,, \qquad (1)$$

where $\rho(r)$ is the microscopic pair density, ρ_0 is the average number density and Q is the magnitude of the scattering vector. For elastic scattering $Q = 4\pi \sin(\theta)/\lambda$ with 2θ being the scattering angle and λ the wavelength of the radiation used.

http://www.totalscattering.org

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The Rietveld method

J. Appl. Cryst. (1969). **2**, 65

A Profile Refinement Method for Nuclear and Magnetic Structures

BY H. M. RIETVELD

Reactor Centrum Nederland, Petten (N.H.), The Netherlands

(*Received* 29 *November* 1968)

A structure refinement method is described which does not use integrated neutron powder intensities, single or overlapping, but employs directly the profile intensities obtained from step-scanning measurements of the powder diagram. Nuclear as well as magnetic structures can be refined, the latter only when their magnetic unit cell is equal to, or a multiple of, the nuclear cell. The least-squares refinement procedure allows, with a simple code, the introduction of linear or quadratic constraints between the parameters.

Hugo M. Rietveld 1932-2016

- Originally written to analyse neutron powder diffraction data
- Both nuclear and magnetic structure refinement
- Adapted for X-ray methods in 1977 by Young
- Thousands of publications per year published using the method
- It is the reason powder crystallography is so successful!!

"NASA would never have sent an X-ray powder diffractometer to Mars without the Rietveld method" (David Blake, 2012)

Rietveld refinement software

Many programs out there. Well used examples include:

- GSAS
- GSAS-II
- Fullprof
- Topas
- Jana
- Maud
- Reitan
- BGMN
- Etc…

The Rietveld method

What it is not:

- A phase identification tool – use databases for this
- For structure solution – it refines a given structural model to data

What it can tell us:

- Phase fractions
- Unit cell dimensions
- Atomic coordinates / bond lengths / substitutions and vacancies
- Strain and texture effects

What you need:

- Good quality data
- A good starting structural model
- An instrument description file

The Rietveld method

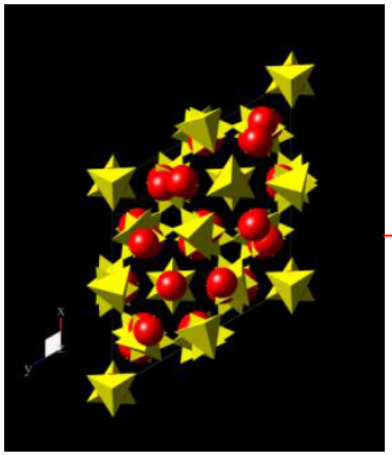
- The intensity, Y_{ic}, of each individual data point *i* is calculated using the equation:

$$Y_{ic} = Y_{ib} + \sum_{k=k1}^{k2} G_{ik} I_k$$

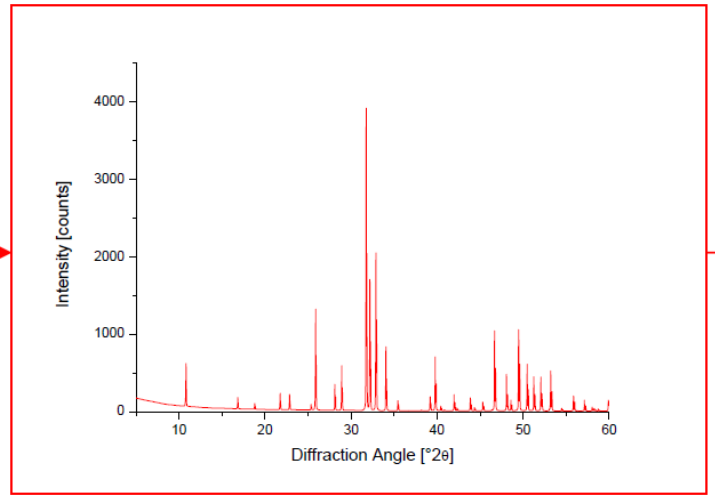
- We already know how to calculate I_K, the intensity of the Bragg diffraction peak k: $I_K = SM_K L_K |F_K|^2 P_K A_K E_K$
- Y_{ib} is the intensity of the background at point *i* in the pattern
- k1 - k2 are the reflections contributing to data point *i* in the pattern
  - sometimes multiple Bragg diffraction peaks overlap, resulting in multiple contributions to the observed intensity at a single data point
- G_{ik} is the peak profile function
  - this describes how the intensity of the diffraction peak is distributed over a range of 2theta rather than at a single point
  - this profile is due to instrument broadening, sample broadening, etc

The Rietveld method

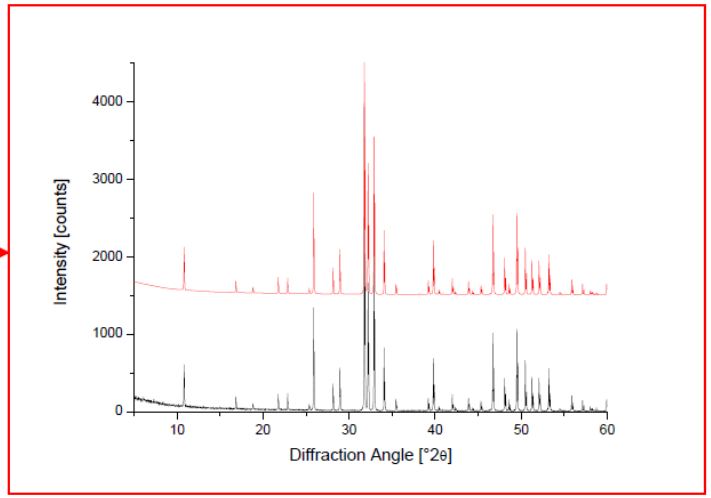
Known structure model



Calculate theoretical diffraction pattern



Compare with measured pattern



Optimize structure model, repeat calculation

Basic refinement procedure

Experimental diffraction pattern

Starting crystal structure (.cif, ICSD)

Instrument file (.inst, LaB_6 standard)

Refine:

- Background
- Lattice parameters
- Peak intensities
- Peak shapes
- Peak positions
- Phase fractions

Assess:

- Goodness of fit/R factors
- Impurity phases
- Peak/background shapes
- Difference pattern

bad peak position

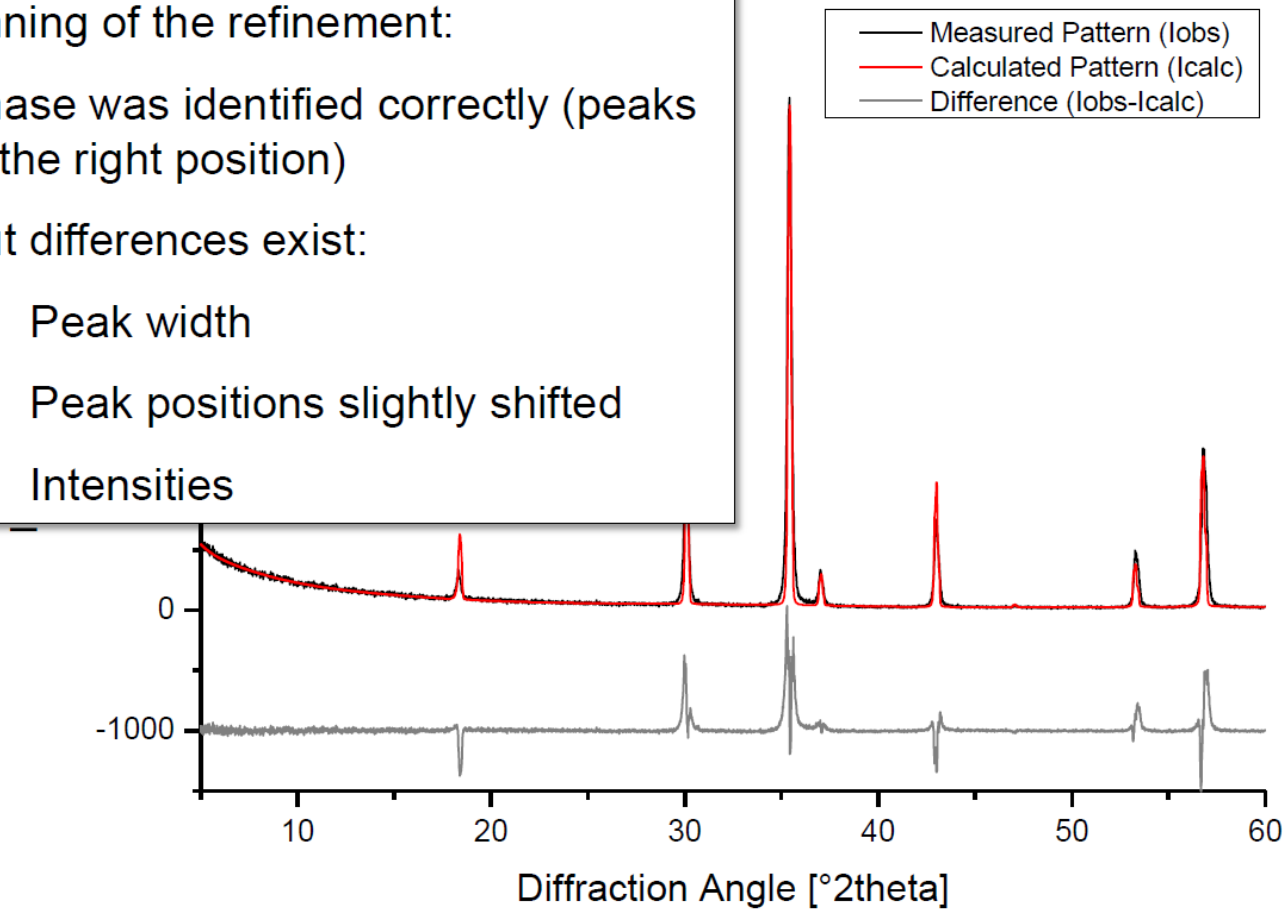
poor peak shape

peak intensities are off

Initial model

Beginning of the refinement:

