EUROPEAN SPALLATION SOURCE

Diffraction and Instruments for Neutron Diffraction

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Neutron School SoNS Francesco Paolo Ricci, Erice 28 July – 4 August 2015

Who am I?

- University education (solid-state chemist)
  - Chemistry Degree (with supplementary Bio-chemistry)
  - D. Phil. in Solid State Chemistry “Fullerene Intercalation Compounds”
  - 7 years Post Doctoral experience
    - High-pressure, zeolites, magnetic materials, superconductors, pigments, isotopes
- Instrument scientist (powder diffraction)
  - 5 Years as co-responsible for D20 at ILL, Grenoble
  - 2.5 Years responsible E9 at HZB, Berlin
  - Since March 2011 responsible for powder diffraction at ESS, Lund
  - Since May 2013 Adjunct Professor in Neutron Scattering at CTH, Göteborg
- Research interests
  - Hydrogenous materials and neutrons
  - In-situ sample environment development
  - Materials research
  - Neutron diffraction community development

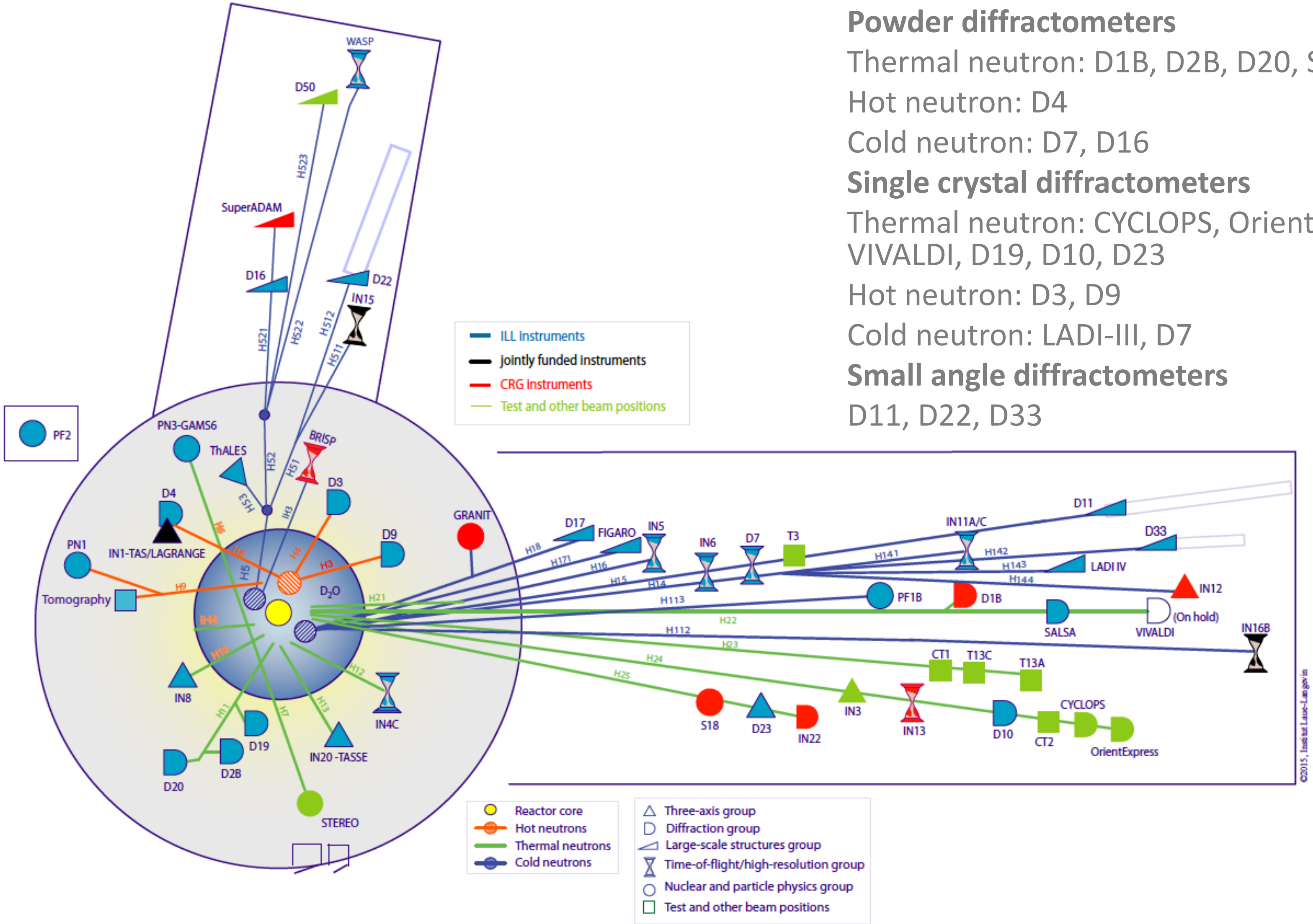
Outline

- Diffraction and structure
- Diffraction instruments at large-scale facilities
- Principles of diffraction
- X-rays v neutrons
- Data collection and analysis
- Total scattering (PDF methods)
- TOF v Monochromatic for diffraction
- Examples of neutron diffractometers
- Design of next generation diffraction instruments
- Examples of uses of diffraction
- Final comments

Diffraction and structure

- Diffraction is the tool we use to determine structure
- Structure determines the physical properties of a material
- To tailor physical properties we must understand structure
- Neutron and X-ray diffraction are complementary tools
- Most diffraction measurements use powders. Why?
  - Many materials are difficult to make as single crystals
  - Practical uses require bulk materials
  - Functional materials may require non-perfect crystals
  - Phase transitions destroy or fracture single crystals

Diffraction instruments at ILL



Powder diffractometers

Thermal neutron: D1B, D2B, D20, SALSA

Hot neutron: D4

Cold neutron: D7, D16

Single crystal diffractometers

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

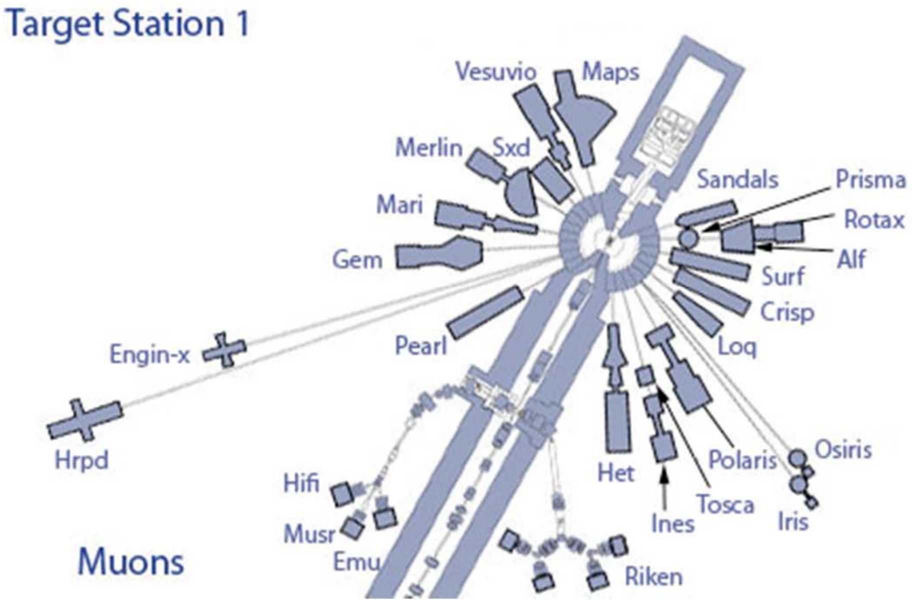
Hot neutron: D3, D9

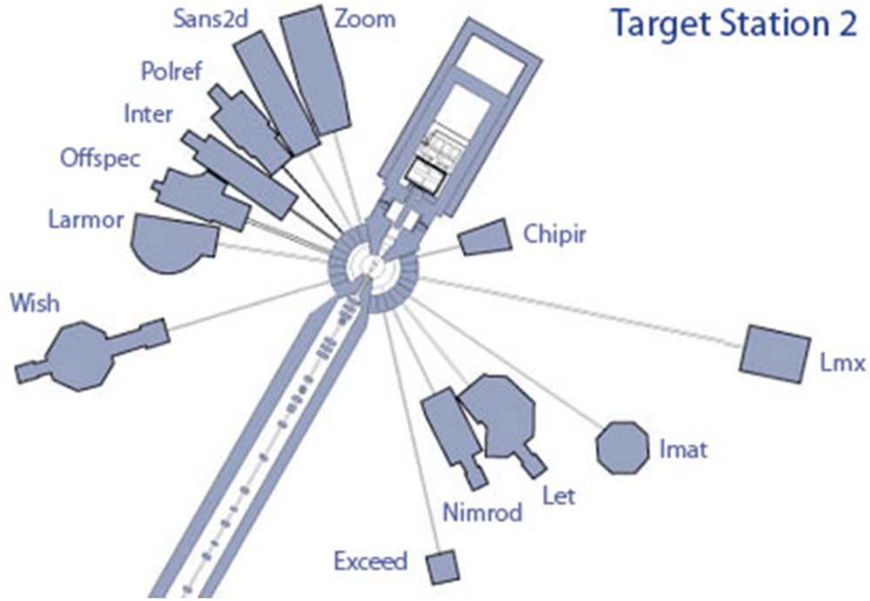
Cold neutron: LADI-III, D7

Small angle diffractometers

D11, D22, D33

Diffraction instruments at ISIS



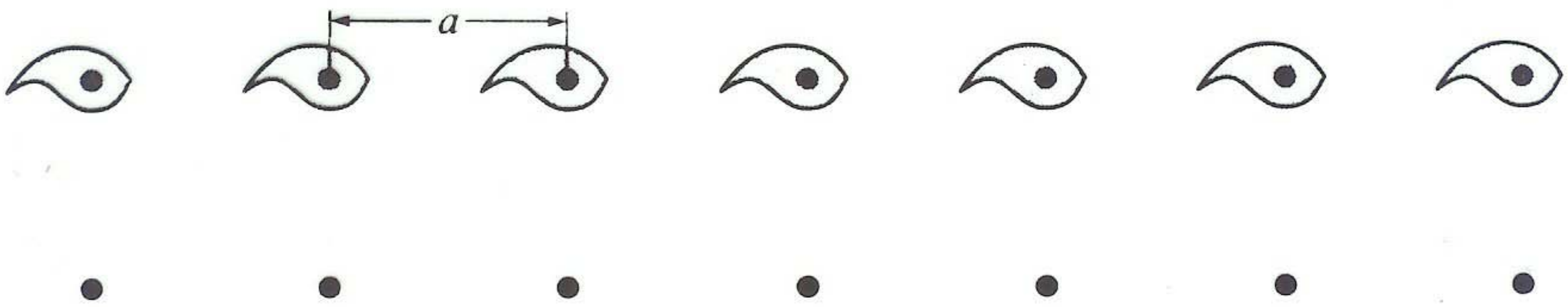


HRPD	PEARL	WISH
ENGIN-X	ROTAX	NIMROD
GEM	LoQ	EXCEED
SXD	OSIRIS	LMX
SANDALS	POLARIS	SANS2D
	INES	ZOOM

Principles of Diffraction

- The lattice
- Crystal systems
- Centering
- 3-D lattice types
- Miller indices/planes
- Bragg equation
- Ewald Sphere
- Reciprocal lattice
- Conditions for observing diffraction
- Laue diffraction

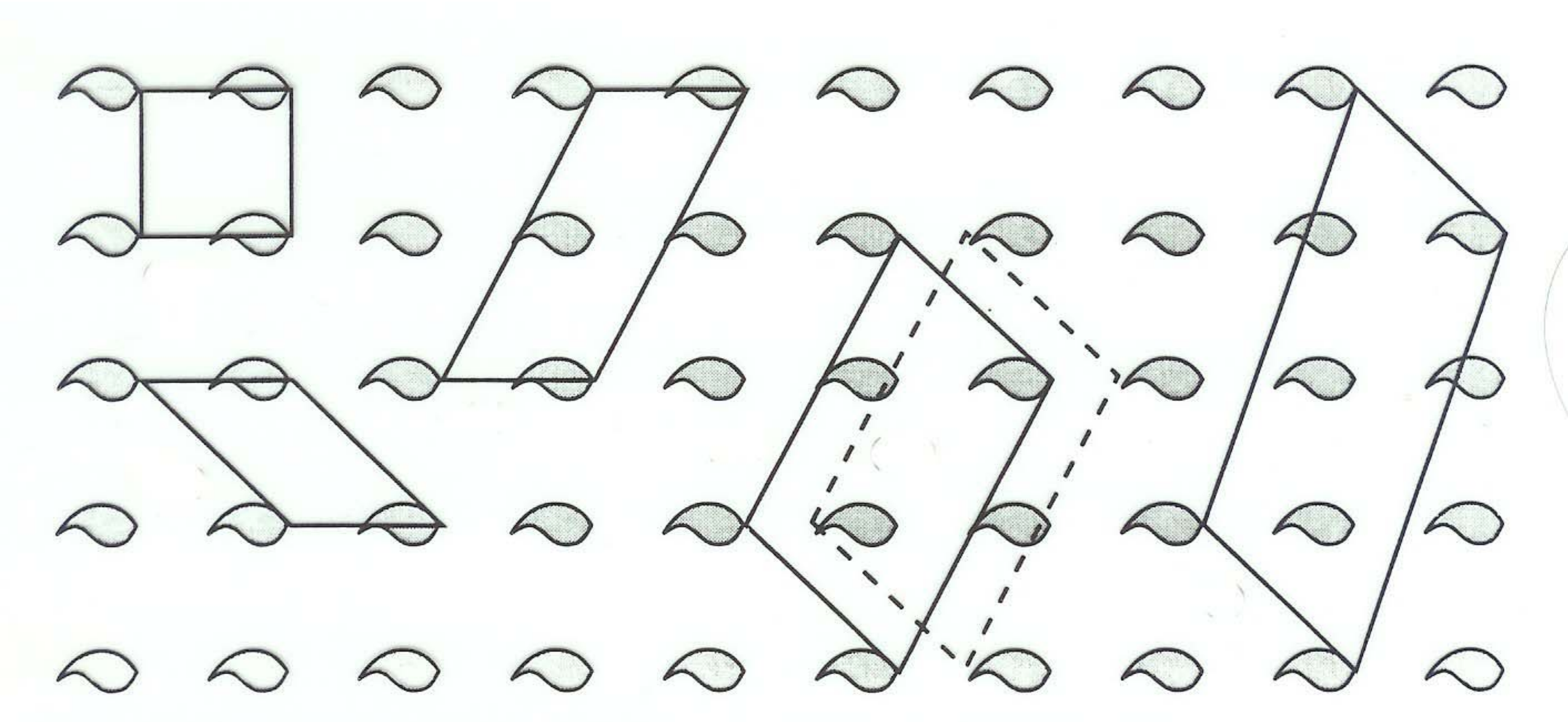
Lattices & Unit Cells: 1-D



Lattice + Motif = Structure

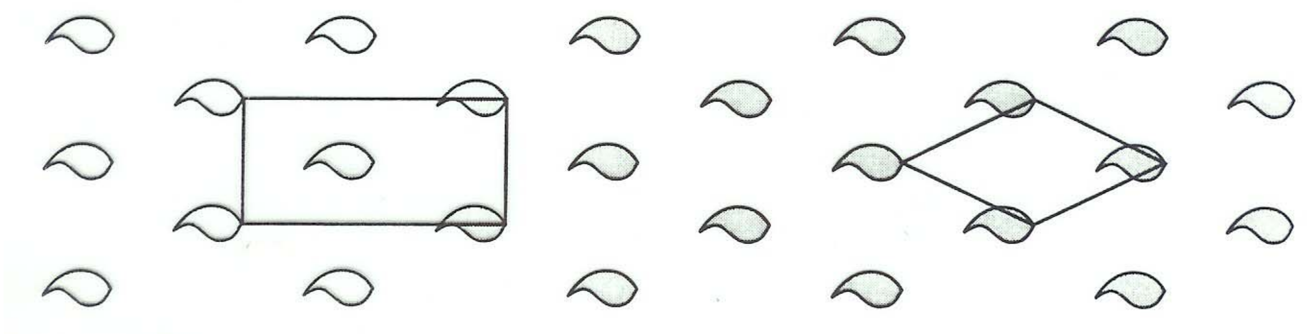
The motif can be an atom, molecule, part of a molecule or several molecules are atoms

Lattices & Unit Cells: 2-D



All the cells highlighted are equally valid. All will reproduce the 2-D lattice array. The convention is too choose the smallest cell that also represents the symmetry of the structure.