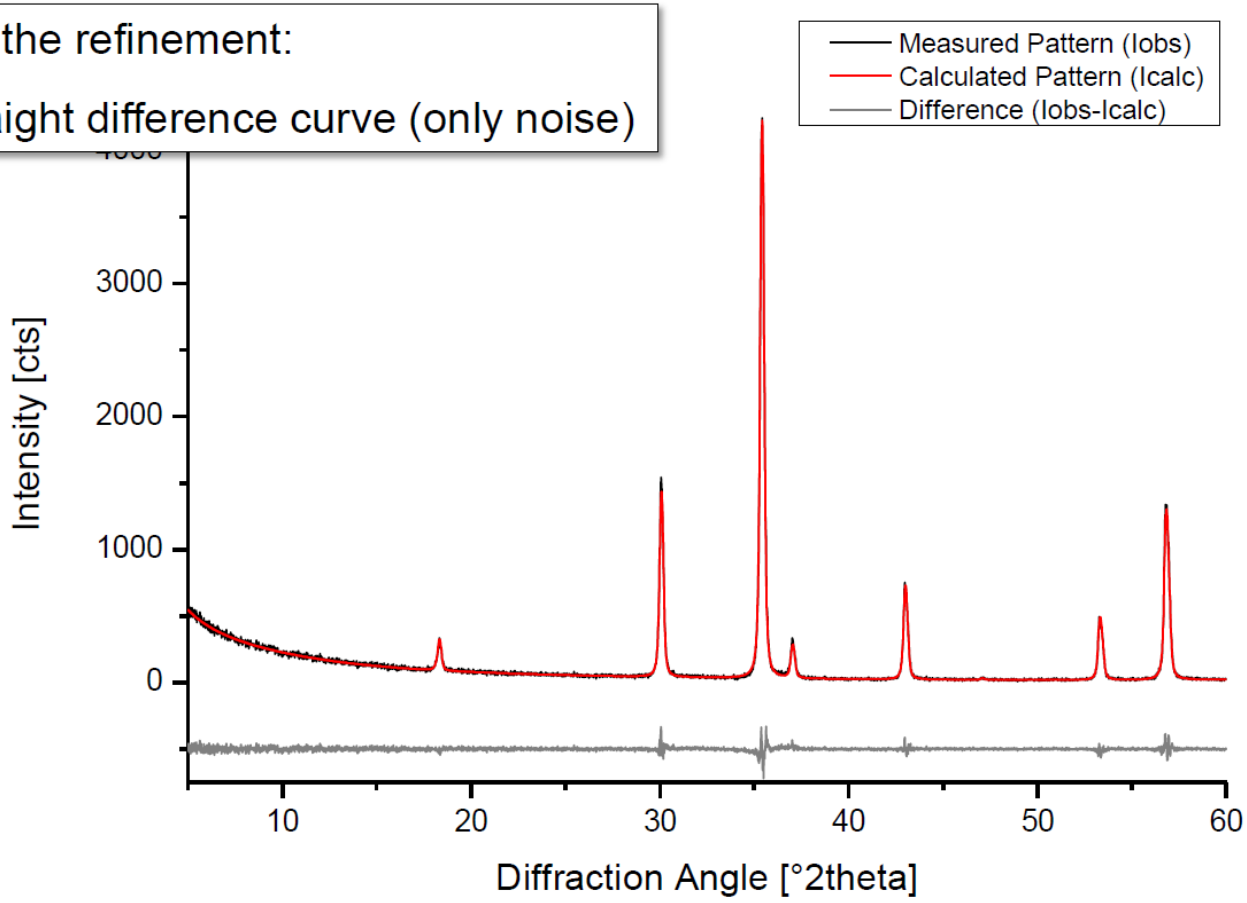
- Phase was identified correctly (peaks at the right position)
- But differences exist:
  - Peak width
  - Peak positions slightly shifted
  - Intensities



Final refined model

After the refinement:

- Straight difference curve (only noise)



Some common challenges/problems

- Incorrect starting crystal structure
- Poor quality data!
- False minimas
- Refinement diverges (“blows up”)
- Over interpretation
- Refine unnecessary variables
- Parameter correlation
- Which goodness of fit to choose? R vs. Chi sq?
- Preferred orientation
- High background
- Ignores non-Bragg diffraction peak information

Summary: complete guide for Rietveld refinement

36

J. Appl. Cryst. (1999). **32**, 36–50

Rietveld refinement guidelines

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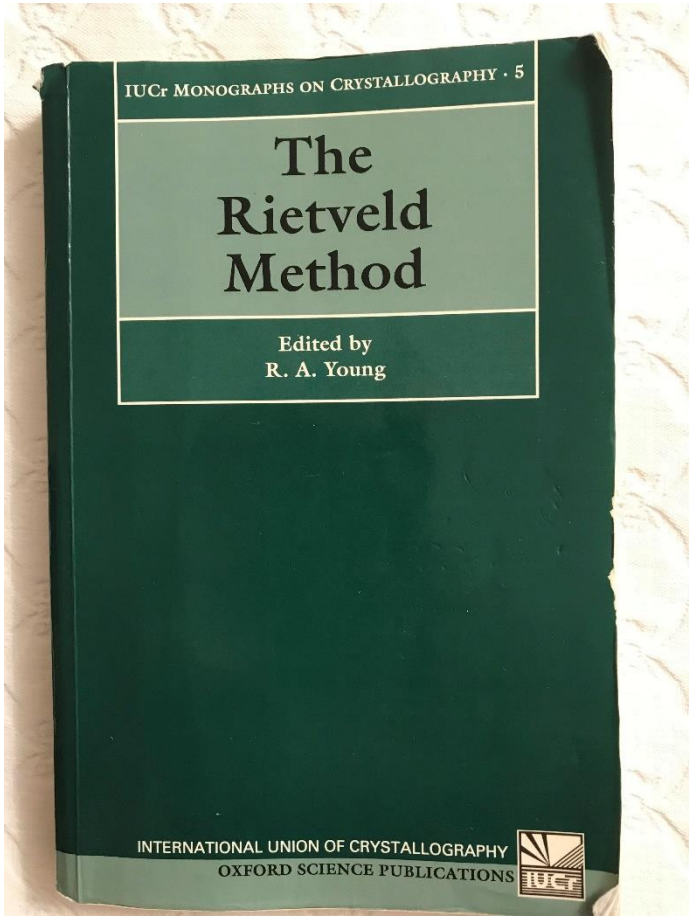
(*Received 23 February 1998; accepted 22 July 1998*)

Background and theory



Extra Information 3

(CW v TOF for resolution)
(ILL and ISIS diffraction suites)

CW or TOF: Q resolution

Monochromatic

$$\frac{\Delta d}{d} = \frac{1}{2}\sqrt{U.\cot^2(\theta) + V.\cot(\theta) + W}$$

- U, V and W are functions of the collimation and U, V also takeoff angle to the monochromator
- Resolution minimum found near the takeoff angle of the monochromator $2\theta_M$
- Higher takeoff angle gives higher resolution for identical wavelength
- Wavelength produced by monochromator is takeoff angle dependent for any particular hkl plane

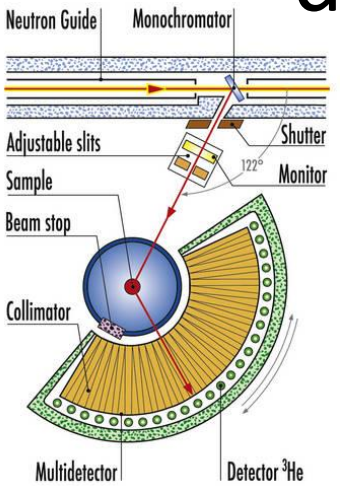
Time-of-flight

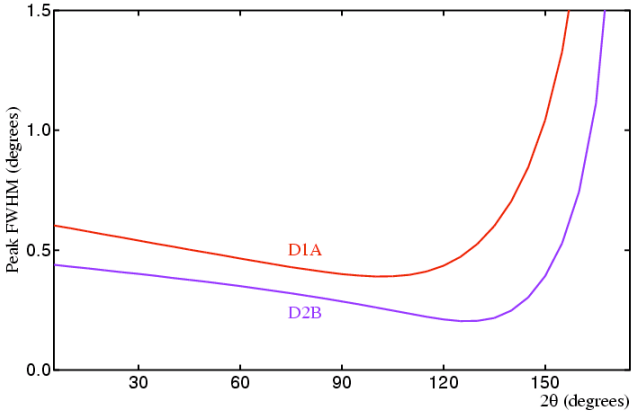
$$\Delta d/d = \left[\Delta\theta^2 \cot^2\theta + \left(\Delta t/t\right)^2 + \left(\Delta L/L\right)^2\right]^{1/2}$$

- $\Delta\theta$ is the angular uncertainty
- The main component of Δt is the moderation time of the neutron
- ΔL is the flight path uncertainty of the neutron mainly due to the finite width of the moderator
- First term can be minimised by moving to higher scattering angle
- Second and third terms minimised by increasing instrument length

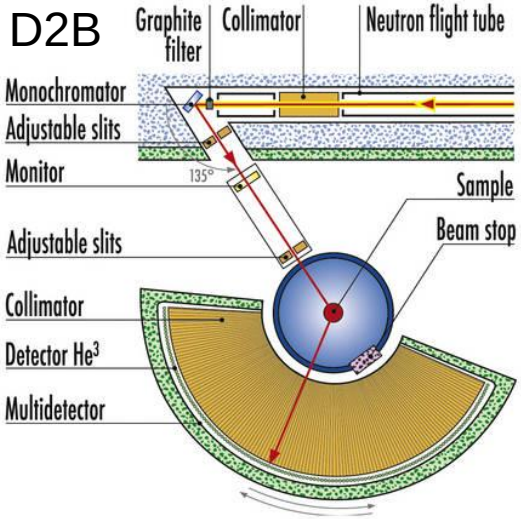
CW, High resolution, thermal powder diffractometers: D1A, D2B

D1A





D2B



Science: Inorganics, small molecule, magnetism,
Q range up to about 12 Å^{-1}

http://www.ill.eu/instruments-support/instruments-groups/

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CW, High resolution powder diffractometers: D1A, D2B

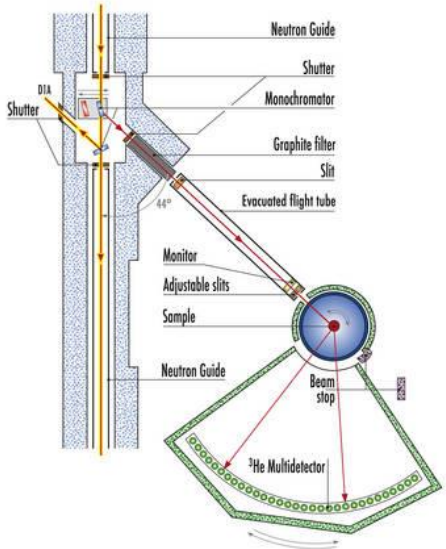
Instrument	D1A	D2B
Takeoff angle / °	122	135
Flux / n cm^{-2} s^{-1}	10^6	10^6 to 10^7
Beam (h × w) / mm	30 × 20	50 × 20
Detectors	25 ^{3}He × 10 cm h	128 ^{3}He × 30 cm h
Wavelengths	Ge(hhl)	Ge(hhl)
Δd/d Resolution	2-3 × 10^{-3}	Min 5 × 10^{-4}
Background	Very Low (60 m)	Low (15 m)
Average data collection time	3-24 hrs	0.25-4 hrs

Similar instruments at all continuous sources:
Echidna (ANSTO), Spodi (FRM-II), BT-1 (NIST), 3T2 (LLB), HB-2A (HFIR) etc…

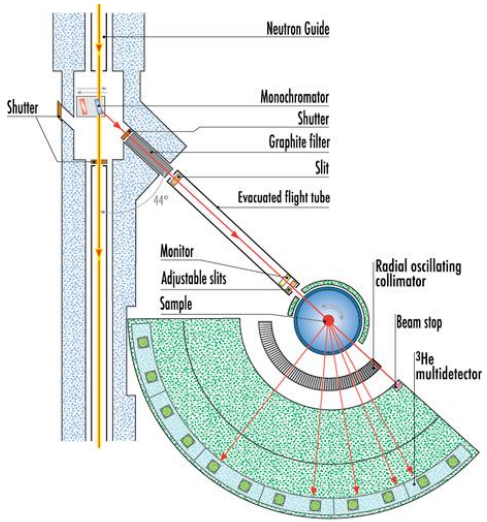
http://www.ill.eu/instruments-support/instruments-groups/