Lattices & Unit Cells: Centering

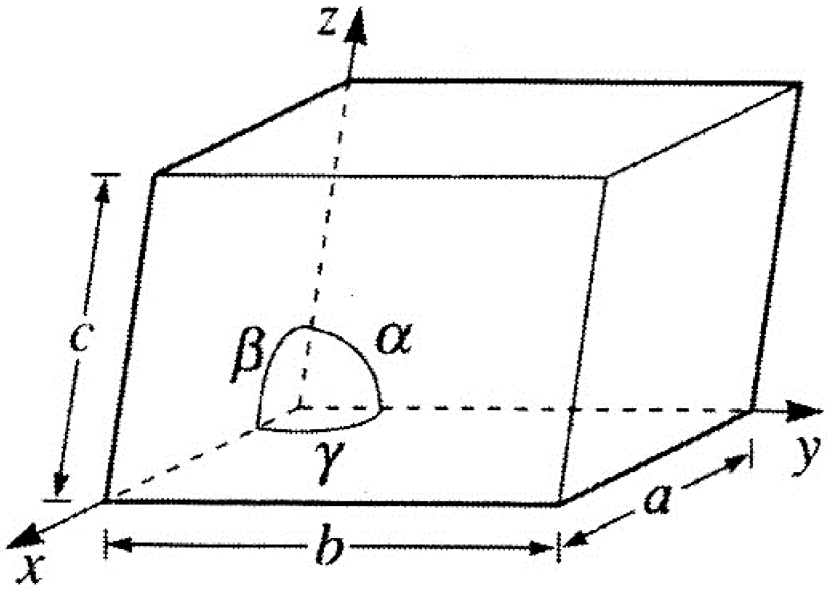


Centred v Primitive unit cell

Rules for unit cell selection:

- Unit cell should show the symmetry of the crystal
- Origin should be a geometrically unique point, priority given to inversion centre.
- Basic vectors should be as short as possible and the angle between them as close to 90° as possible.
- ALL angles diverting from 90° should be larger or smaller (convention is larger)

Lattices & Unit Cells: 3-D



Conventions

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

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:

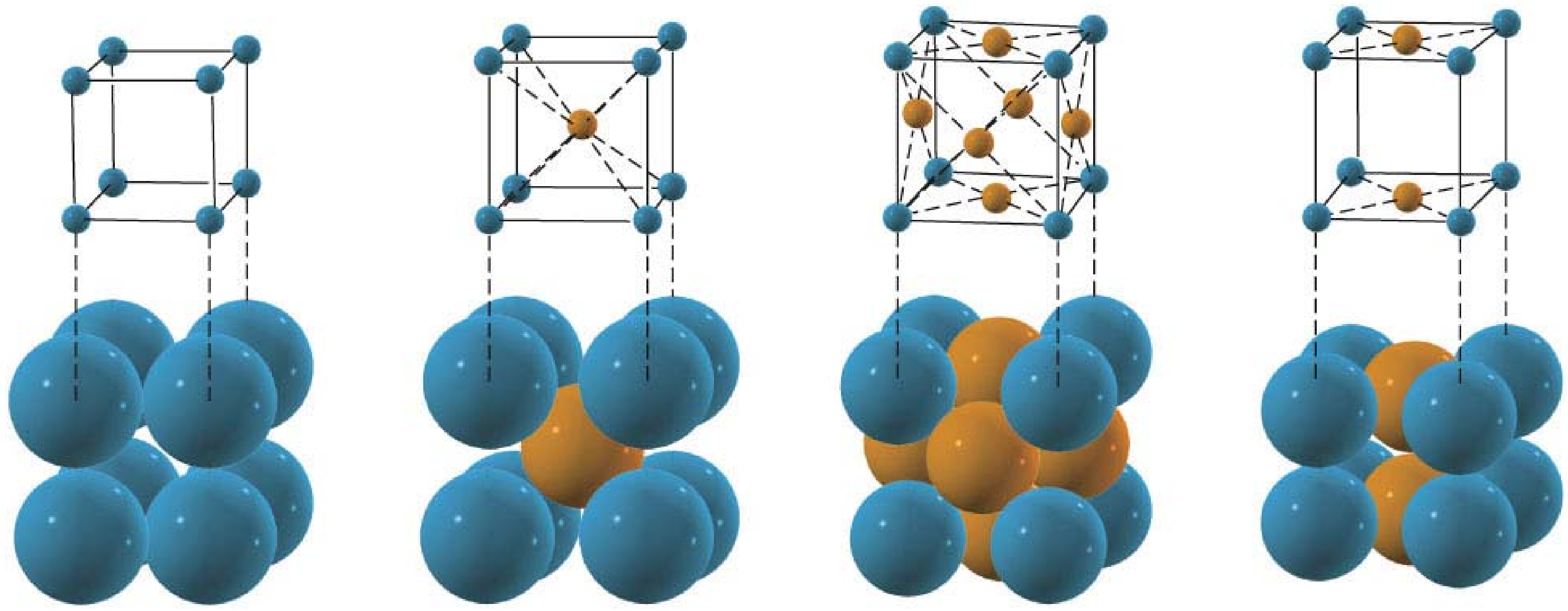
- x is fraction of *a* axis
- y is fraction of *b* axis
- z is fraction of *c* axis

Lattices & Unit Cells: 3-D 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	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$
Trigonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°$ $\gamma = 120°$
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$

Lattices & Unit Cells: 3-D Cell Setting

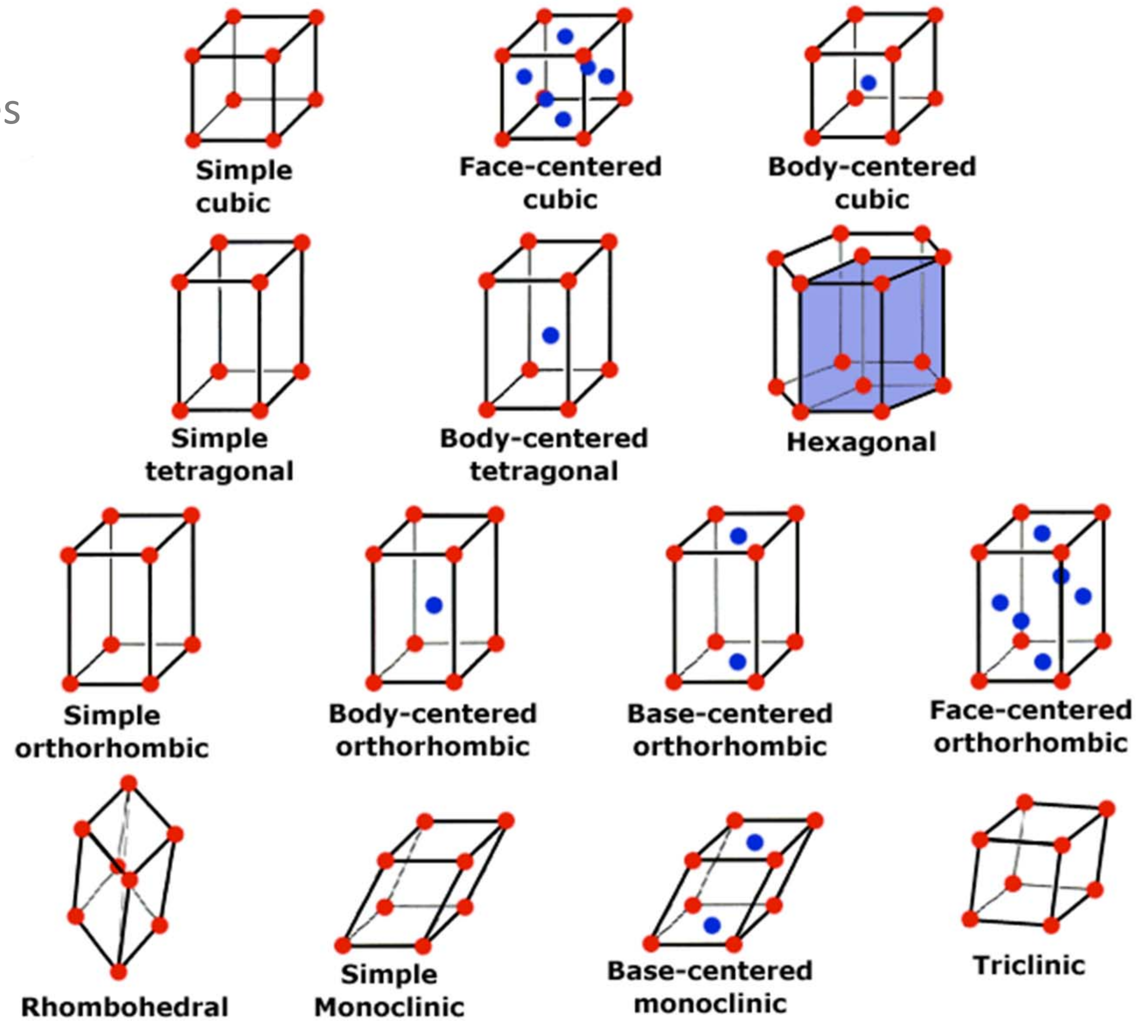
Primitive	Body-Centred	Face-Centred	Side-Centred
P	I	F	C



Atoms are identical even though coloured differently.

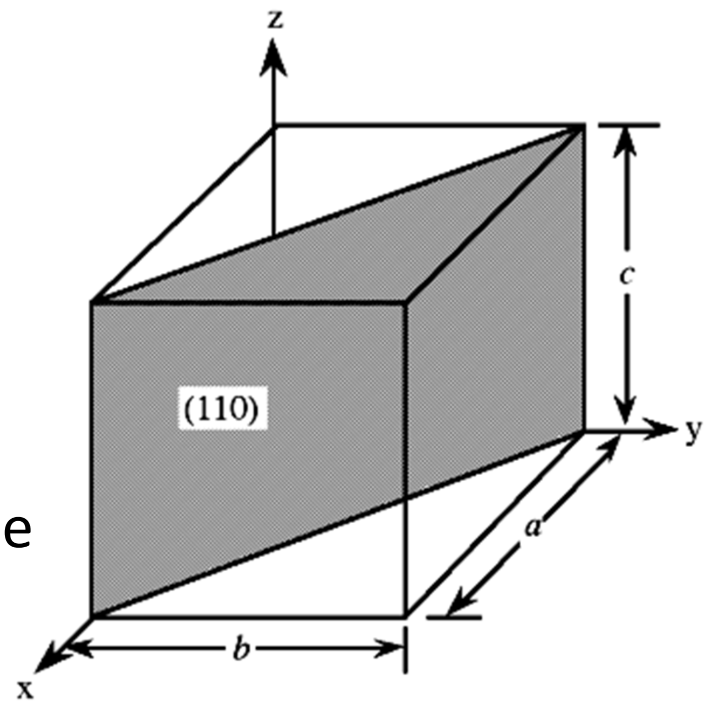
Lattices & Unit Cells: 3-D lattice types

7 crystal classes
14 Bravais Lattice types
230 space groups



Miller indices / planes

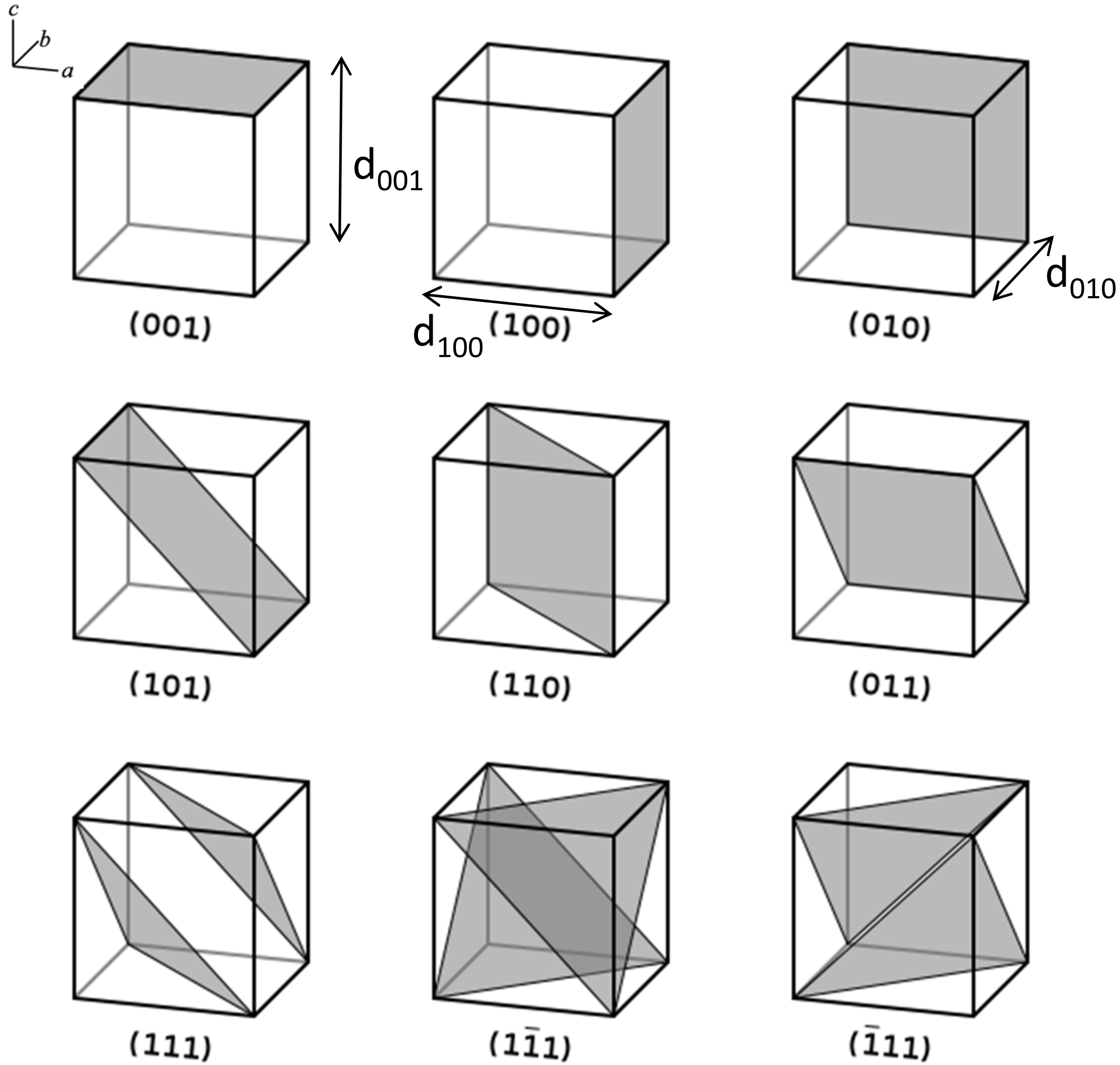
Unit cell planes can be defined by the notation called Miller indices. The Miller index is given as a hkl number where *h*, *k*, and *l* are reciprocals of the plane with the *x*, *y*, and *z* axes.



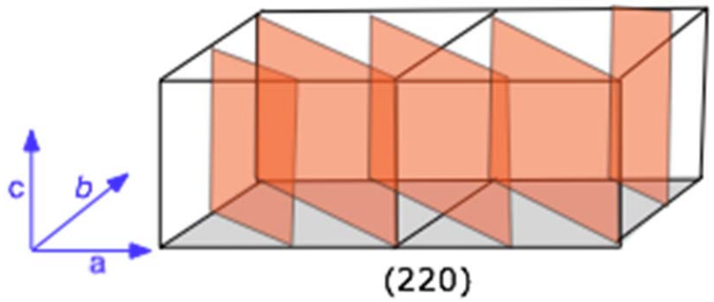
To obtain the Miller indices of a given plane requires the following steps:

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

More Miller indices



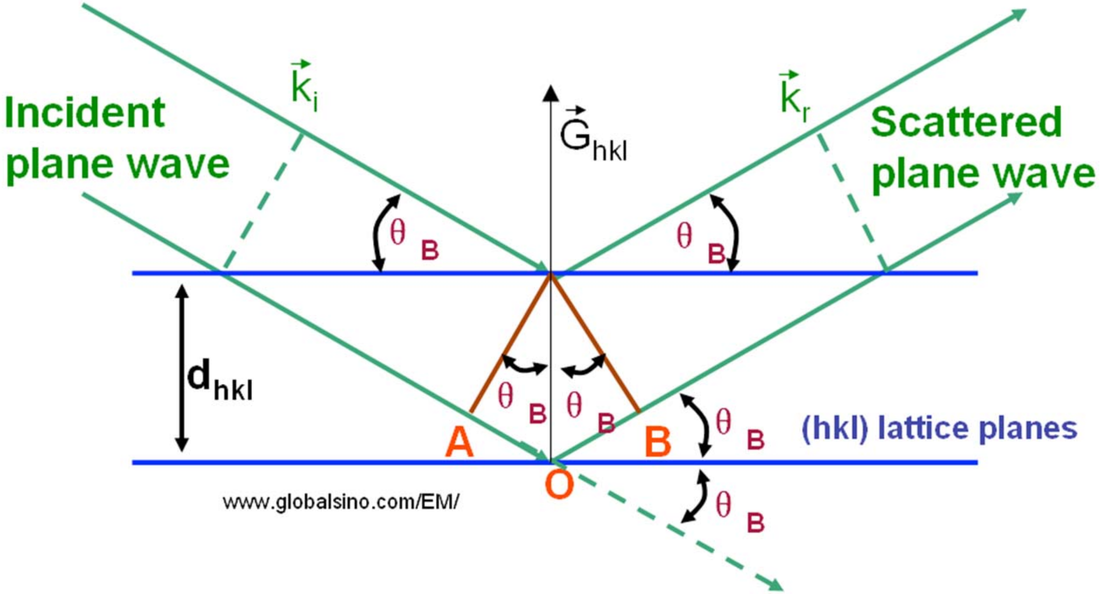
The higher the Miller index the less distance there is between equivalent planes, dividing the unit cell into ever smaller slices



For higher symmetry cells interplane distances are identical

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

Diffraction: The Bragg Law



- Constructive interference occurs when the waves reflected from adjacent scattering planes remain in phase – diffraction peak is observed
- The path difference travelled by waves between adjacent planes must be an integral multiple of the wavelength

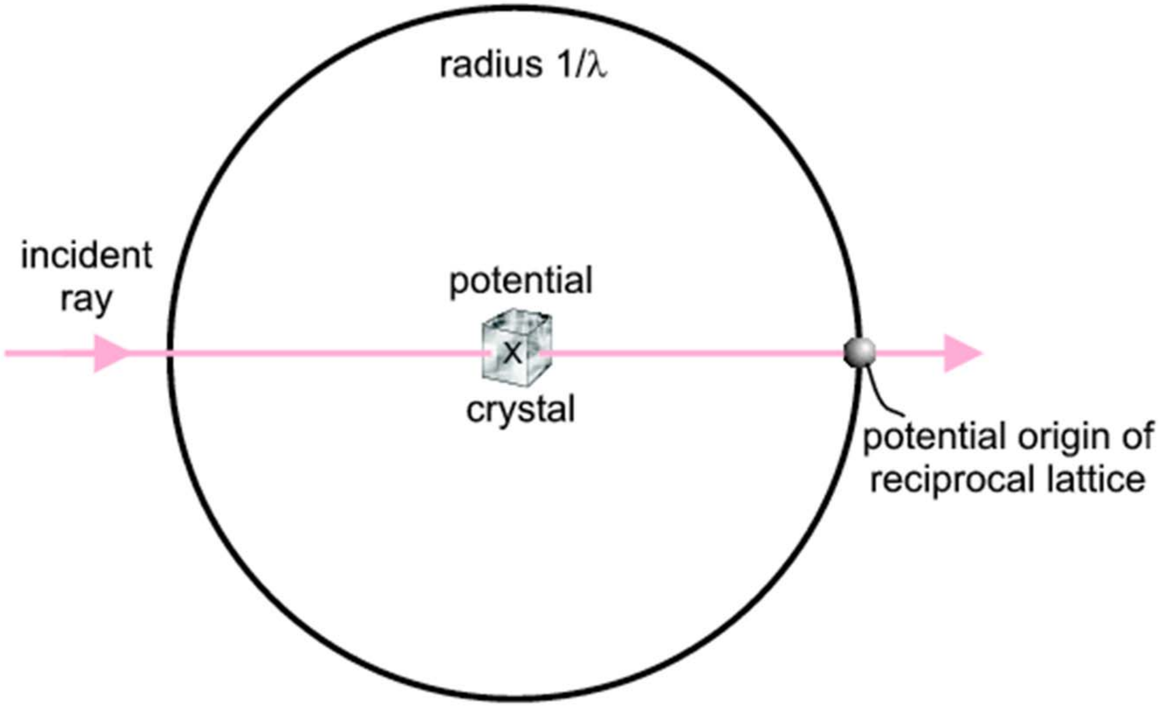
$$n\lambda = 2d\sin\theta$$

Distances Between Miller Planes

d-spacings in different crystal systems

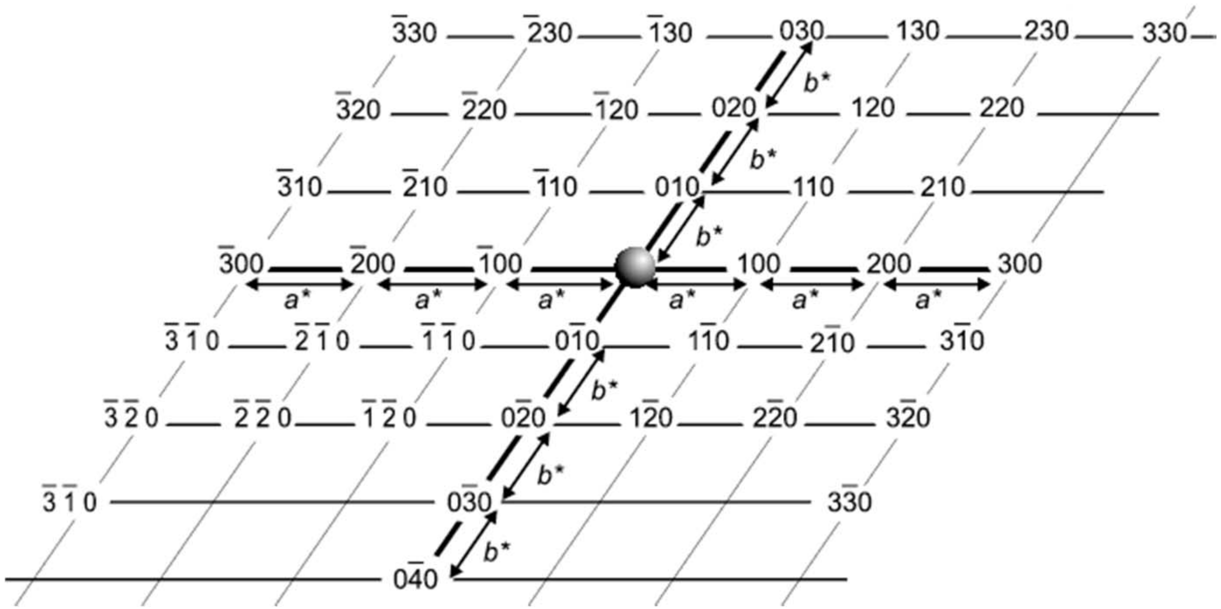
Crystal system	d_{hkl} as a function of Miller indices and lattice parameters
Cubic	$\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2}$
Tetragonal	$\frac{1}{d^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2}$
Orthorhombic	$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$
Hexagonal	$\frac{1}{d^2}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

The Ewald Sphere



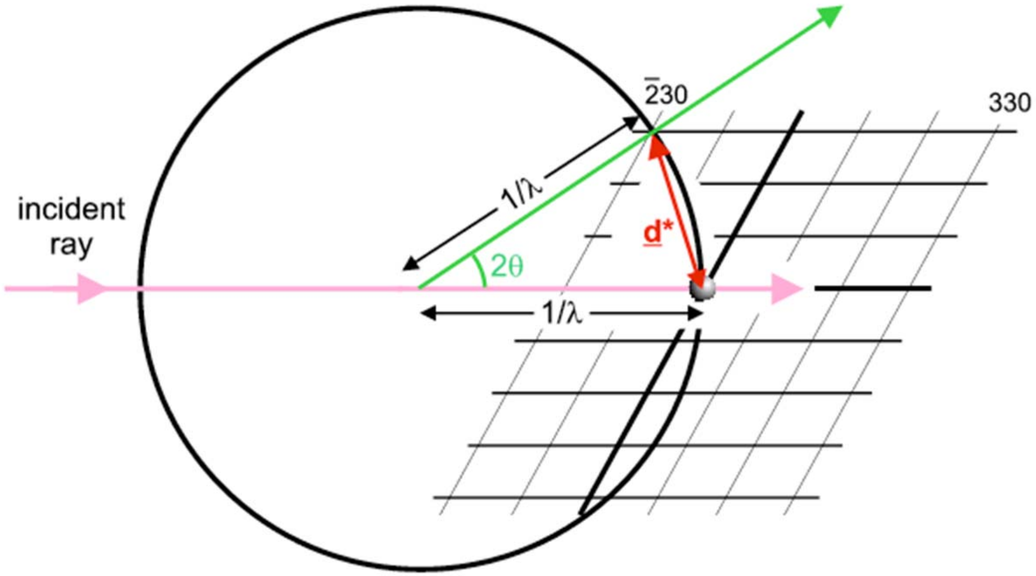
- Convenient visualisation tool especially for single crystal diffraction
- A sphere of radius 1/λ (2-D projection shown above)
- Potential diffracted X-rays/neutrons can be along any radius from the centre of the sphere to the circumference (including out of plane in the projection above). This represents the experimental possibilities (λ, possible 2θs)

The Reciprocal Lattice



- Alternative view of the crystal structure (hk0 plane illustrated)
- The reciprocal lattice consists of points which represent diffraction possibilities
- Each point can be labelled with a Miller index
- The units of this lattice are a*, b* and c* and any point can be reached using the vector equation d* = ha* + kb* + lc*

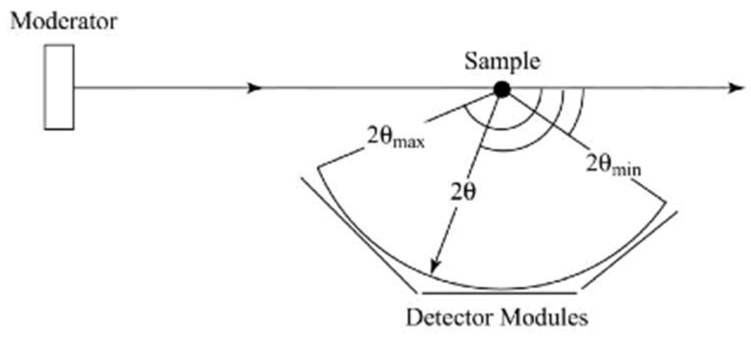
Condition for Observing Bragg Diffraction