CW, High flux, thermal powder diffractometers: D1B, D20

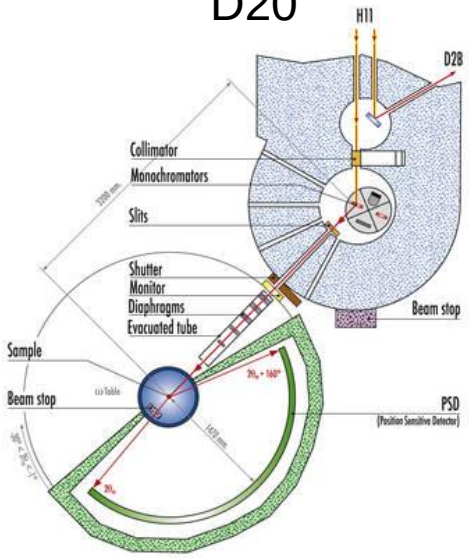
D1B

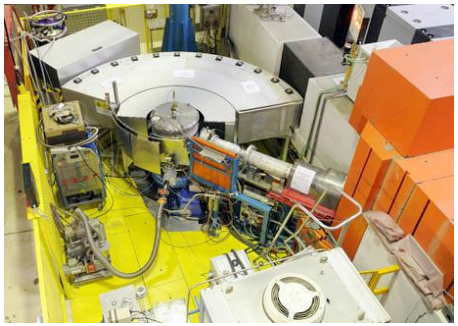


newD1B



D20



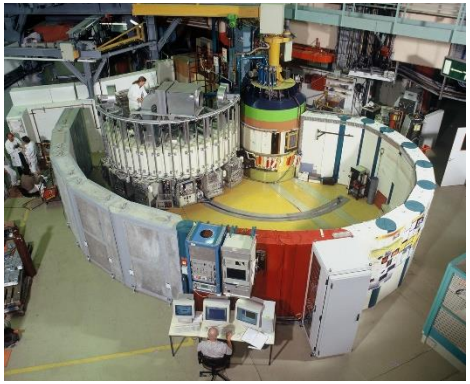


CW, High flux, thermal powder diffractometers: D1B, D20

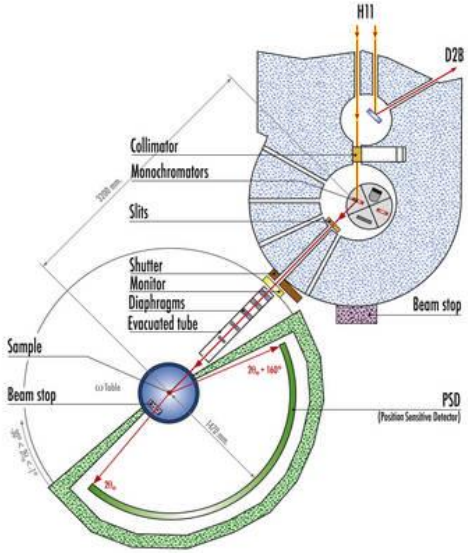
Instrument	D1B (old) / D1B (new)	D20
Takeoff angle / °	44	28, 42 (±2)
Flux / n cm^{-2} s^{-1}	6.5×10^6 HOPG(002) 0.4×10^6 Ge(311)	4.2×10^7 HOPG(002) 9.8×10^7 Cu(200) 42° 3.2×10^7 Cu(200) 28°
Beam (h × w) / mm	50 × 20	50 × 20
Detectors	80° multi-wire / 128° multi-wire 0.2° separation / 0.1° separation 400 channels / 1280 channels	153.6° micro-strip detector 0.1° separation 1536 channels
Wavelengths / Å	2.52, 1.28	2.42, 1.30, 0.87
Δd/d Resolution	$> 1 \times 10^{-2}$	$> 1 \times 10^{-2}$
Background	Medium (low with ROC)	Medium/High (low with ROC)
Average data collection time	5-10 mins / 1-5 mins	<1 min

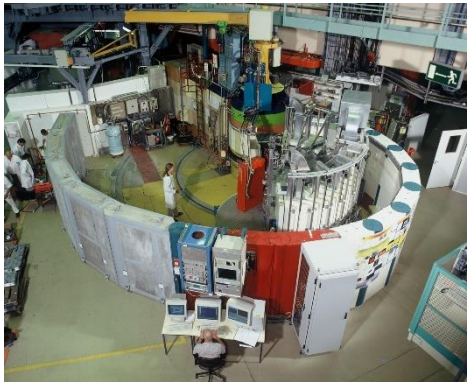
Fewer comparable instruments: Wombat (ANSTO), G4.1 (LLB), HB-2C (HFIR)

CW, variable resolution, thermal powder diffractometer: D20

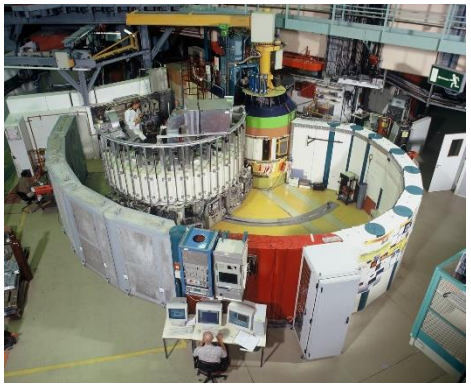


120°



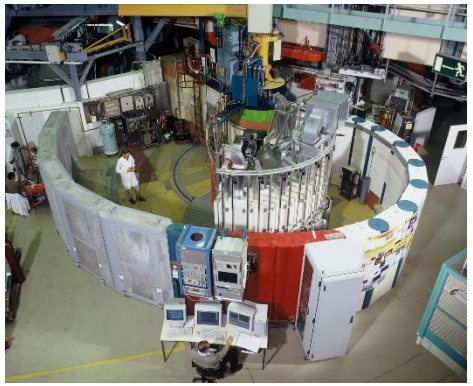


28°



90°

65°



42°

Photos courtesy T. Hansen ILL

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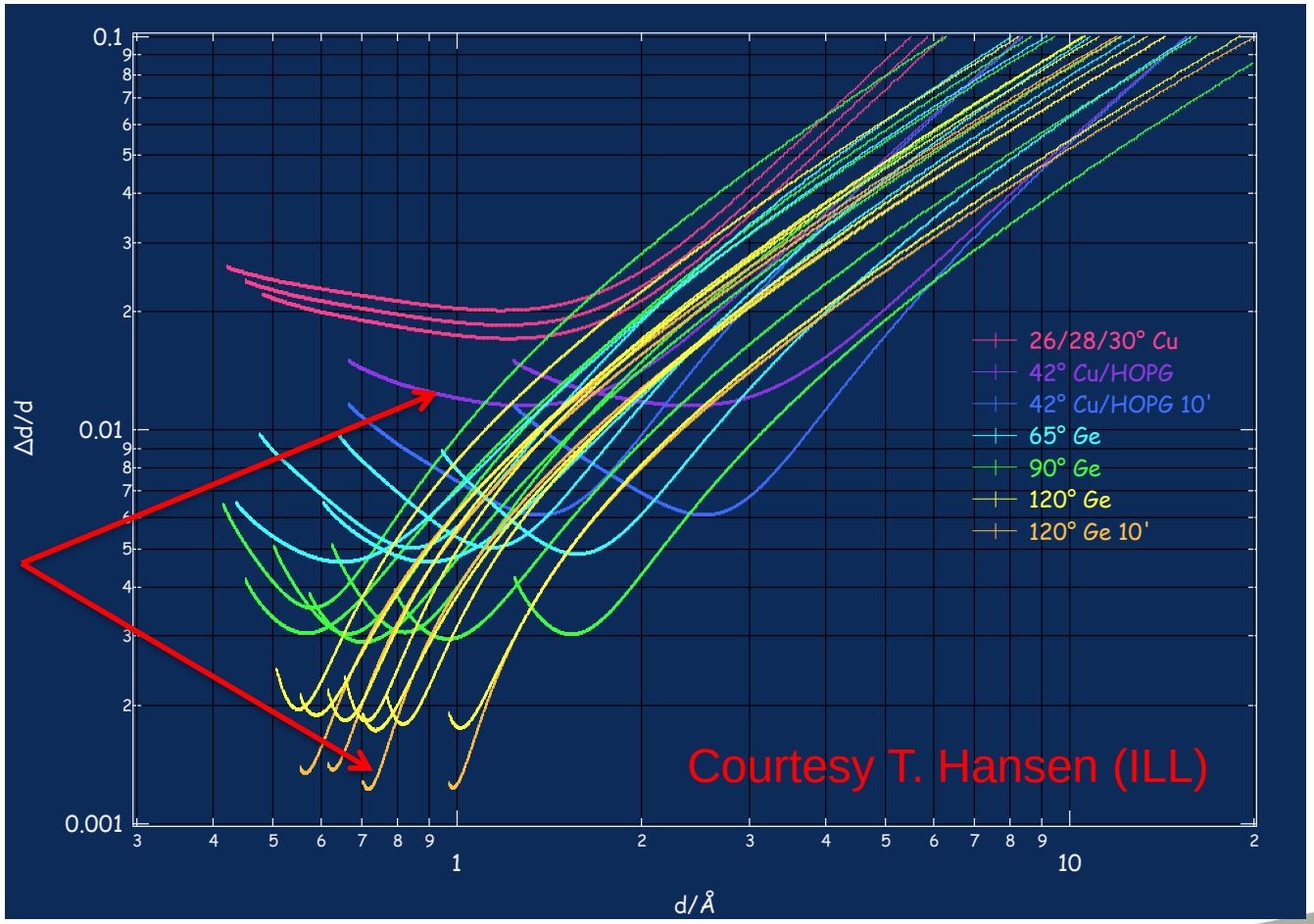
CW, variable resolution, thermal powder diffractometer: D20

Instrument	D20 (high flux)	D20 (high takeoff angle)
Takeoff angle / °	28, 42 (±2)	65, 90, 120 (±2)
Flux / n cm^{-2} s^{-1}	4.2×10^7 HOPG(002) 9.8×10^7 Cu(200) 42° 3.2×10^7 Cu(200) 28°	8.0×10^6 Ge(115) 7.5×10^6 Ge(117) 4.0×10^6 Ge(119)
Beam (h × w) / mm	50 × 20	50 × 20
Detectors	153.6° micro-strip detector 0.1° separation 1536 channels	153.6° micro-strip detector 0.1° separation 1536 channels
Wavelengths / Å	2.42, 1.30, 0.87	variable 0.8-3 Ge(hhl/00l/hhh)
Δd/d Resolution	$> 1 \times 10^{-2}$	See next slide
Background	Medium/High (low with ROC)	Medium/High (low with ROC)
Average data collection time	<1 min	5-15 mins (30 times faster than similar counting statistics on D2B)