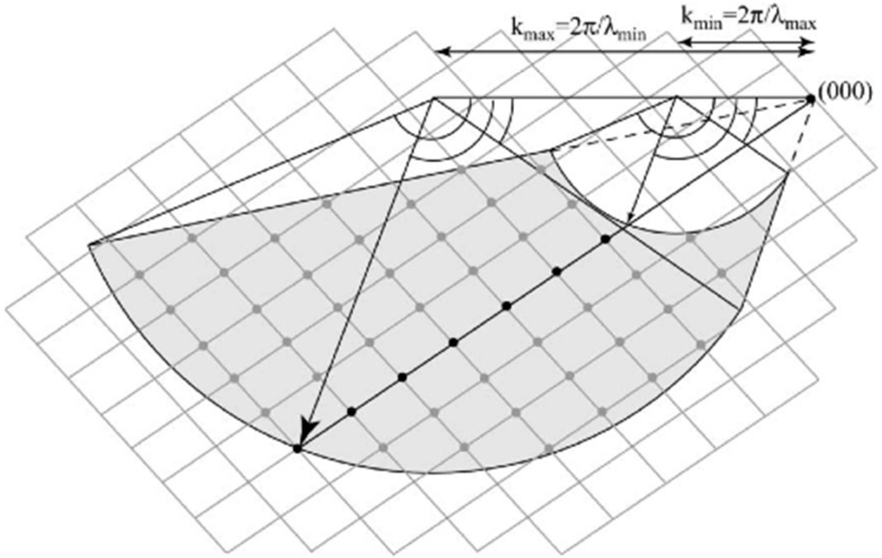


- Diffraction is observed whenever a reciprocal lattice point intersects the Ewald sphere (when Bragg condition is satisfied). Rotating the crystal will bring different lattice points into contact with the Ewald sphere.
- The direction of the diffracted ray is indicated in green
- The vector from origin 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

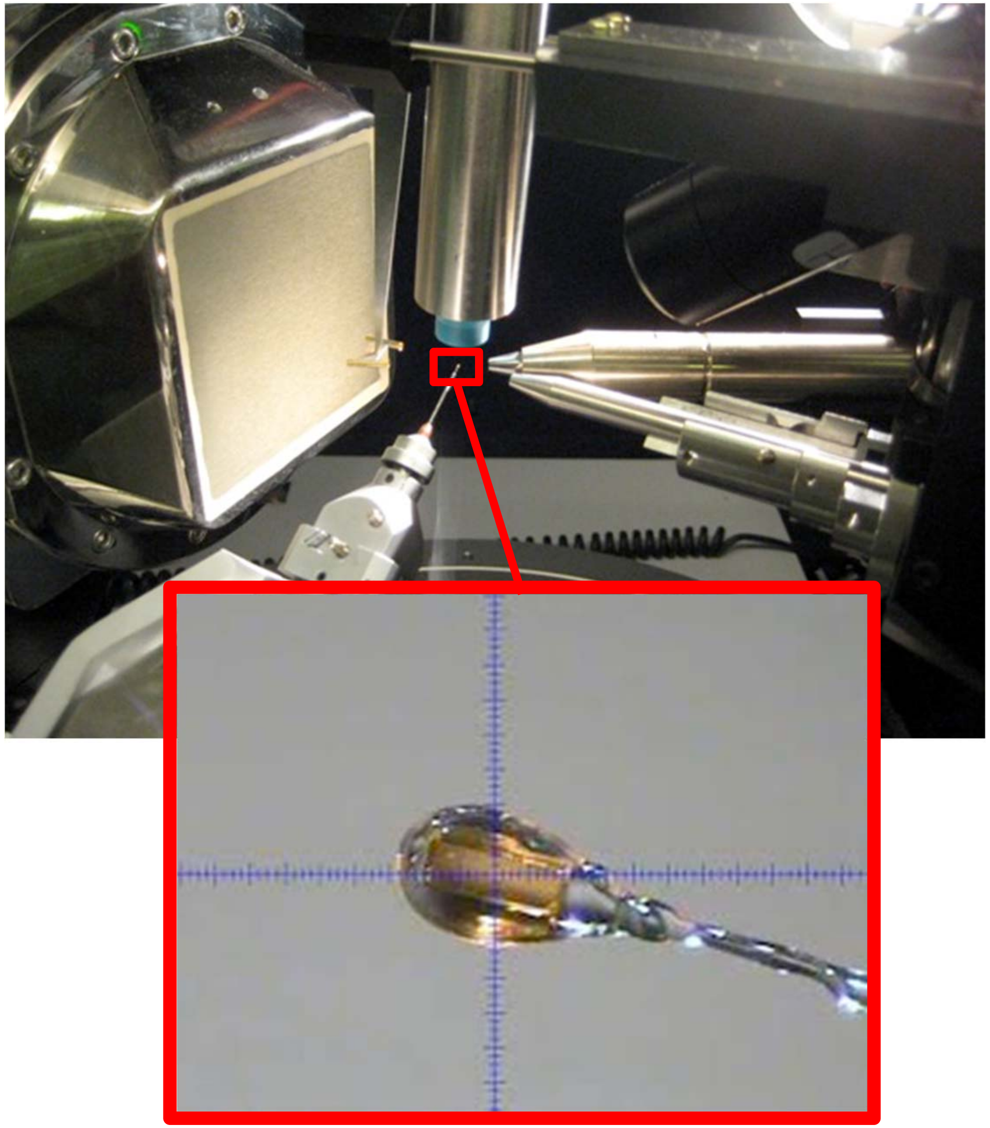
The Laue method

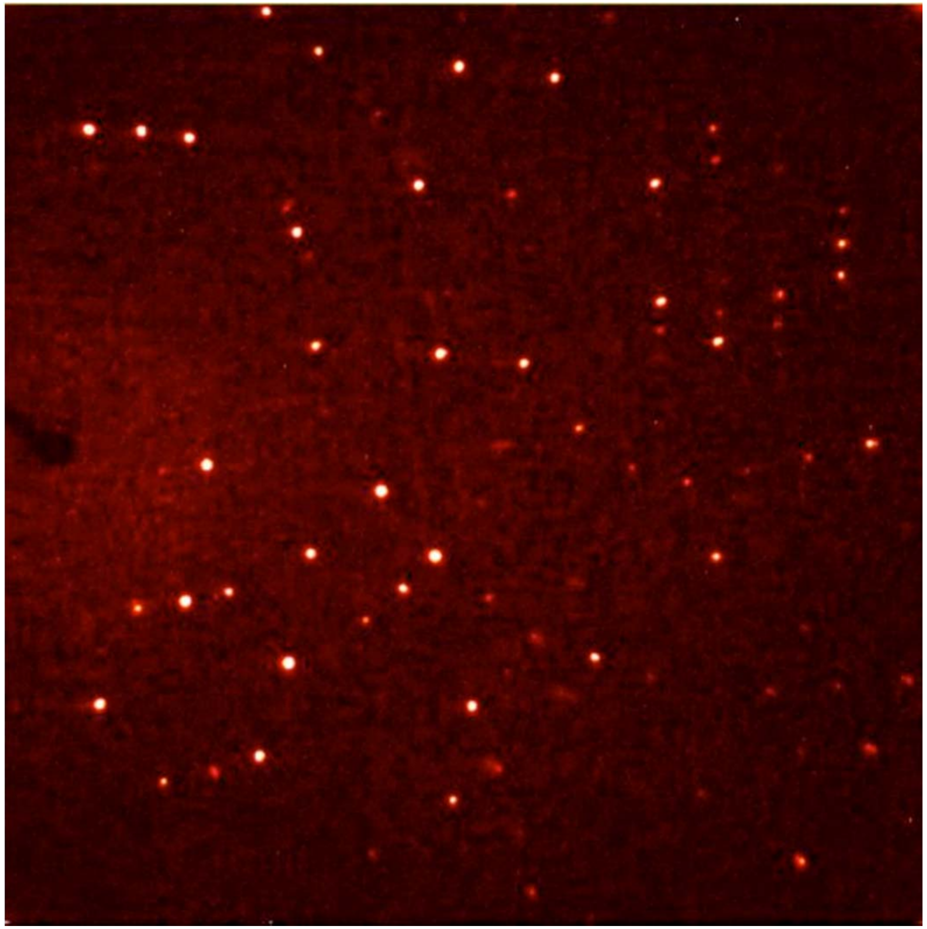
- Use a wavelength band to sample larger volume of reciprocal space
- A wide wavelength band covers a large reciprocal space volume
- Limits are λ_{min}, λ_{max}, the accessible scattering angle of the instrument and the diffraction limit of the crystal
- All reciprocal lattice points that lie in the shaded region will be sampled simultaneously
- More chance of spatial overlap of reflections, particularly with large unit cells
- Detector technology becomes paramount – image plate v continuous output
- Wavelength band must be well characterised for data normalisation



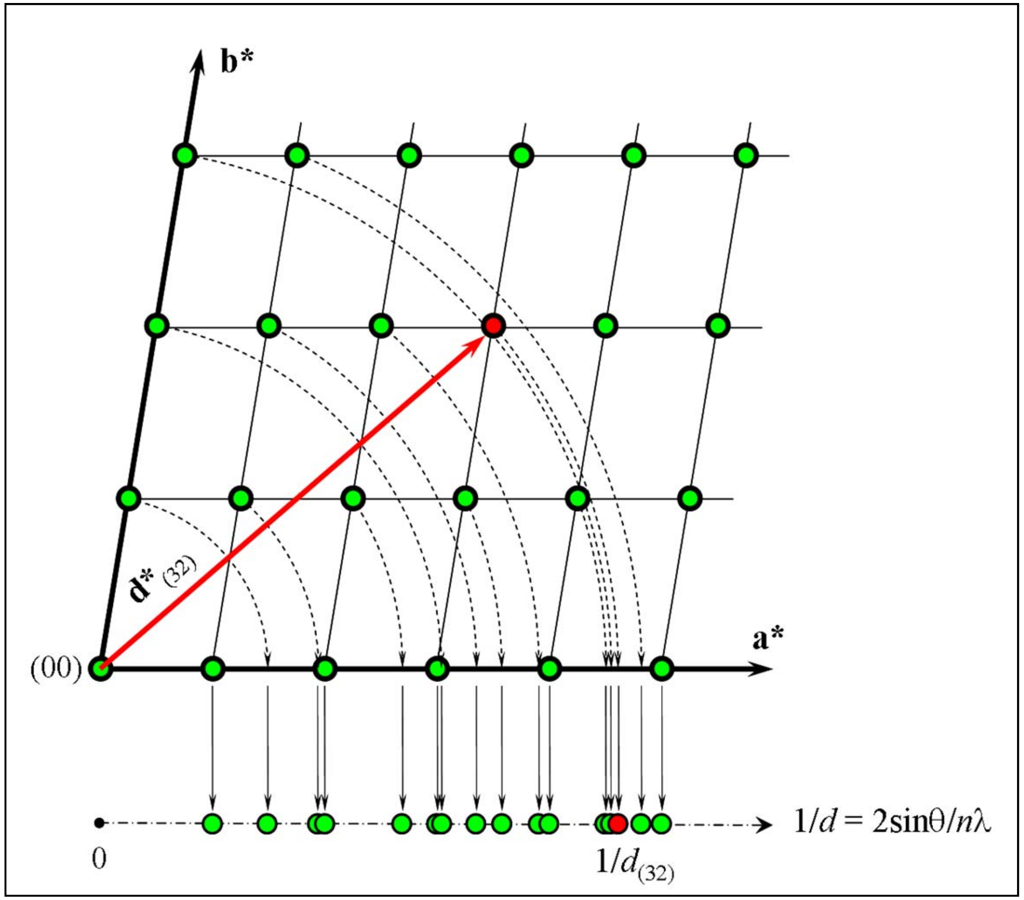


Diffraction set-up for a single crystal



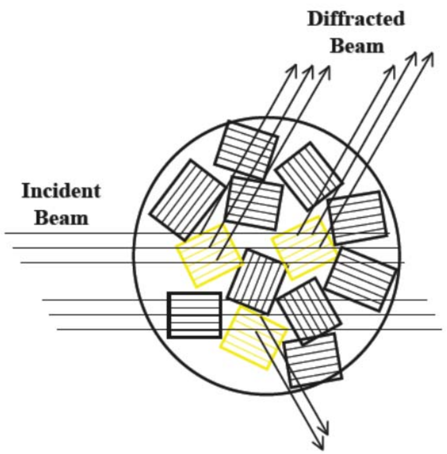


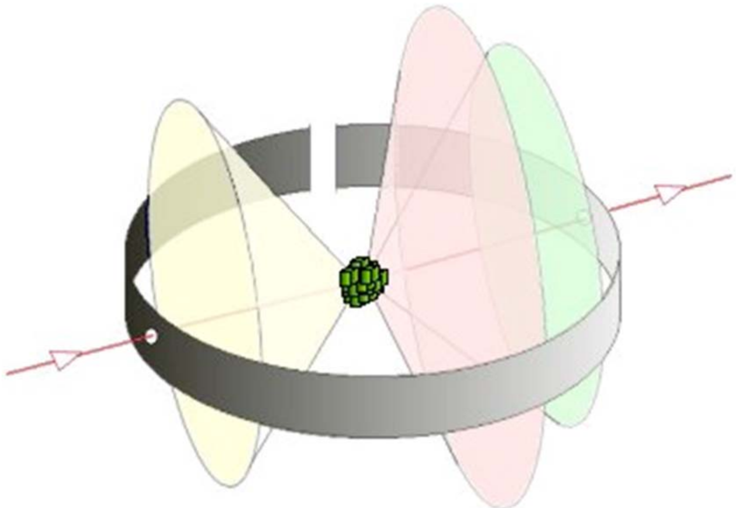
Powder diffraction in reciprocal space

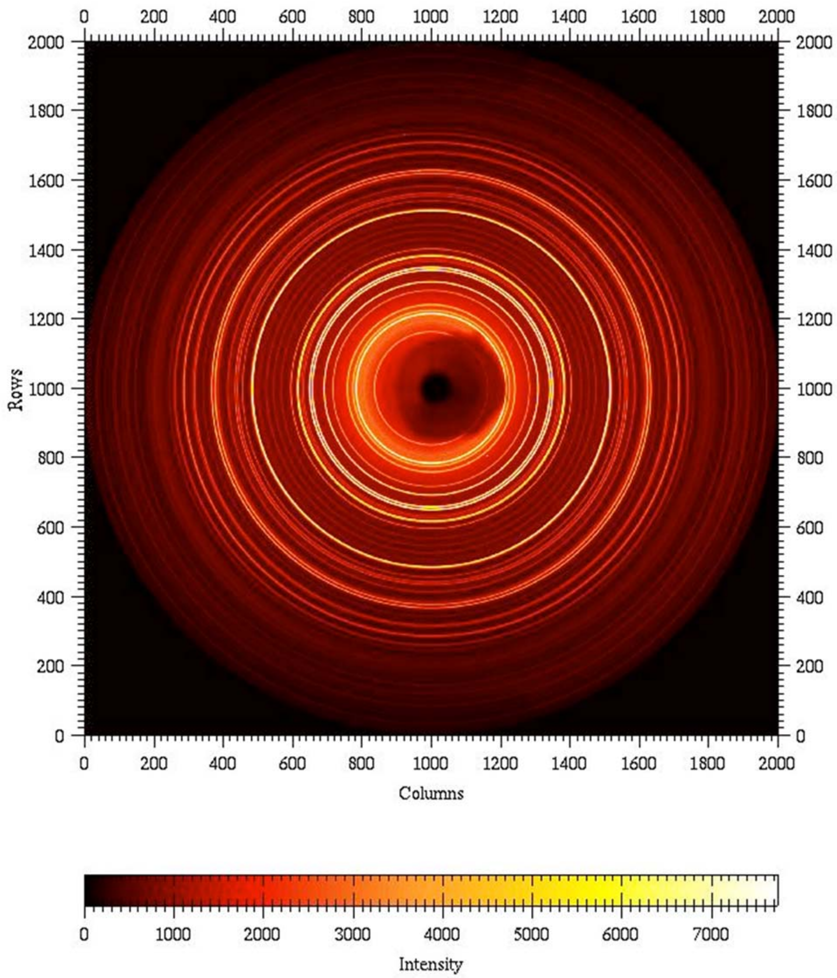


- Many crystallites with random orientation mean that each reciprocal lattice point will occur in every orientation possible, broadening into the surface of a sphere with radius d*
- The intersection of the Ewald sphere and the reciprocal lattice becomes a cone (intersection of 2 spheres)
- The directions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

Diffraction from a powder







Diffraction from a powder

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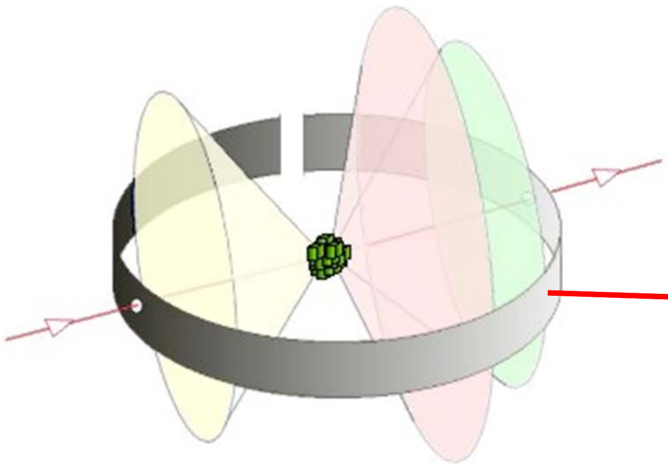
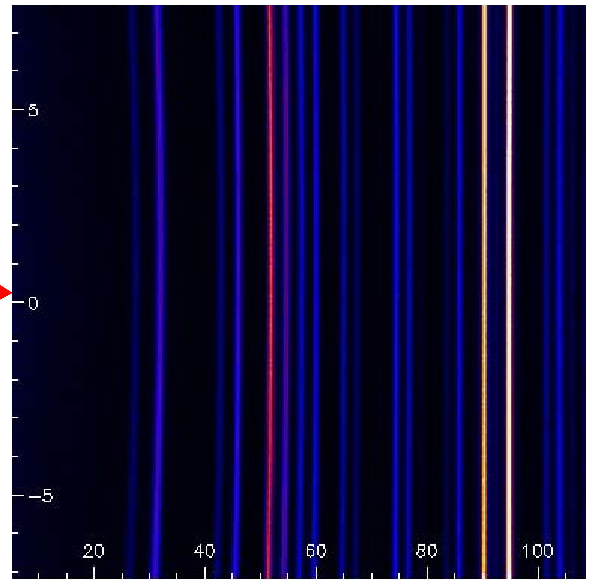
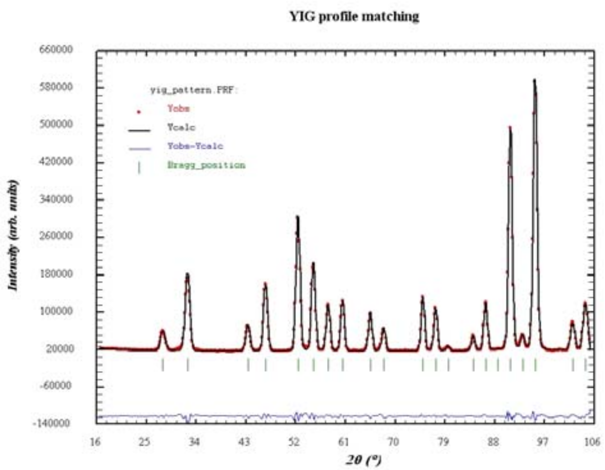


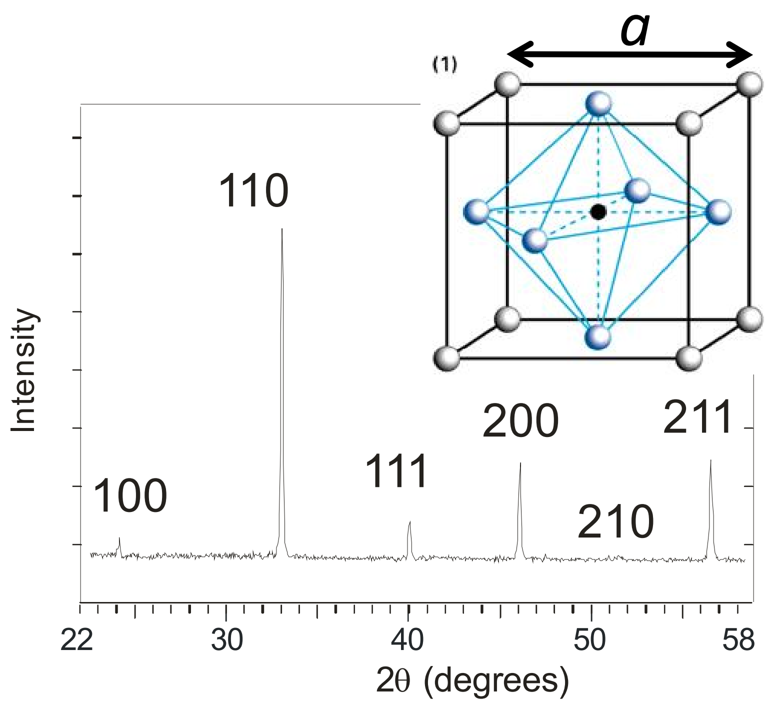


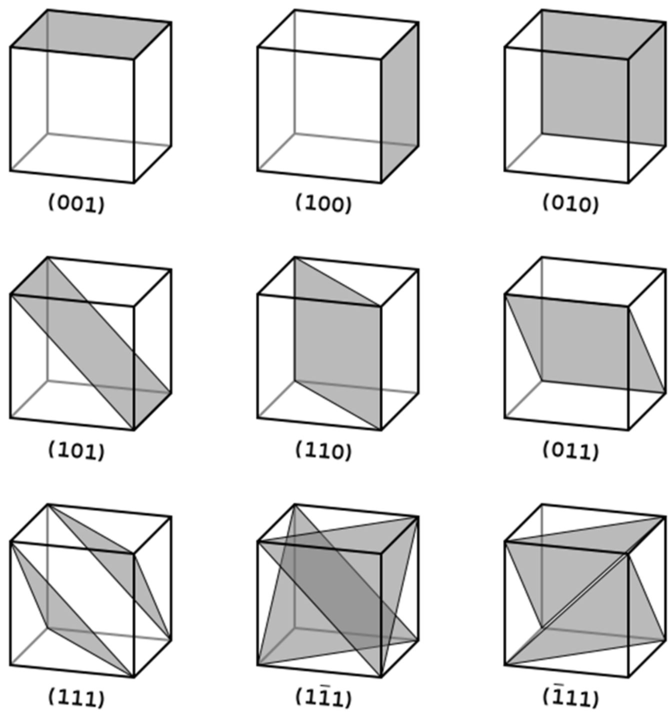


Typical monochromatic powder diffractometer

- Area or point detector and scans scattering angle intersecting the Debye-Scherrer cones
- Collapse into 1-D diffraction pattern

Miller Planes and Powder Diffraction



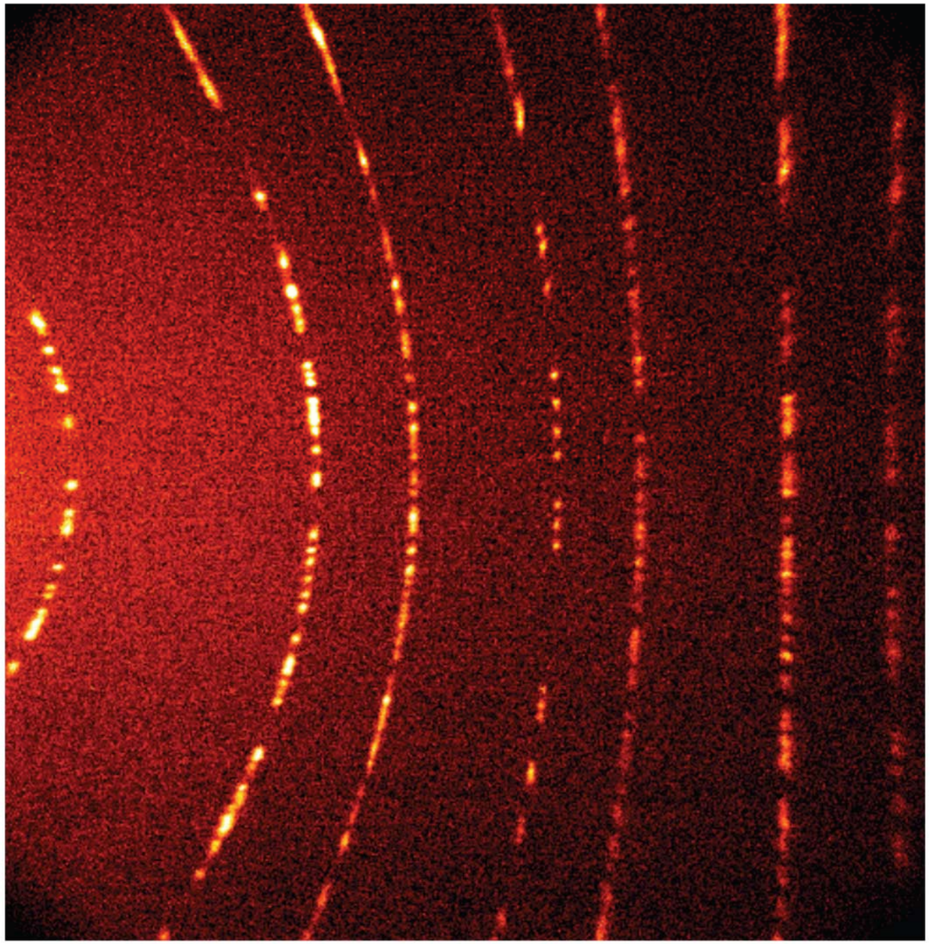


All equivalent planes occur at same scattering angle

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

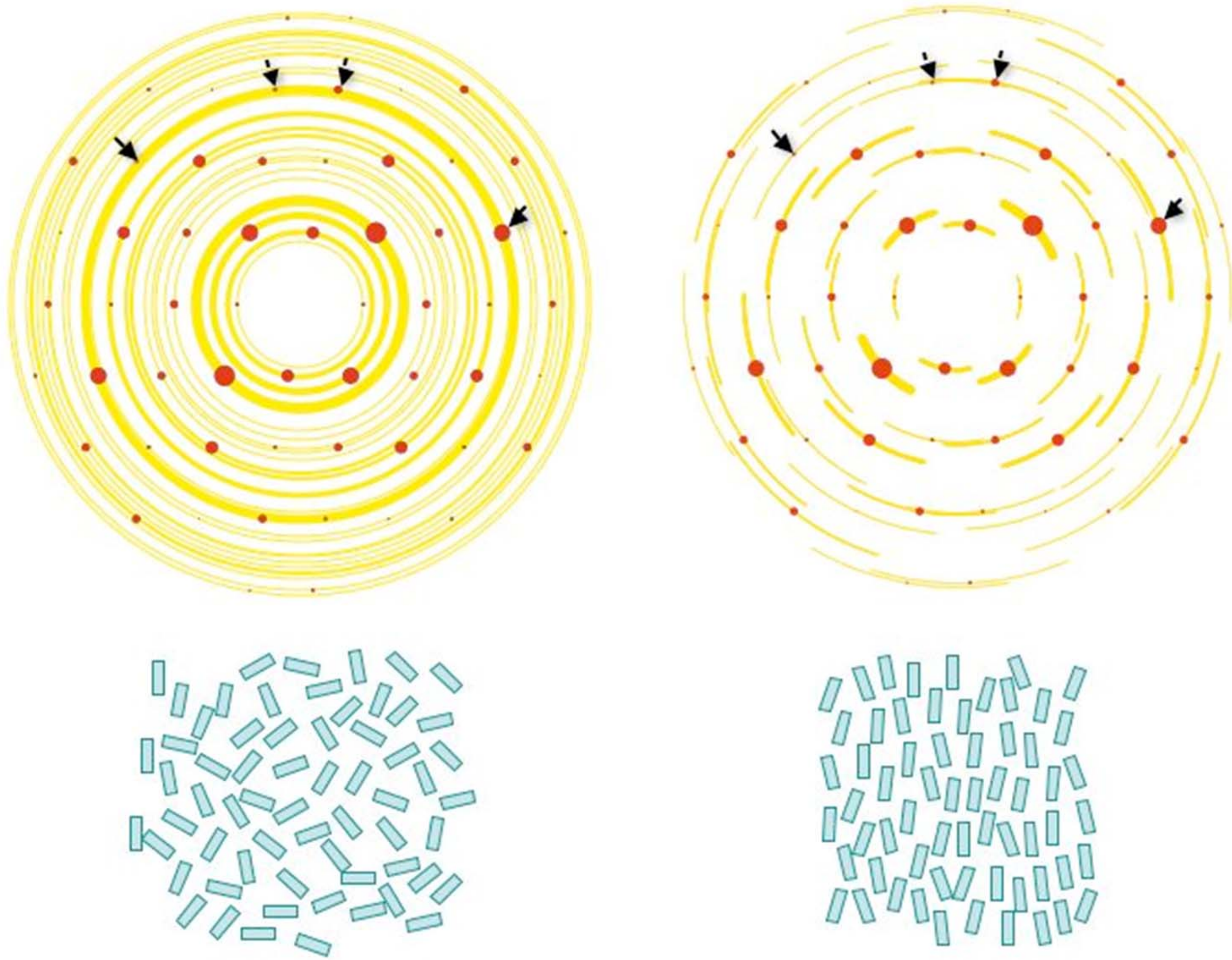
e.g. (511) and (333) occur at same 2θ for a cubic material

Diffraction from a few crystals or a non-powder average (preferred orientation)