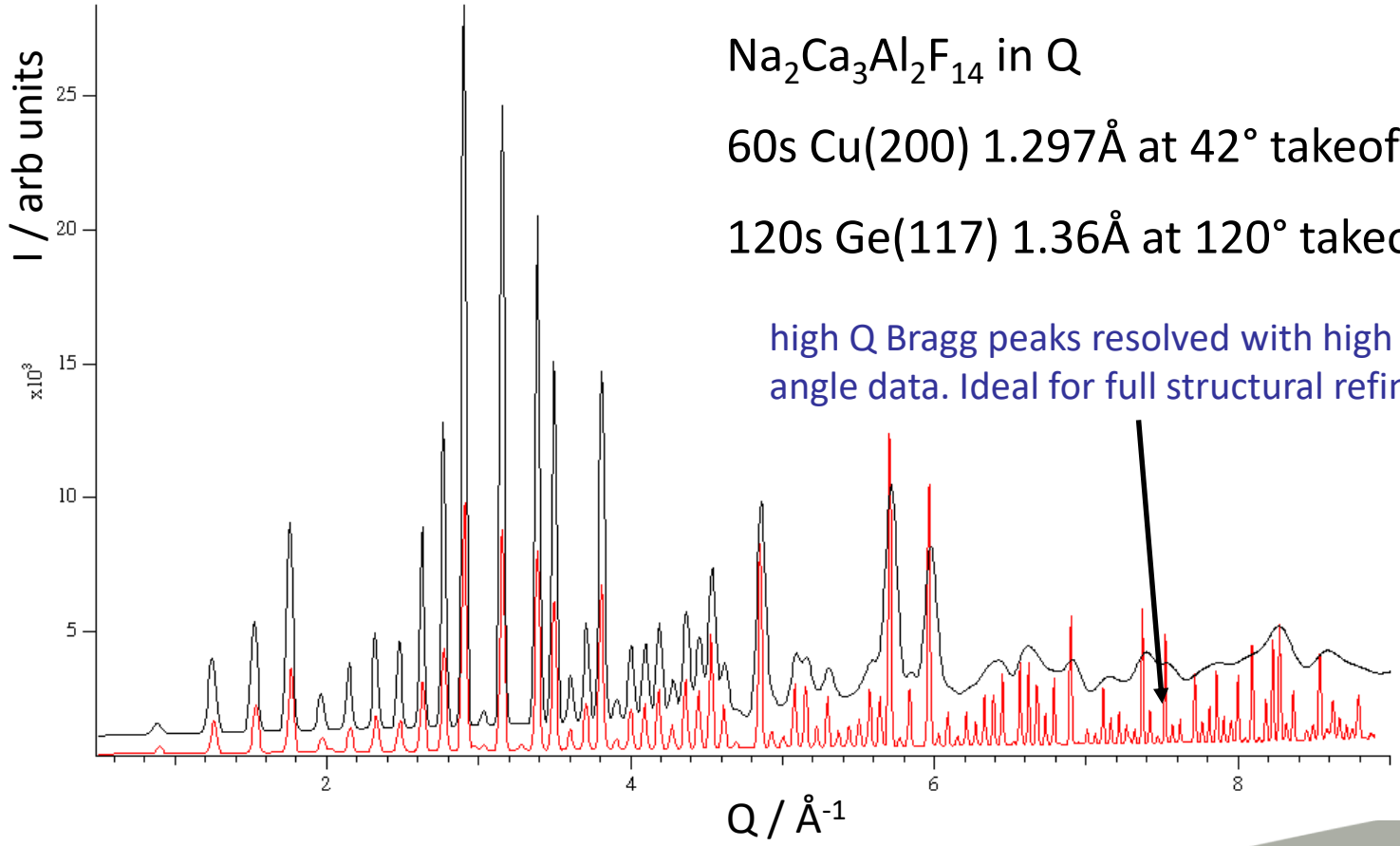
Few contemporary instruments: HRPT (PSI), Wombat (ANSTO has potential)

Tune resolution using θ_B

compare



Low θ_B v high θ_B: Q resolution v count-rate



$Na_2Ca_3Al_2F_{14}$ in Q

60s Cu(200) 1.297Å at 42° takeoff (black)

120s Ge(117) 1.36Å at 120° takeoff (red)

high Q Bragg peaks resolved with high take off angle data. Ideal for full structural refinement

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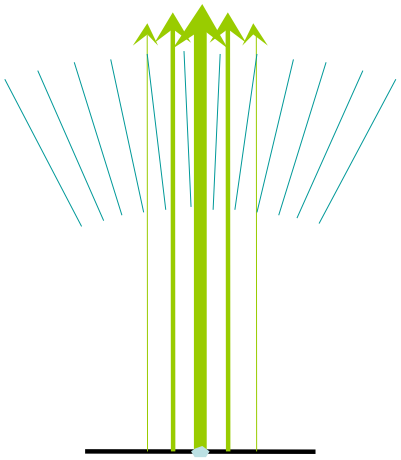
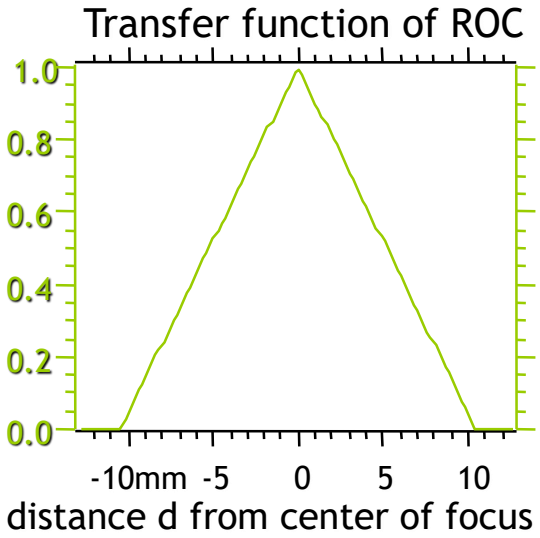
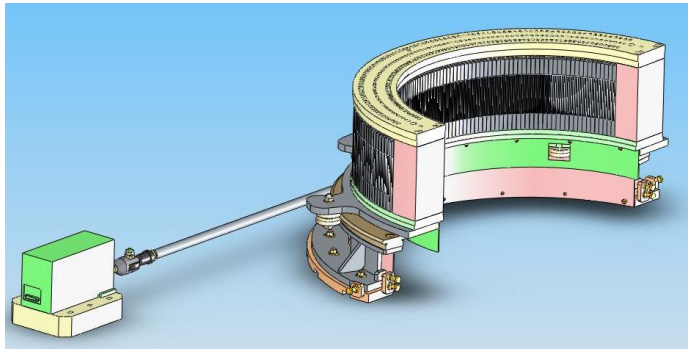
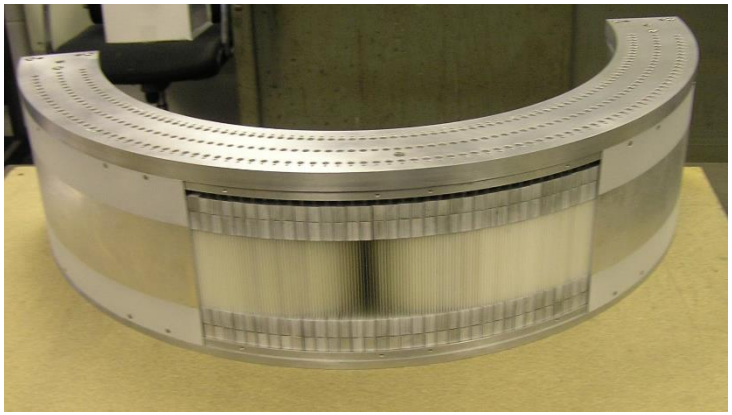
Parasitic scattering on instruments with area detectors: D20 collimator

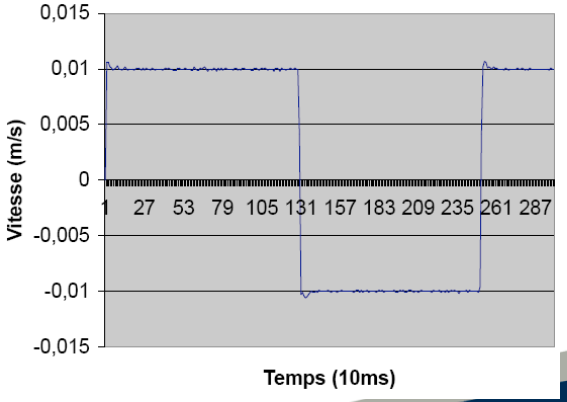






Photos Courtesy ILL





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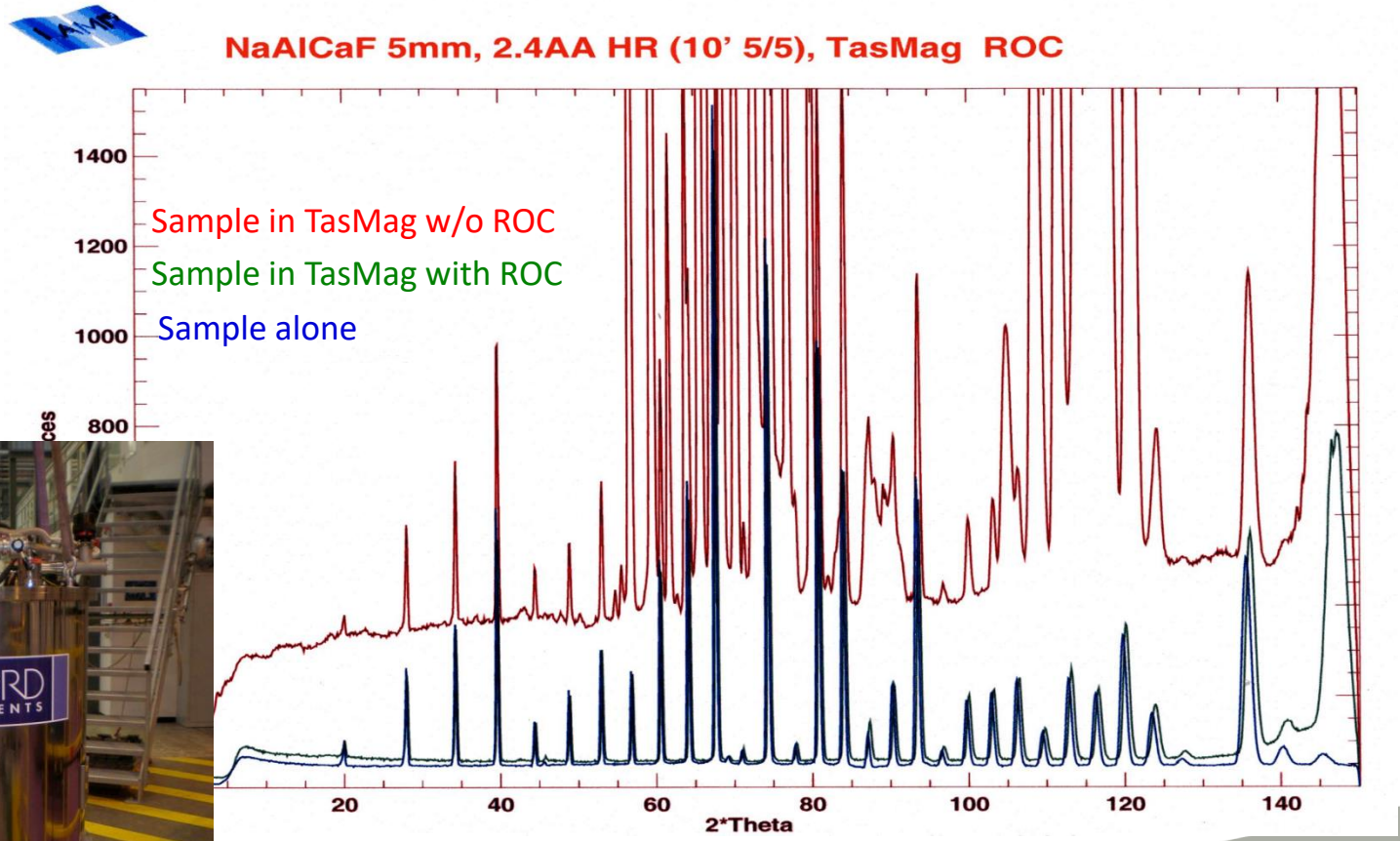
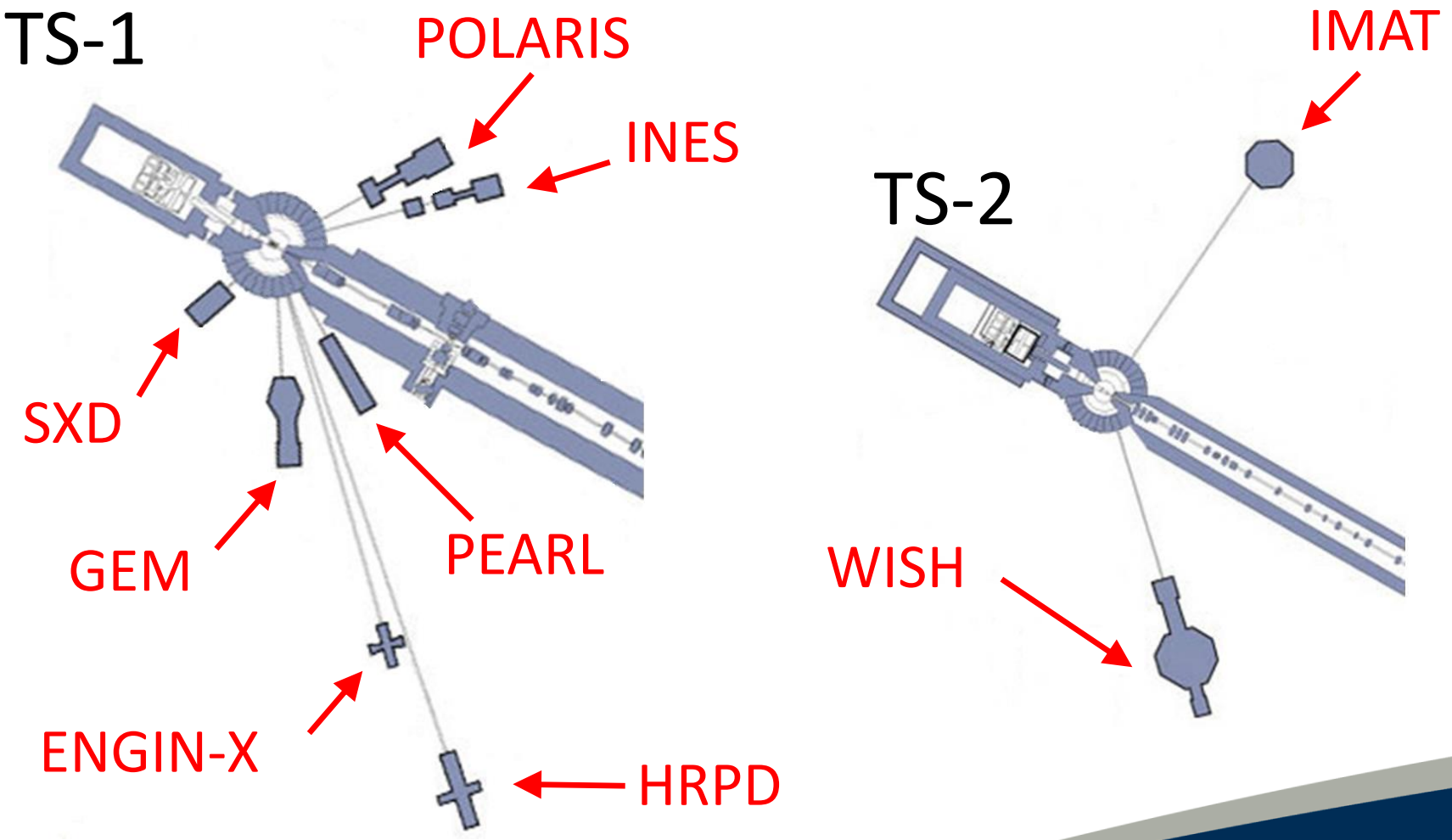
Parasitic scattering on instruments with area detectors: D20 example