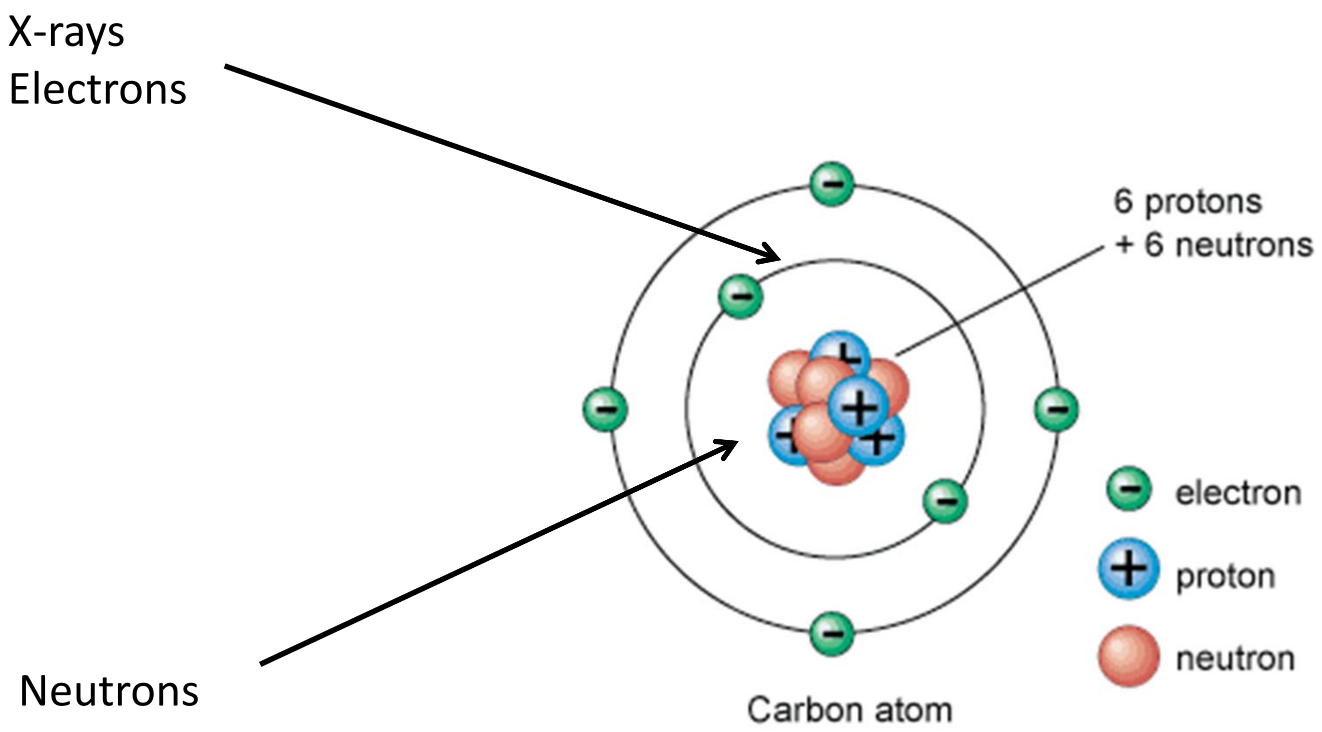


- When number of crystals is too small, the pattern becomes "grainy" -- diffraction from individual crystals dominate.
- Increase sample size
- Grind the sample to decrease domain size
- Oscillate or rotate the sample
- Use area detection & integrate the entire ring.

Diffraction from a few crystals or a non-powder average (preferred orientation)



X-rays and Neutrons are Complementary Probes for Diffraction

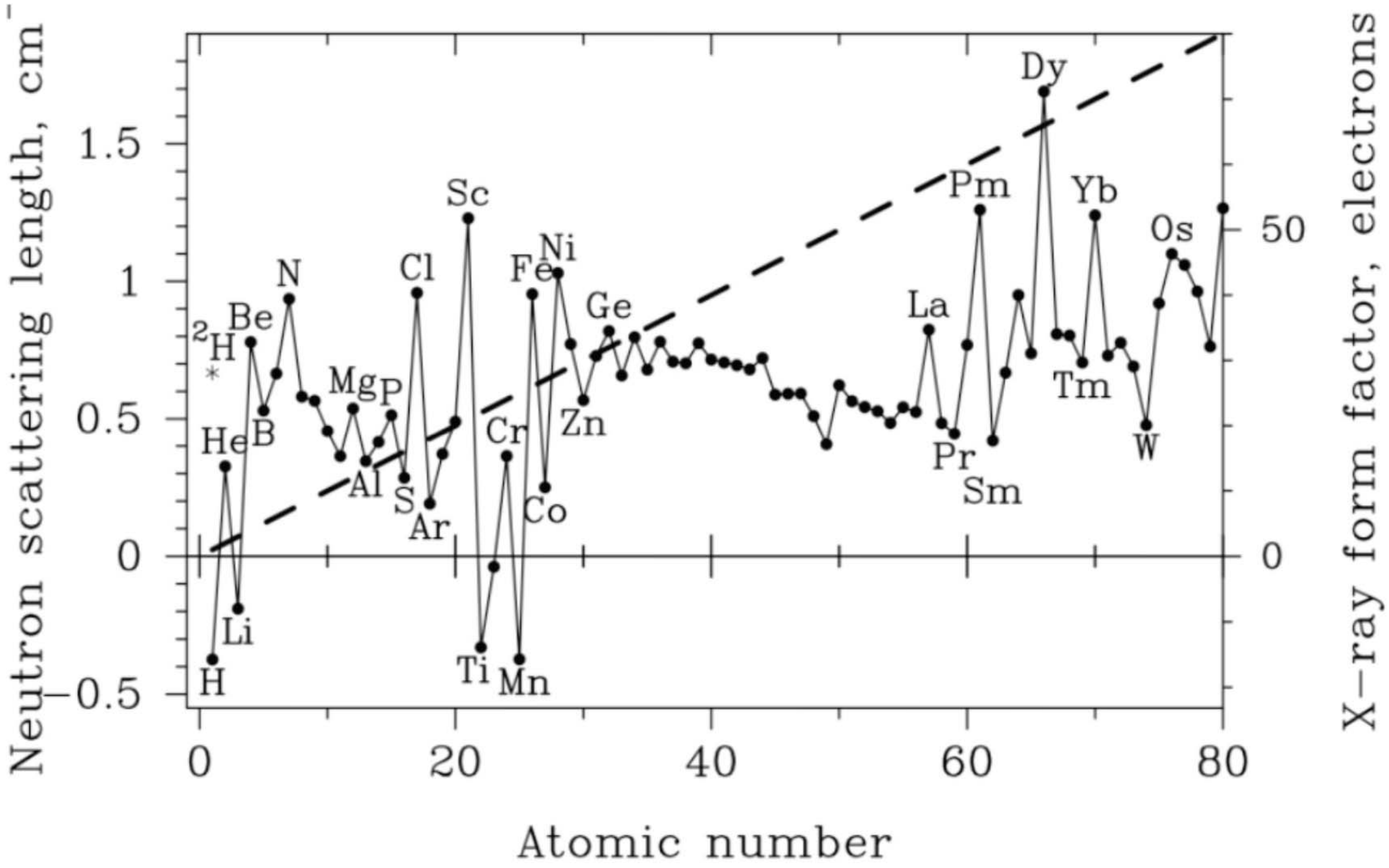


Neutron diffraction is used for problems that X-rays cannot address or inadequately address

X-rays vs neutrons for Diffraction

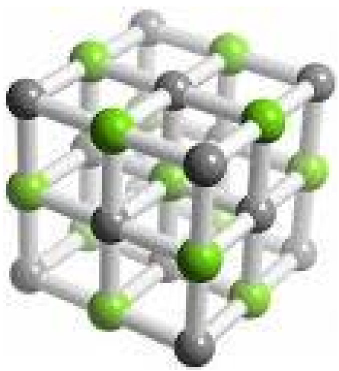
X-rays	Neutrons
Small samples	Large samples
Strong absorption	Low absorption
High energy (1 Å – 12.4 keV)	Low energy (1 Å = 81.81 meV)
Low penetration depth	High penetration depth
Light elements hard to detect	Light elements can be seen
Scattering power highly Q dependent	Scattering power almost Q independent
Neighbouring elements cannot be discriminated	Neighbouring elements can be discriminated
High availability (lab)	Low availability (large scale fac)
Cannot distinguish isotopes	Isotopes can be distinguished
	Magnetic structures easily probed

X-ray vs neutron scattering power



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

Neighbouring Element Discrimination



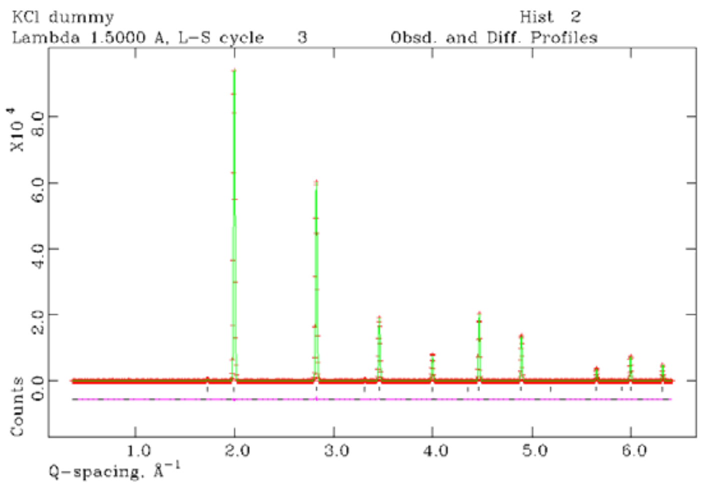
KCl

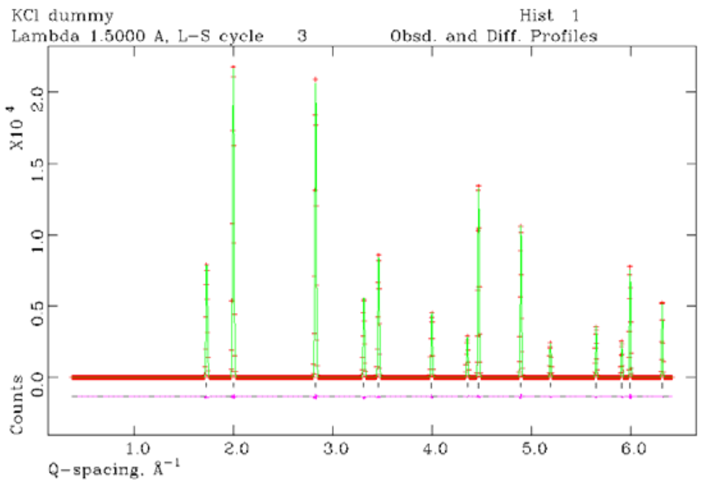
Fm-*3*m *a* = 6.29 Å

K z = 19

Cl z = 17

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



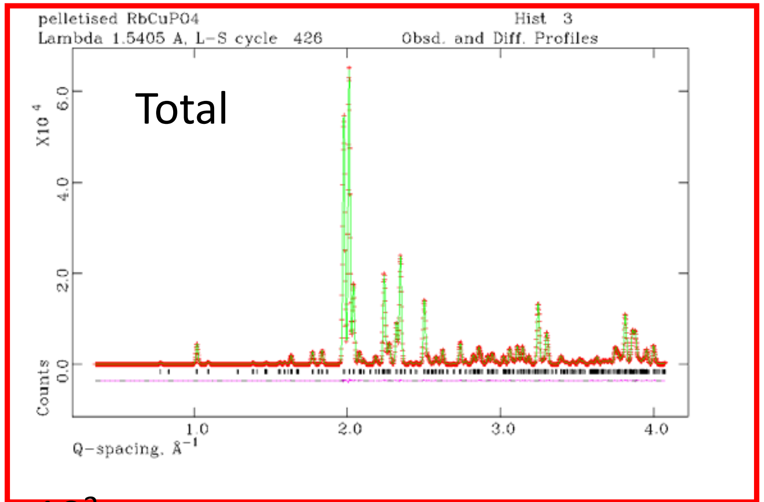


Without care KCl indexes from X-ray data on a cell that is ½ that from neutron data as elements are identical to X-rays as both have 18 e^-

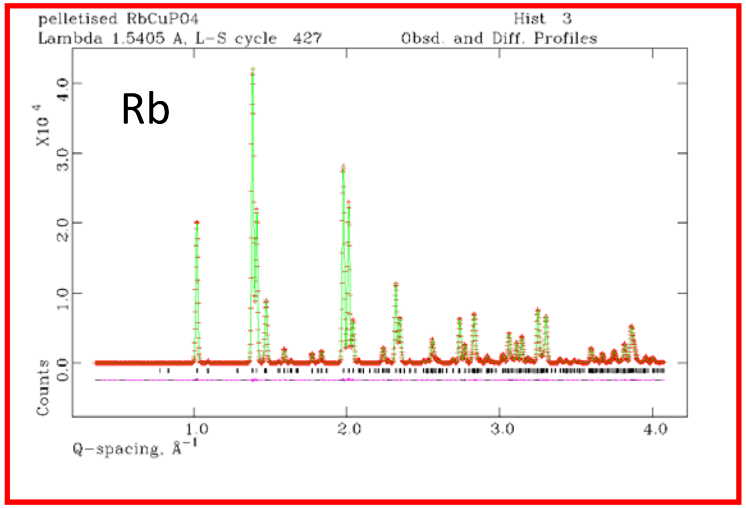
The non-linear relationship of neutron scattering length between neighbouring elements is crucial

Scattering contributions $RbCuPO_4$ (X-rays)

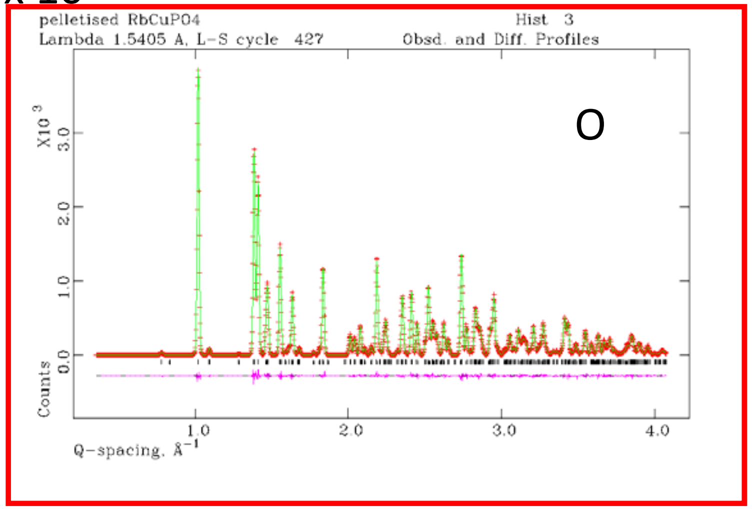
6×10^4



4×10^4



3.5×10^3



- Rb scattering contribution is factor 10 higher
- Cu and P contributions not shown
- Total is not just a simple sum of the contributions
- Evidence of the differing phase of the Rb and O to F_{hkl} hence I_{hkl}