Diffraction at a pulsed source: ISIS



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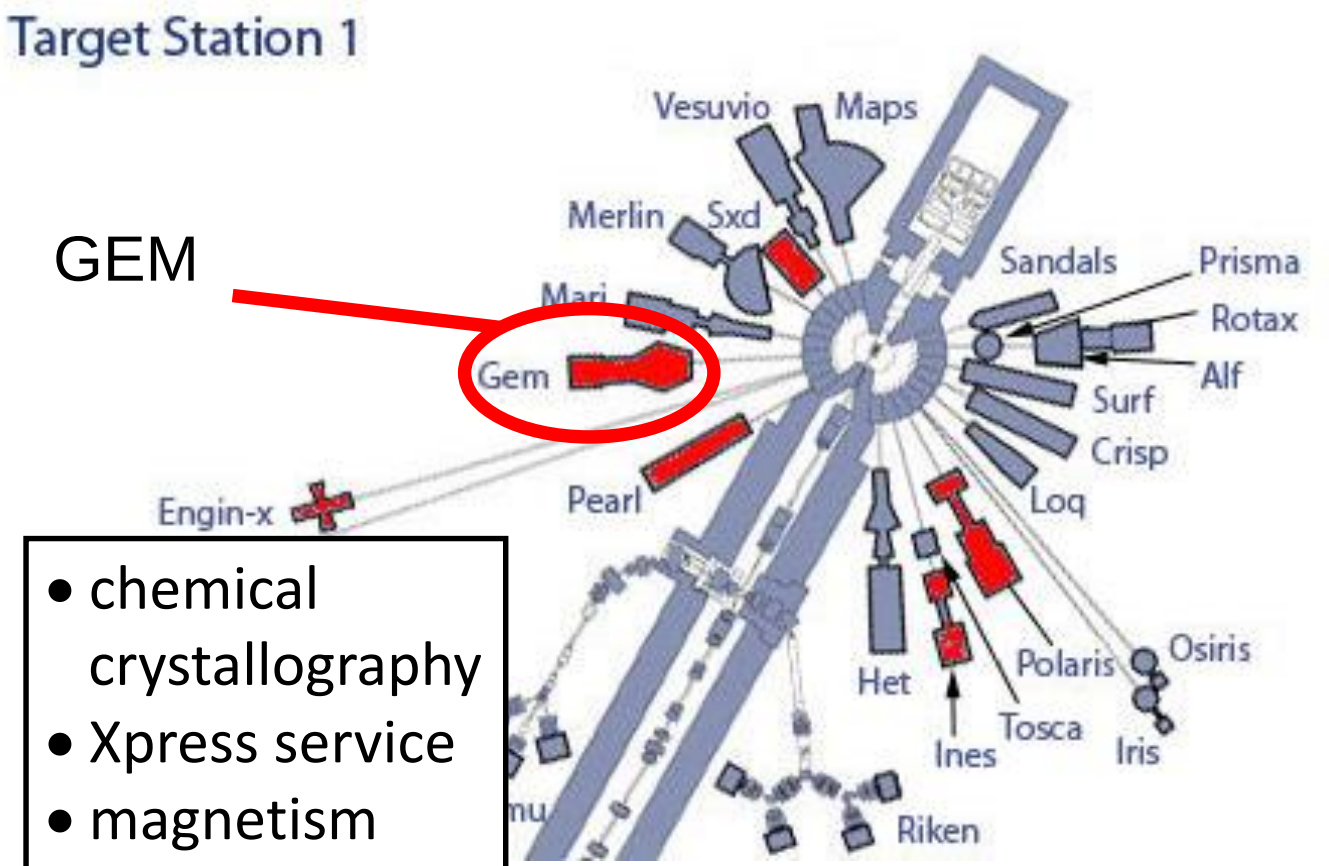
GEM: high intensity powder diffraction



- chemical crystallography
- Xpress service
- magnetism
- PDF studies
- glasses

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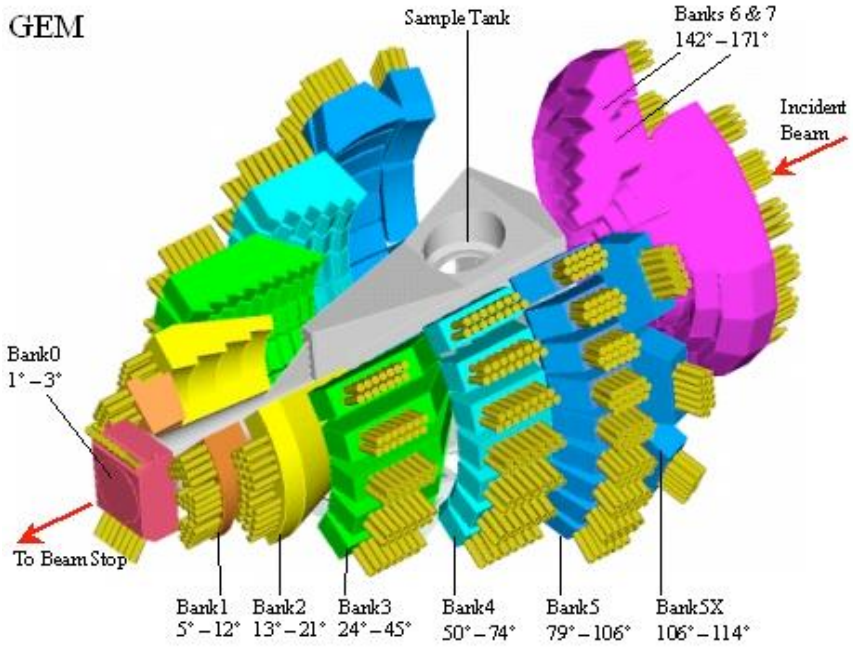
GEM: high intensity powder diffraction

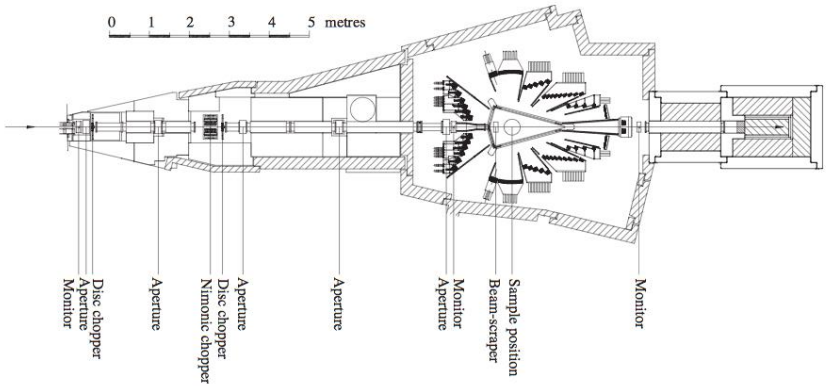


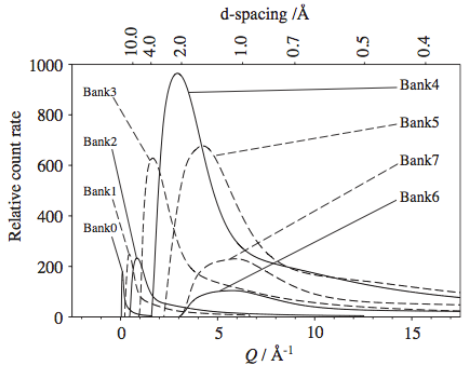
Initially constructed in the late 1990s this powder/liquids diffractometer hybrid changed the way TOF diffraction instruments were designed and built

http://wwwisis2.isis.rl.ac.uk/disordered/gem/gem_home.htm

GEM: high intensity powder diffraction

Detector Bank	Scattering angle 2θ (deg)	Range in azimuthal angle ϕ (deg)	Secondary flight path L_2 (m)	Number of detector elements/ modules	Solid angle Ω (sr)	Resolution $\Delta Q/Q$(%)	Minimum accessible momentum transfer Q_{min} ($Å^{-1}$)
Bank0	1.21–3.18	±90.0	2.757–2.767	80/4	0.008	5–10	0.04
Bank1	5.32–12.67	±45.0	2.365–2.376	330/6	0.056	4.7	0.17
Bank2	13.44–21.59	±43.4	1.477–2.100	320/4	0.093	2.4	0.43
Bank3	24.67–45.61	±42.5	1.077–1.893	900/10	0.478	1.7	0.79
Bank4	50.07–74.71	±44.4	1.028–1.436	1400/14	0.988	0.79	1.56
Bank5	79.07–106.60	±44.5	1.376–1.383	2160/18	1.135	0.51	2.35
Bank5X	106.02–114.19	±42.7	1.377–1.387	720/18	0.378	0.5	2.95
Bank6	142.50–149.72	±69.3	1.544–1.738	560/14	0.280	0.34	3.50
Bank7	149.98–171.40	±66.6	1.035–1.389	800/10	0.443	0.35	3.57