Scattering contributions $RbCuPO_4$ (neutron)

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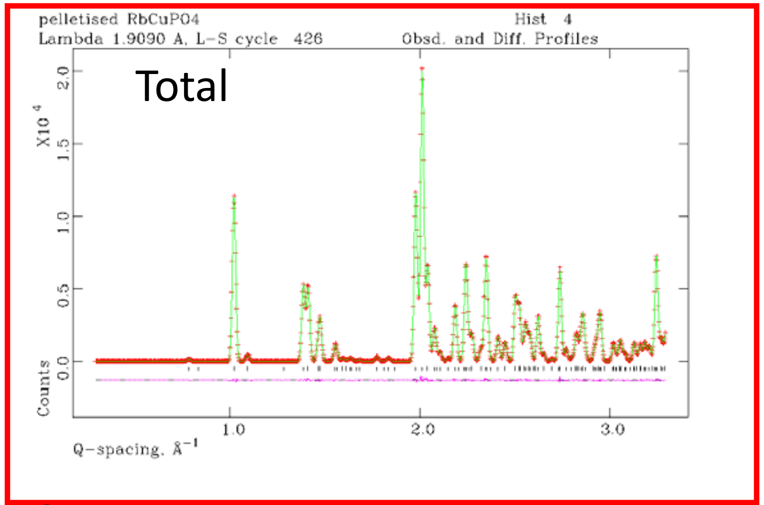
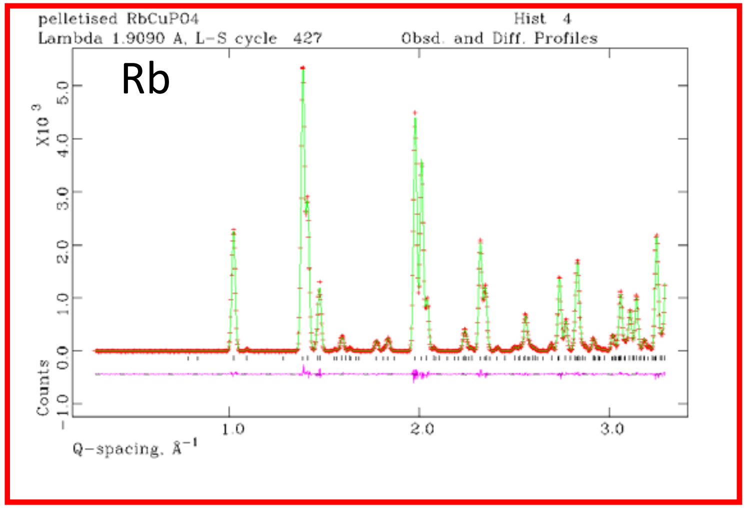
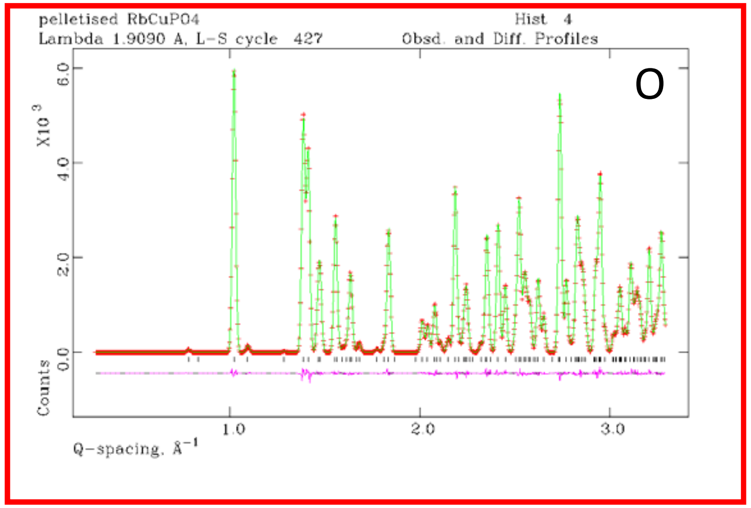
2 x 10^4



5 x 10^3



6 x 10^3



- Rb and O scattering contributions similar
- Cu and P contributions not shown
- Total is not just a simple sum of the contributions
- Evidence of the differing phase of the Rb and O to F_{hkl} hence I_{hkl}

Scattering contrast isotopes

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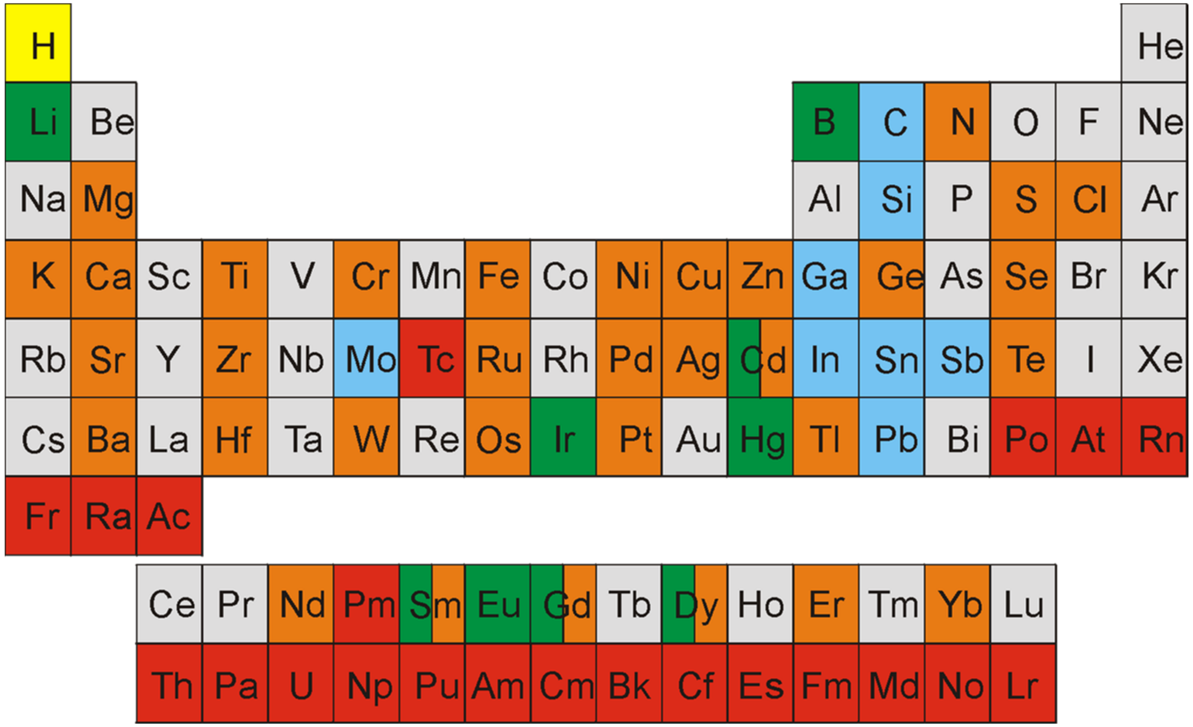


> 20% scattering length contrast isotopes

5-20% scattering length contrast isotopes

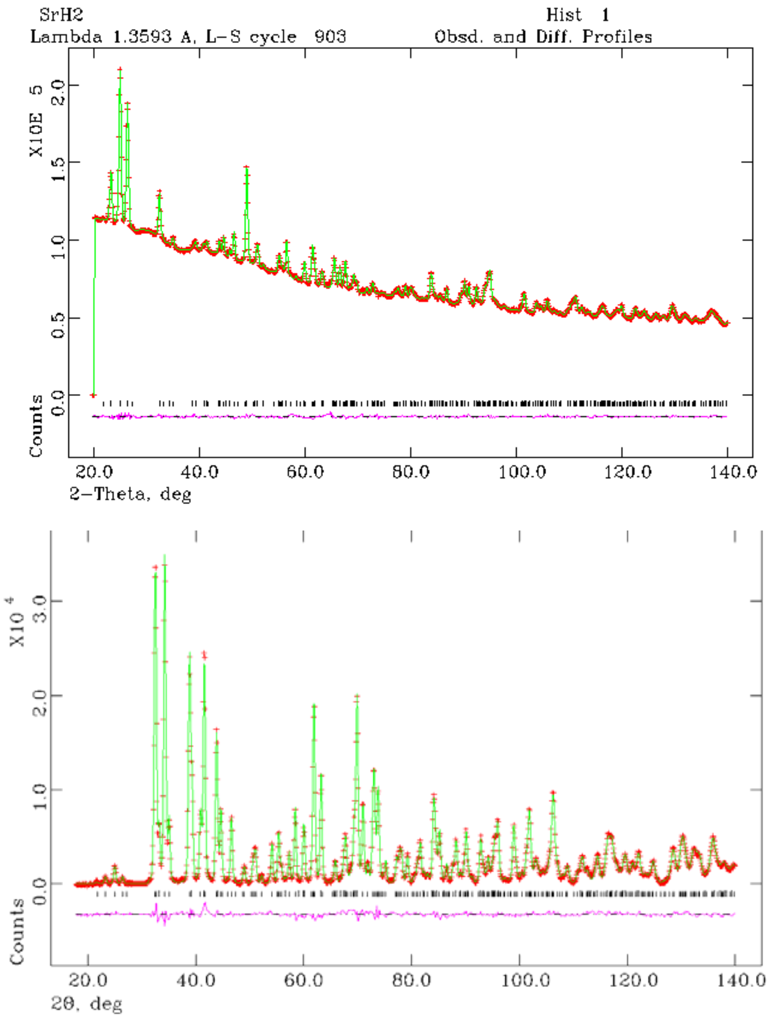
Non-absorbing isotopes available

Non-incoherent scattering isotope available

Mono-isotopic elements

Radioactive elements

Isotope coherent scattering length contrast



SrH_2 (top) v SrD_2 (bottom)

Structures are identical

Scattering lengths

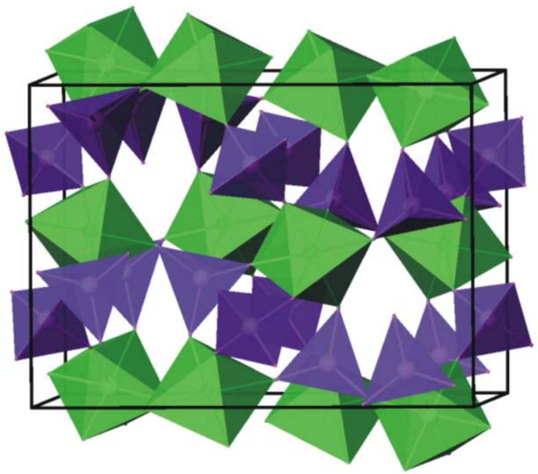
H -3.739 fm

D 6.67 fm

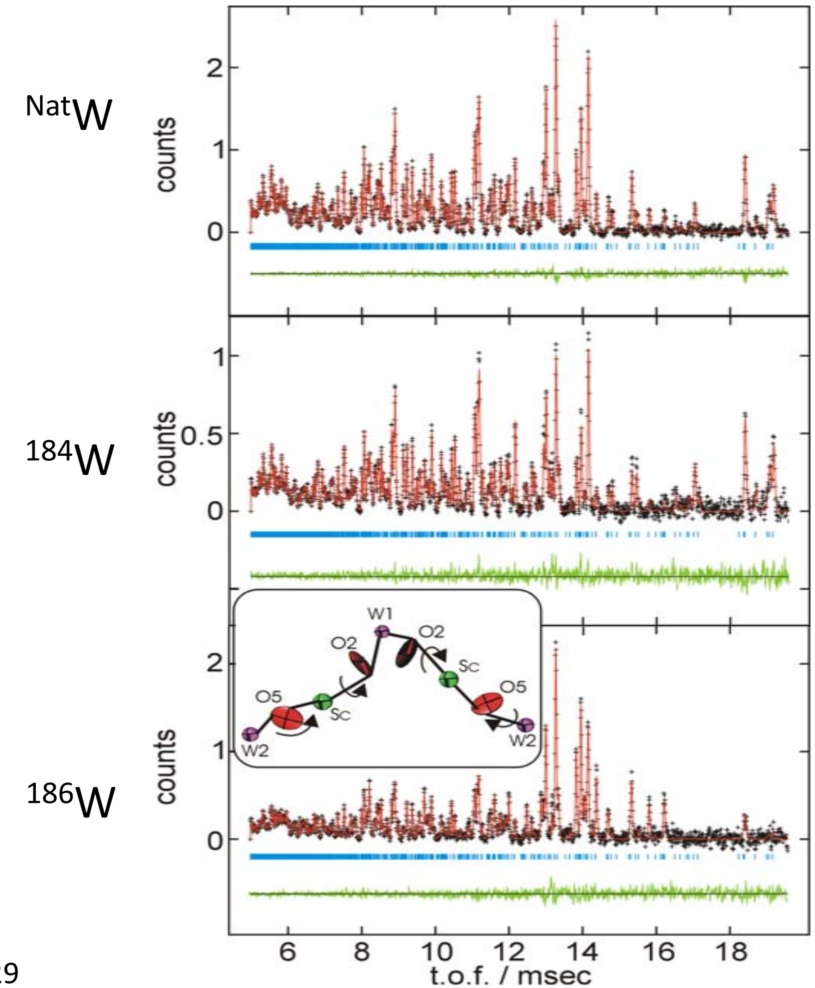
Negative scattering length signifies a change in the phase of the scattered neutron

X-ray patterns are identical and H contribution is negligible to total scattering intensity

Origin of NTE in $Sc_2(WO_4)_3$



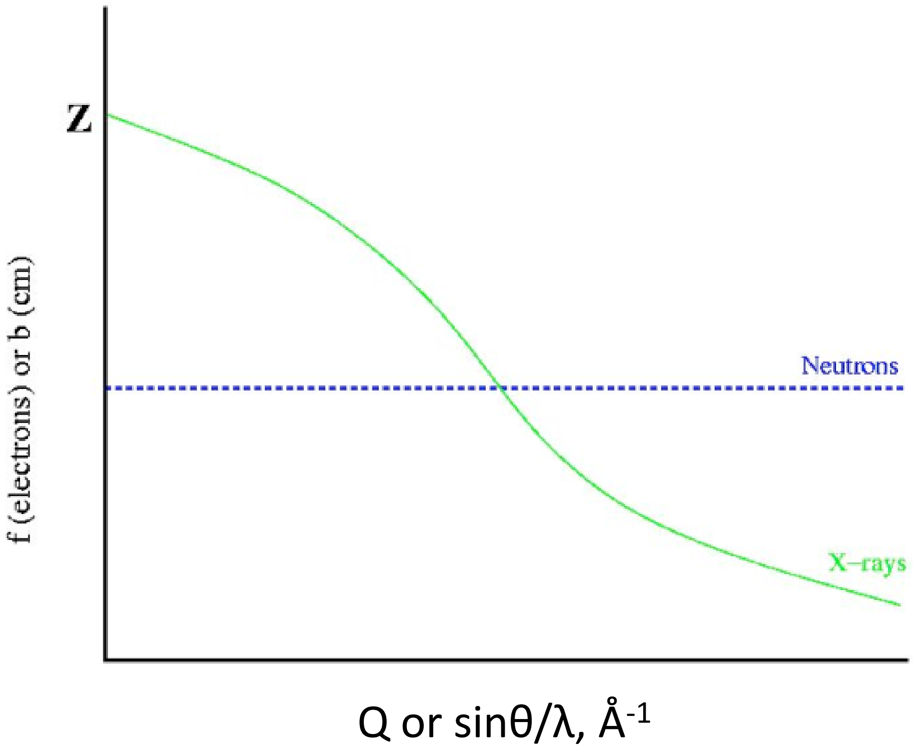
- Resolved co-operative atomic displacements
- First example using PND
- 10 years later same experiment possible without ISND on upgraded instrument HRPD