From Hannon, NIMA (2005), **551**, 88-107

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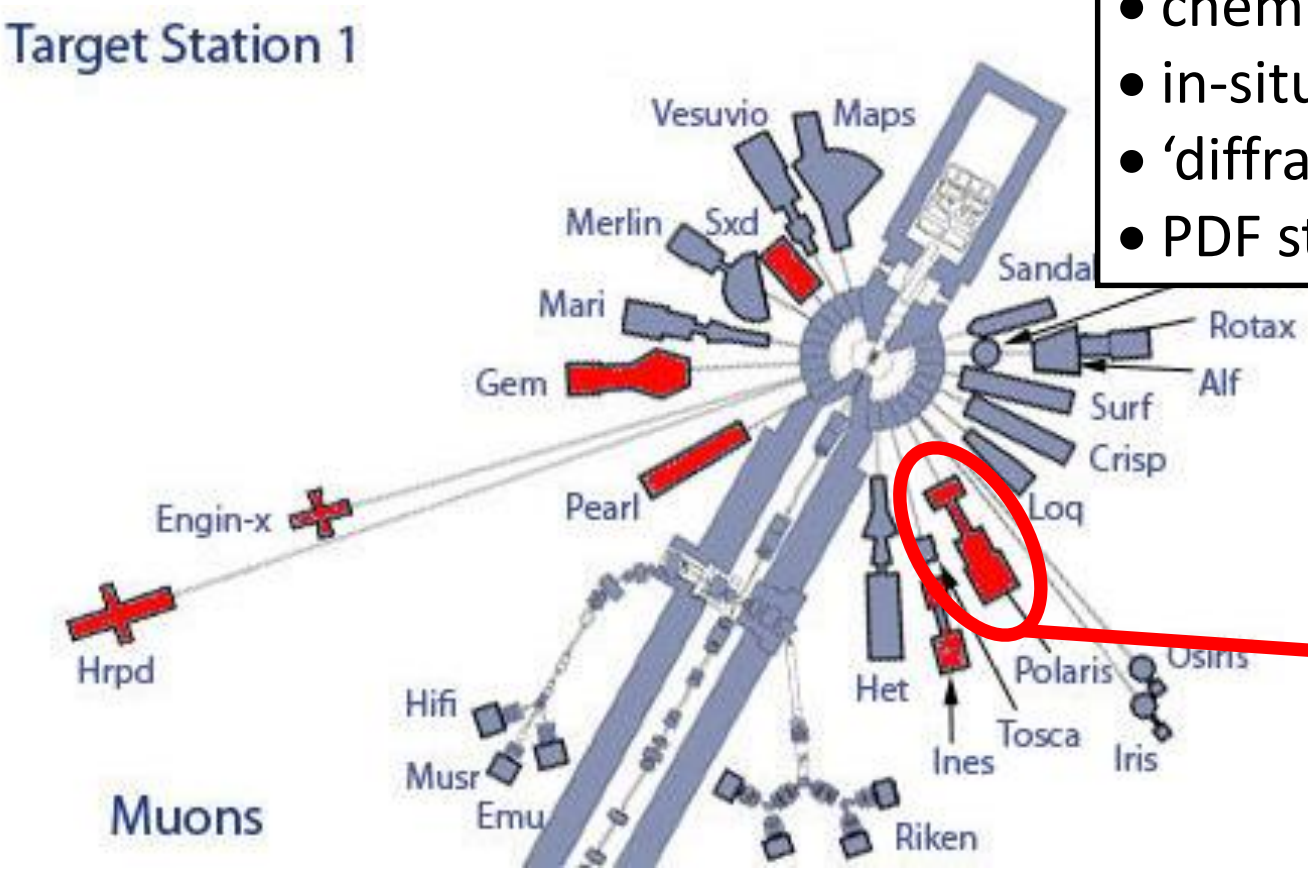
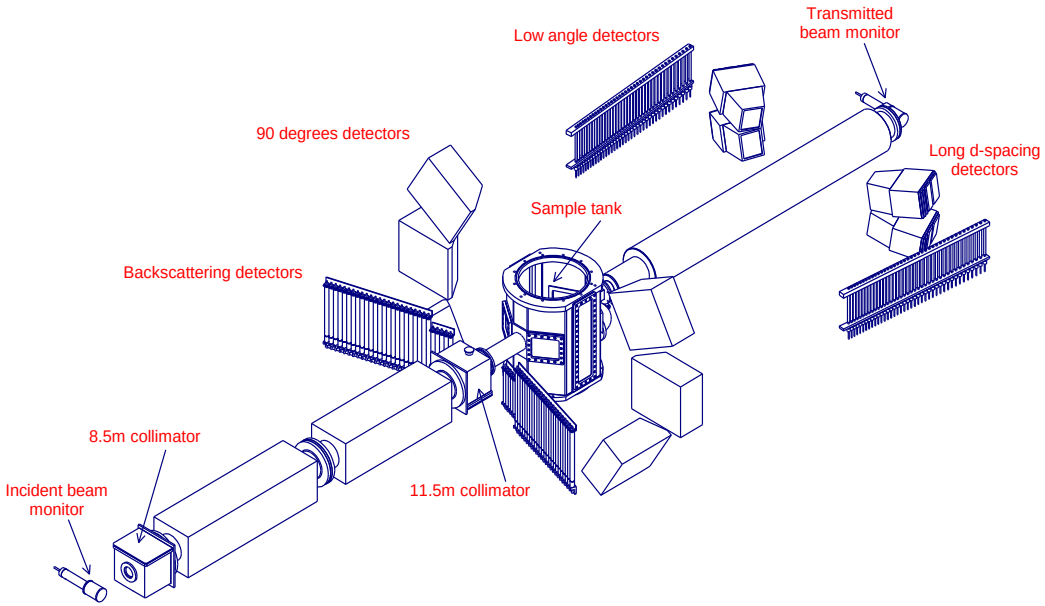
Polaris: high intensity powder diffraction

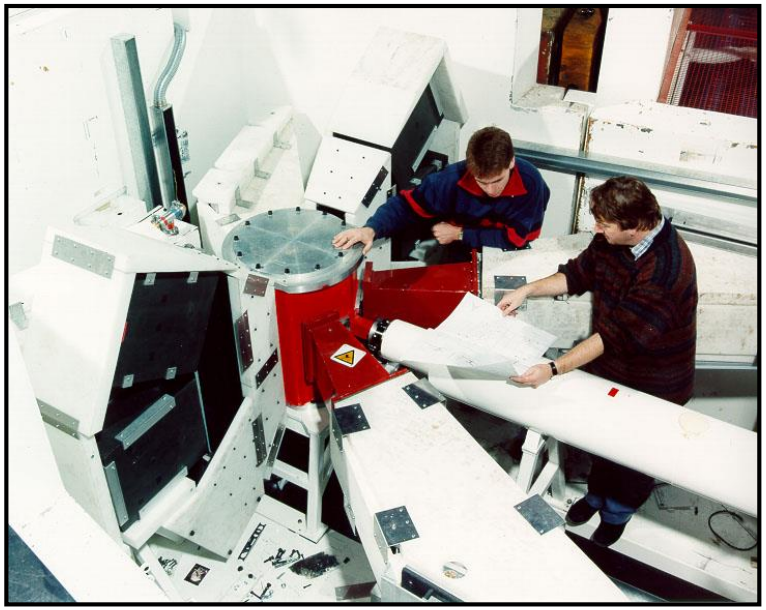
- chemical crystallography
- in-situ studies
- ‘diffraction plus’
- PDF studies



Polaris

Polaris: old configuration





Compare with GEM:

- Higher sample flux
- Wider bandwidth
- Lower resolution
- Hotter spectrum
- Lower detector coverage

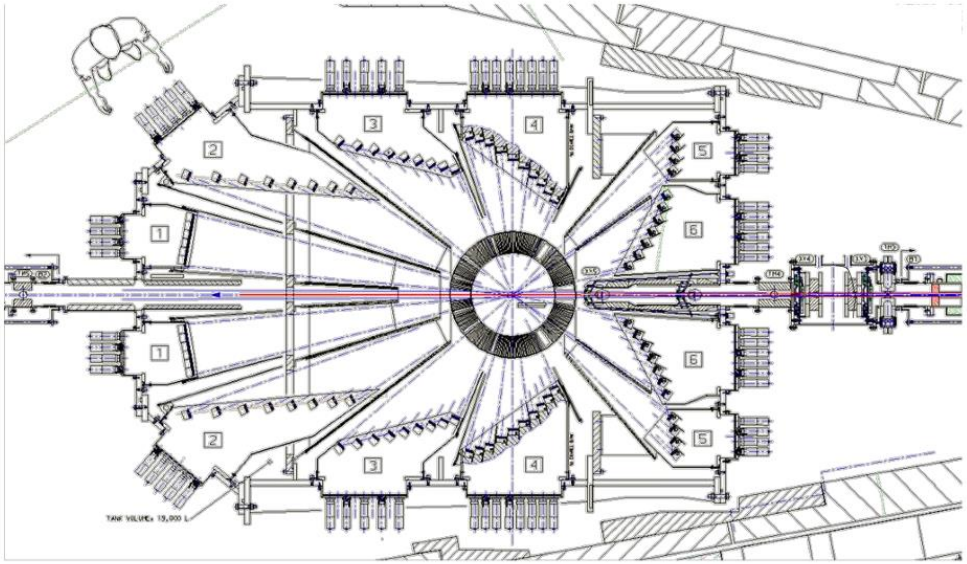
http://www.isis.stfc.ac.uk/instruments/polaris/polaris4643.html

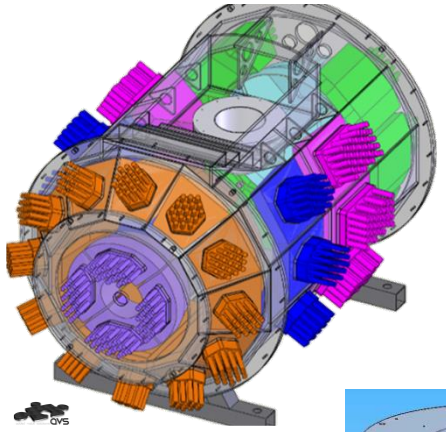
Polaris: old configuration

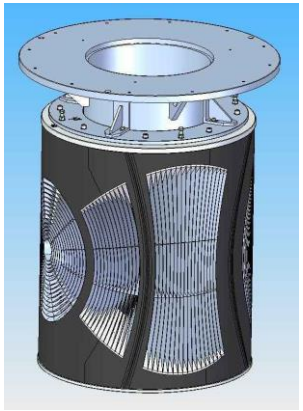
bank position (label)	low angle (A)	low angle (B)	backscattering (C)	90 degrees (E)
detector type	^{3}He	ZnS	^{3}He	ZnS
no. of elements	2 x 40 = 80	4 x 20 = 80	2 x 29 = 58	6 x 36 = 216
L_2 (m)	1.72 - 2.65	~2.2	0.65 - 1.35	~0.80
2θ range	28°< 2θ < 42°	13°< 2θ < 15°	130°< 2θ < 160°	83°< 2θ < 97°
Ω (ster)	0.046	0.009	0.29	0.48
Δd/d	~1x10^{-2}	~3x10^{-2}	~5x10^{-3}	~7x10^{-3}
d-range (Å)	0.5 - 8.3	0.5 - 21.6	0.2 - 3.2	0.2 - 4.0
Q-range (Å^{-1})	0.75 - 12.6	0.3 - 12.6	2.0 - 31.4	1.5 - 31.4

- Good workhorse instrument for powder diffraction
- High Q accessible for disordered materials investigation using the PDF method
- Some in situ capability but limited by count-rate
- Compatible with a wide range of restricted geometry sample environment

Polaris upgrade







- Increase primary flight path to 14 m
- Optimise each detector bank to give constant resolution
- Increase detector coverage
- Design a collimator to reduce background and parasitic scattering

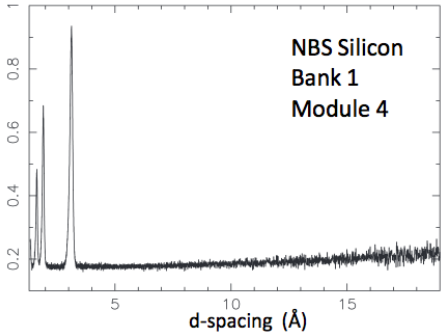
http://www.isis.stfc.ac.uk/instruments/polaris/polaris-upgrade-poster11575.pdf

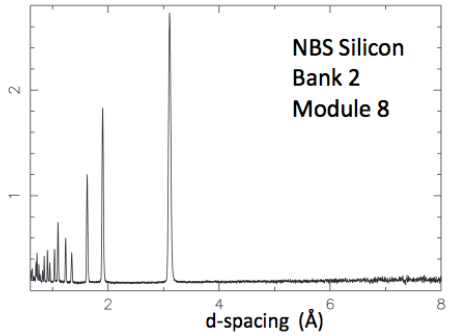
Polaris upgrade

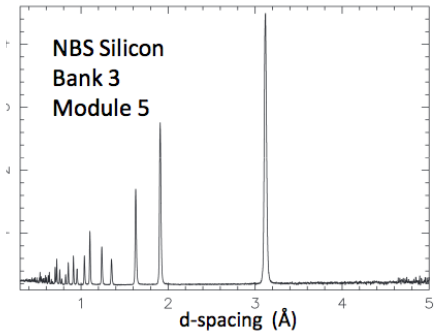
http://www.isis.stfc.ac.uk/instruments/polaris/polaris4643.html

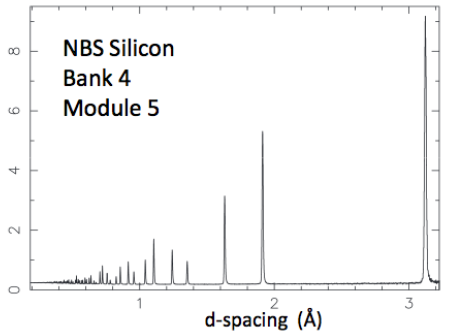
Current Polaris

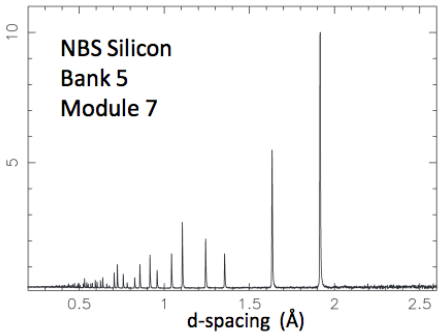
http://www.isis.stfc.ac.uk/instruments/polaris/polaris-upgrade---first-diffraction-pattern12763.pdf

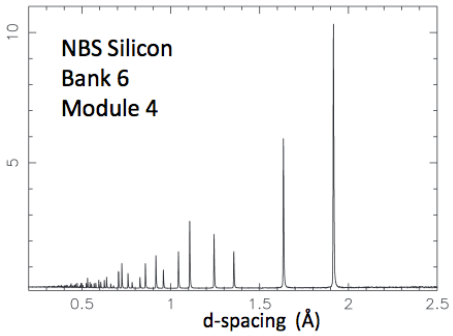


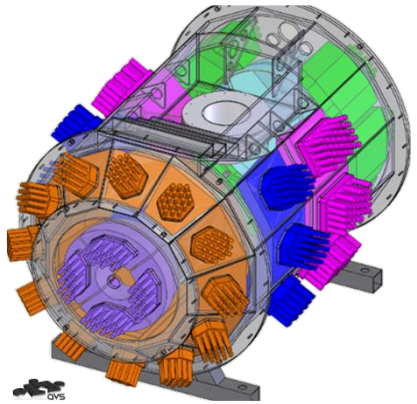












Bank 1 – cyan
Bank 2 – green
Bank 3 – pink
Bank 4 – blue
Bank 5 – orange
Bank 6 - purple

- Increased count rate ×3 at high scattering angle to >20 for low angle banks
- Resolution improvement e.g. bank 5 and 6 of 3×10^{-3} cf. 5×10^{-3}
- Improvement in data at high Q

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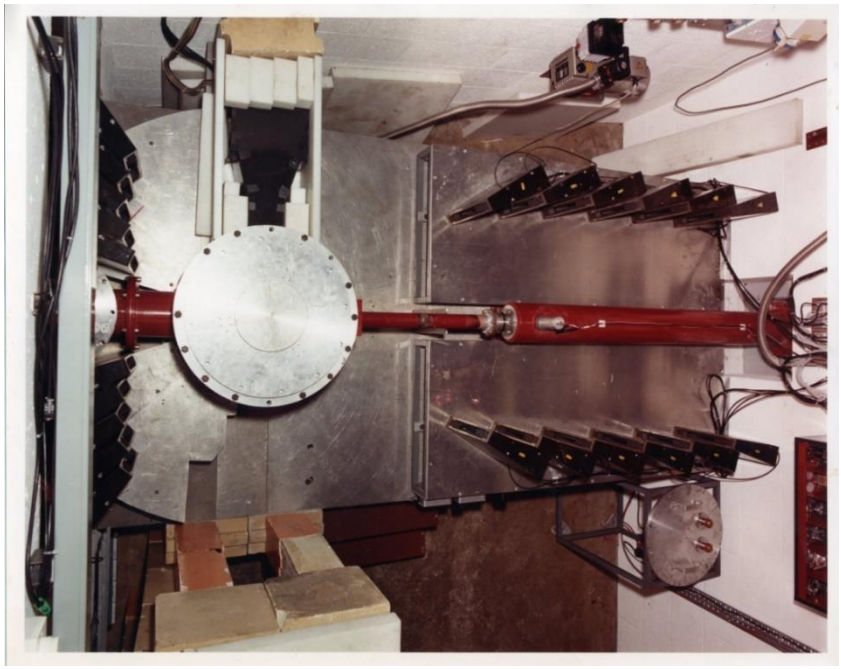
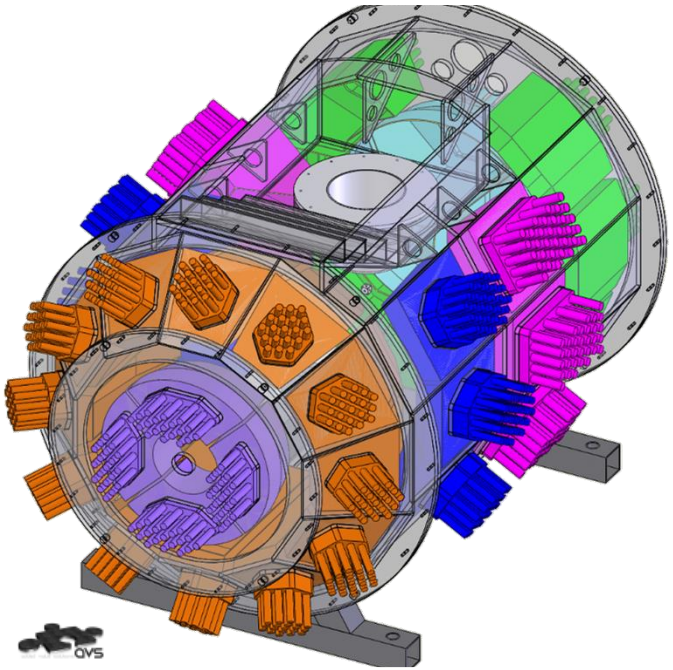
Polaris 1995 v 2013

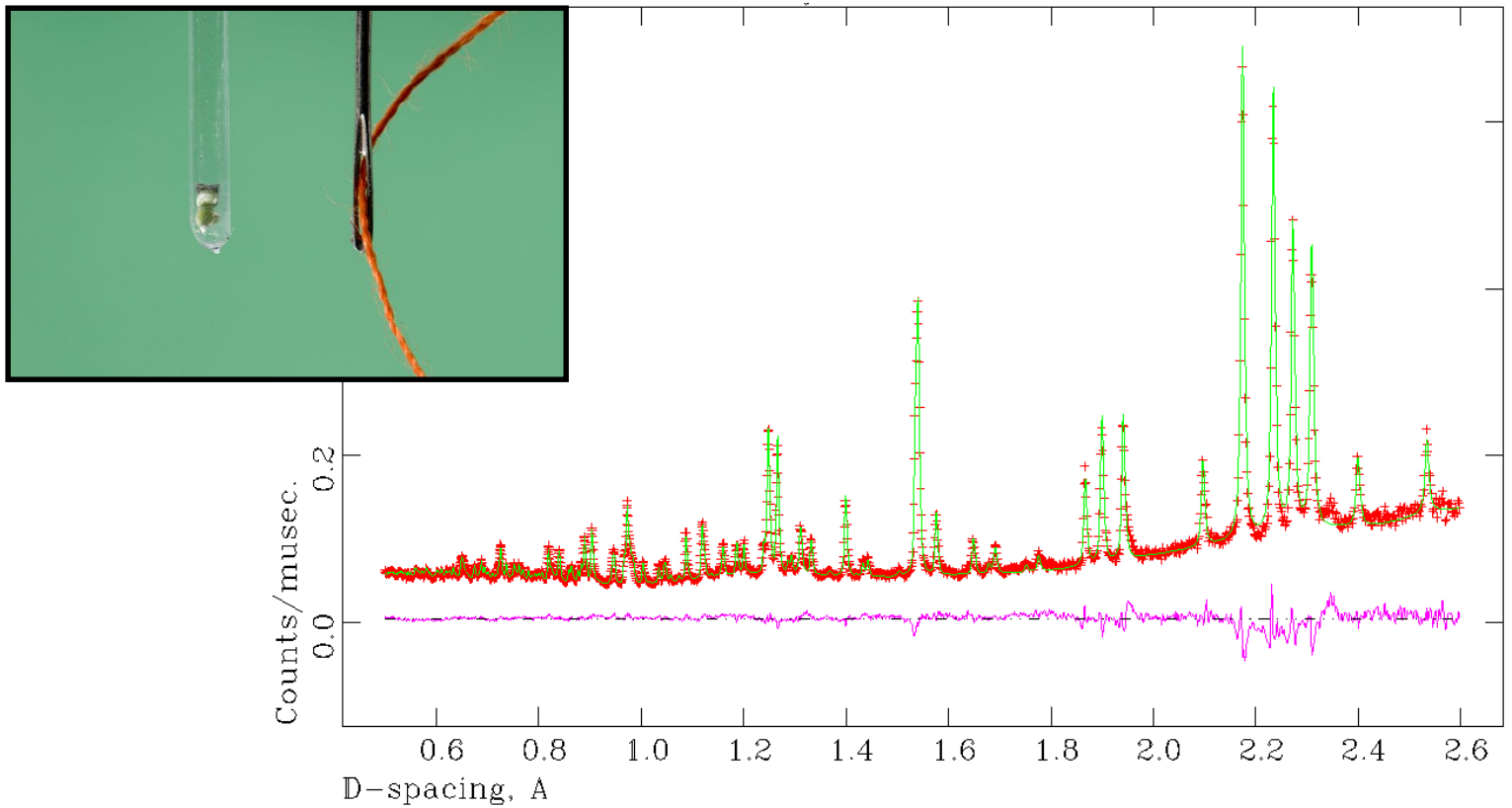




- 1995 500 mg 24+ hrs
- 2013 500 mg 15-20 minutes with increased Q-range

Contemporary instruments NOVA and iMateria (J-PARC), POWGEN-3 (SNS)

Polaris: pushing boundaries in sample size

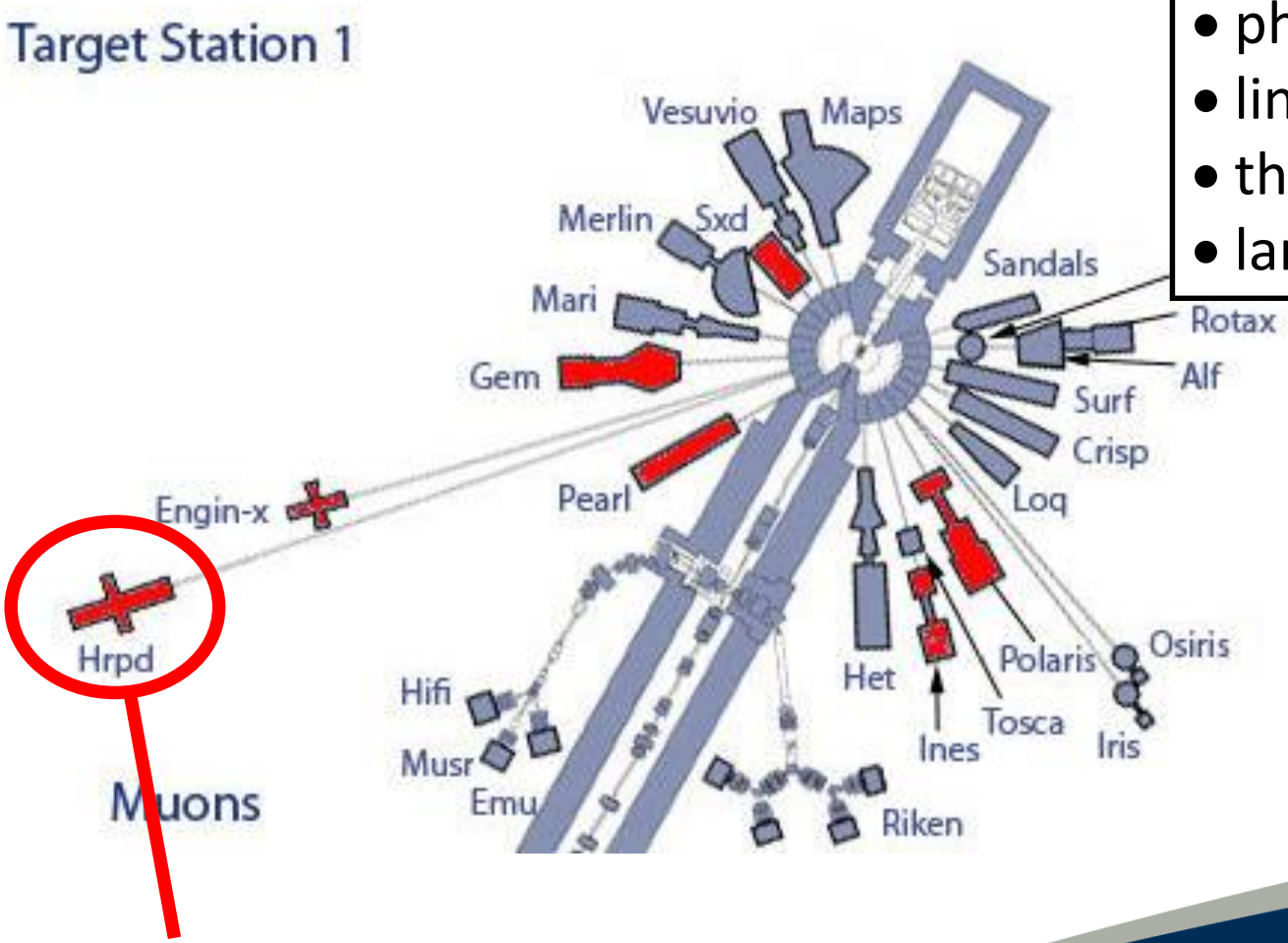


~1mm^3 sample of $NaNiF_3$ phase prepared at high *p* + high T

Lindsay-Scott *et al*, J. Appl. Cryst., **47**, 1939 (2014)

HRPD: high resolution powder diffraction

- phase transitions
- line broadening
- thermal expansion
- large unit cells



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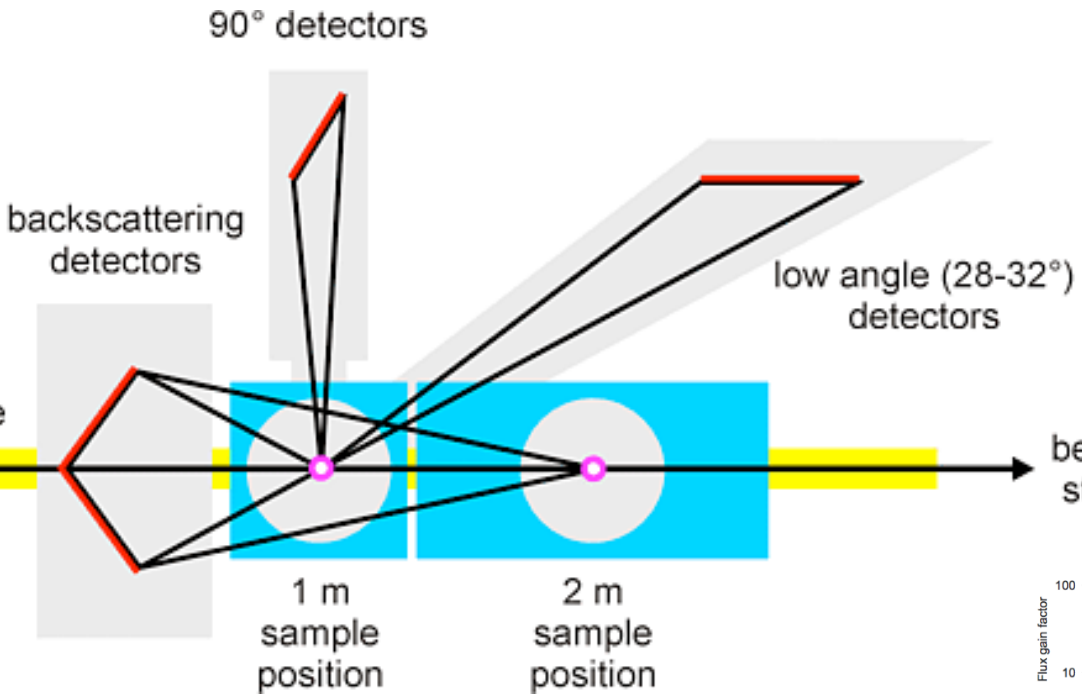
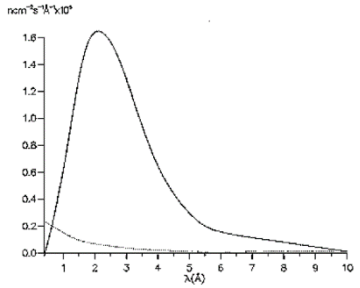
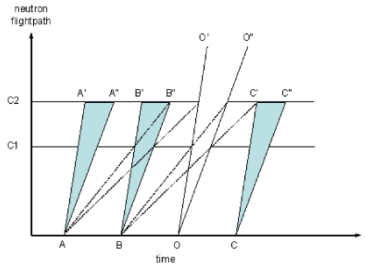
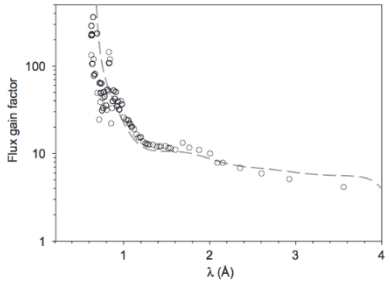
HRPD: high resolution powder diffraction









- Approximately 100 m primary flight path
- 100K methane moderator – peak flux around 2 Å
- Operates at 5 or 10 Hz cf. TS-1 50 Hz

http://www.isis.stfc.ac.uk/instruments/hrpd/hrpd.html

HRPD: high resolution powder diffraction

Table 1. HRPD Detector Bank Details			
	Backscattering	**90°**	**Low Angle**
Detector Specification	ZnS scintillator	ZnS scintillator	½" 10atm He^3 gas tubes
Geometry	60 rings: $7 < r_1 < 8.5$cm $35.5 < r_{60} < 37$cm 8 Octants: 4147cm^2	Slab: 20 x 20cm 66 x 3mm elements 6 Modules: 2400cm^2	72 tubes: (20cm active length) 8 tubes/module 9 Modules: 1800cm^2
Fixed Scattering Angle	$160° < 2\theta < 176°$ (1m)	$87° < 2\theta < 93°$	$28° < 2\theta < 32°$
Solid Angle (Ω)	0.41 ster (1m)	0.08 ster	0.01 ster
Resolution ($\Delta d/d$)	~ 4-5 x 10^{-4}	~ 2 x 10^{-3}	~ 2 x 10^{-2}
***d*-spacing range (30-230ms)**	~ 0.6 - 4.6Å 0.25 – 4.6 Å	~ 0.9 - 6.6Å 0.4 – 6.6 Å	~ 2.2 - 16.5Å 1.0 – 16.5 Å

- Large backscattering detector to minimise $\cot^2\theta$ in resolution term
- High resolution at intermediate Q
- Long flight path to reduce $\Delta t/t$ and $\Delta L/L$ uncertainties
- Pulse skipping to increase bandwidth (@50 Hz 0.4 Å)
- Good combination of parameters for a high resolution TOF diffractometer

Contemporary instrument sHRPD (J-PARC), no current analogue at SNS