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

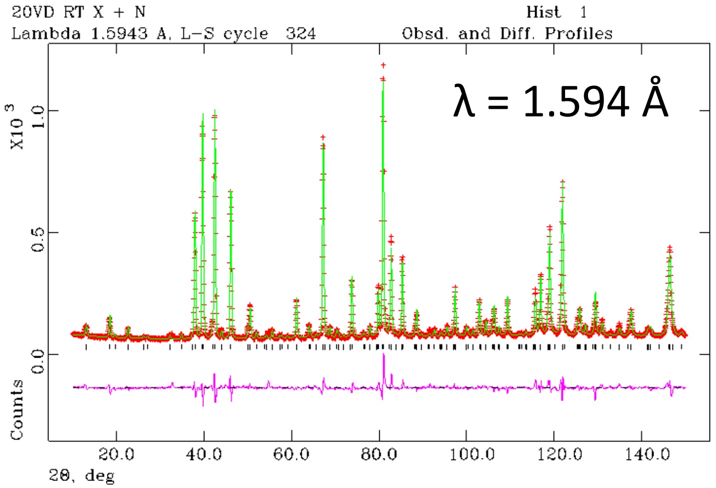
Form factor

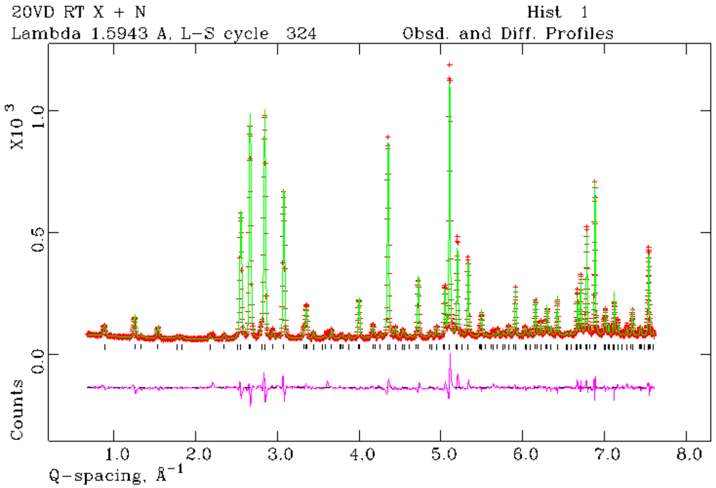
- Neutrons scatter primarily from the nucleus and form factor is almost Q-independent
  - Atom vibrations still reduce scattering at high Q
- The neutron can also interact with unpaired electrons to probe magnetism
  - Q-dependent form factor
  - Magnetic reflections are most intense at low Q

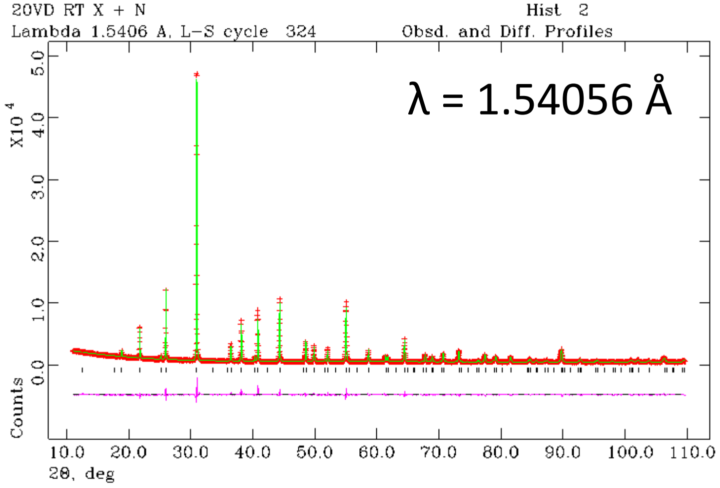


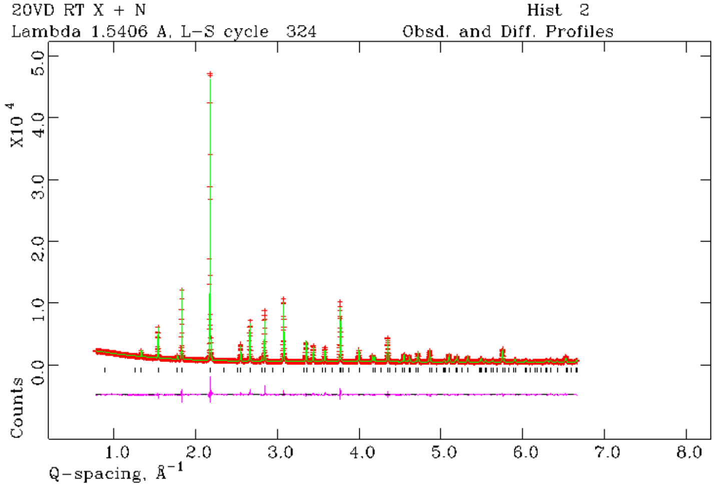
Form factor, scattering power and complementarity of neutrons and X-rays

EUROPEAN SPALLATION SOURCE



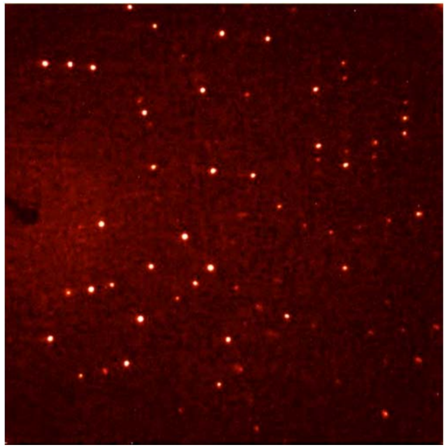


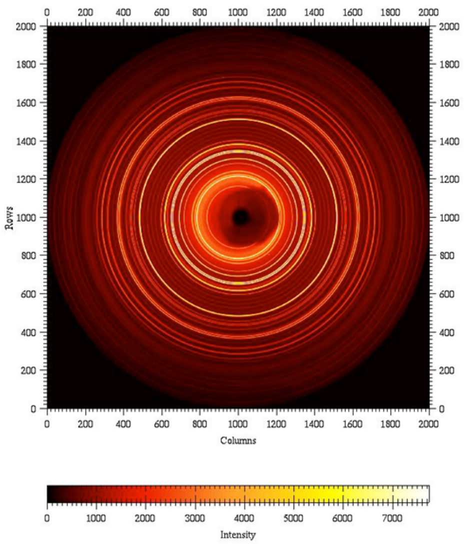


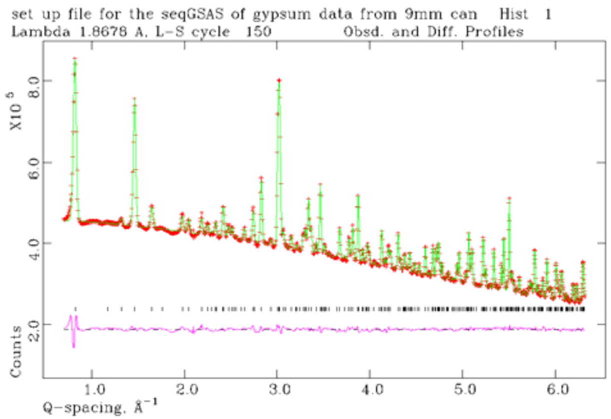


Structure Solution/refinement

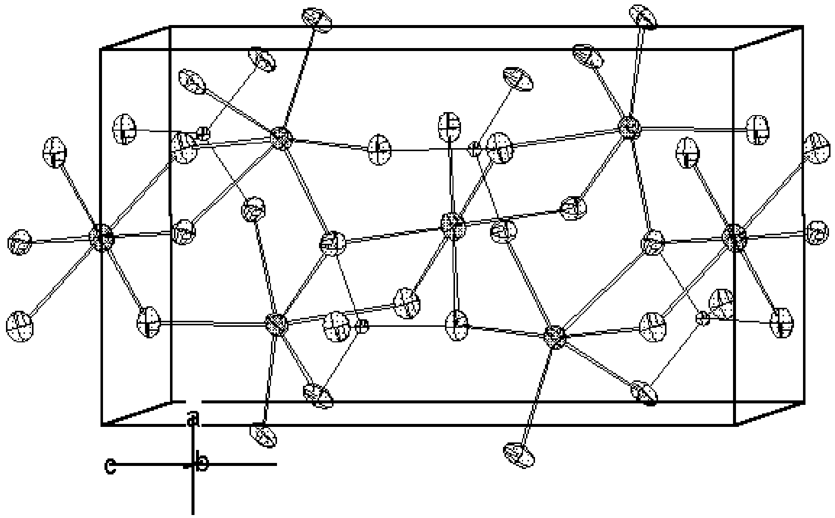
How to go from



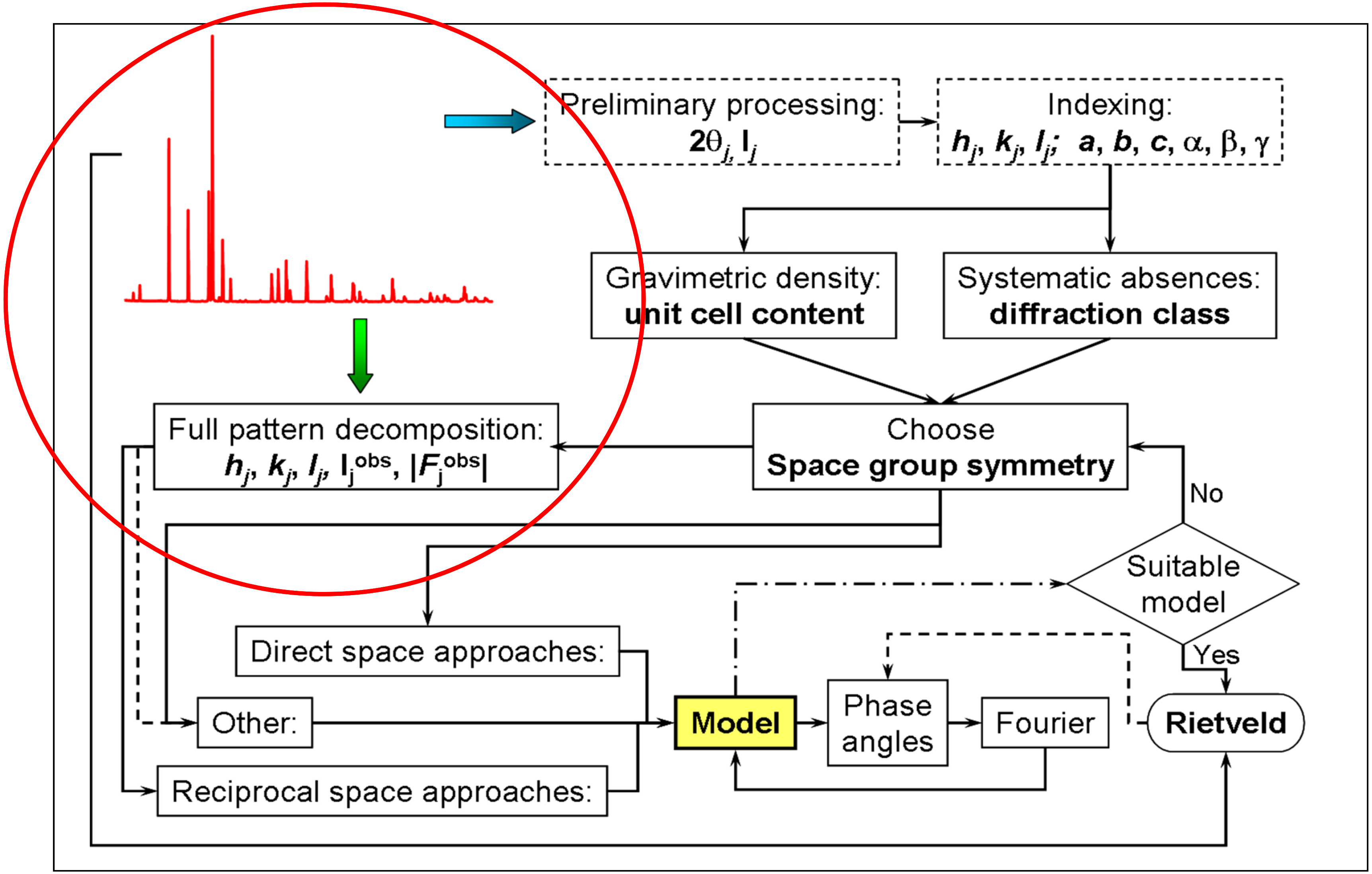




to this?



Process for structure solution and refinement from powders using Bragg scattering



Measured 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

Centrosymmetry

Since adding 1 to x_i,y_i or z_i does not change the structure factor it can be simplified to sum over the atoms of ***one unit cell.***

Also, since $e^{i\phi} = i\sin\phi + \cos\phi$

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

When an atom at x,y,z generates another atom by symmetry at -x,-y,-z

(centrosymmetric with a centre of symmetry at the origin)

We know that:

$$e^{i\phi} = i\sin\phi + \cos\phi$$

$$\cos(-\phi) = \cos\phi$$

$$\sin\phi = -\sin(-\phi)$$

This means $e^{i\phi} + e^{-i\phi} = 2\cos\phi$

Centrosymmetry continued

This allows the simplification of the structure factor to:

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

Where now the sum only includes one atom in each pair

Systematic absences occur when other symmetry conditions are met. Reflections are only observed when:

- For body centering h+k+l=2n
- For face centering h, k and l must all be odd or all be even
- Screw axes and glide planes give further conditions

These reduce the number of observed reflections in a diffraction pattern and is an integral part of choosing monochromator materials

See tutorial session after coffee break where you will prove this yourselves

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.

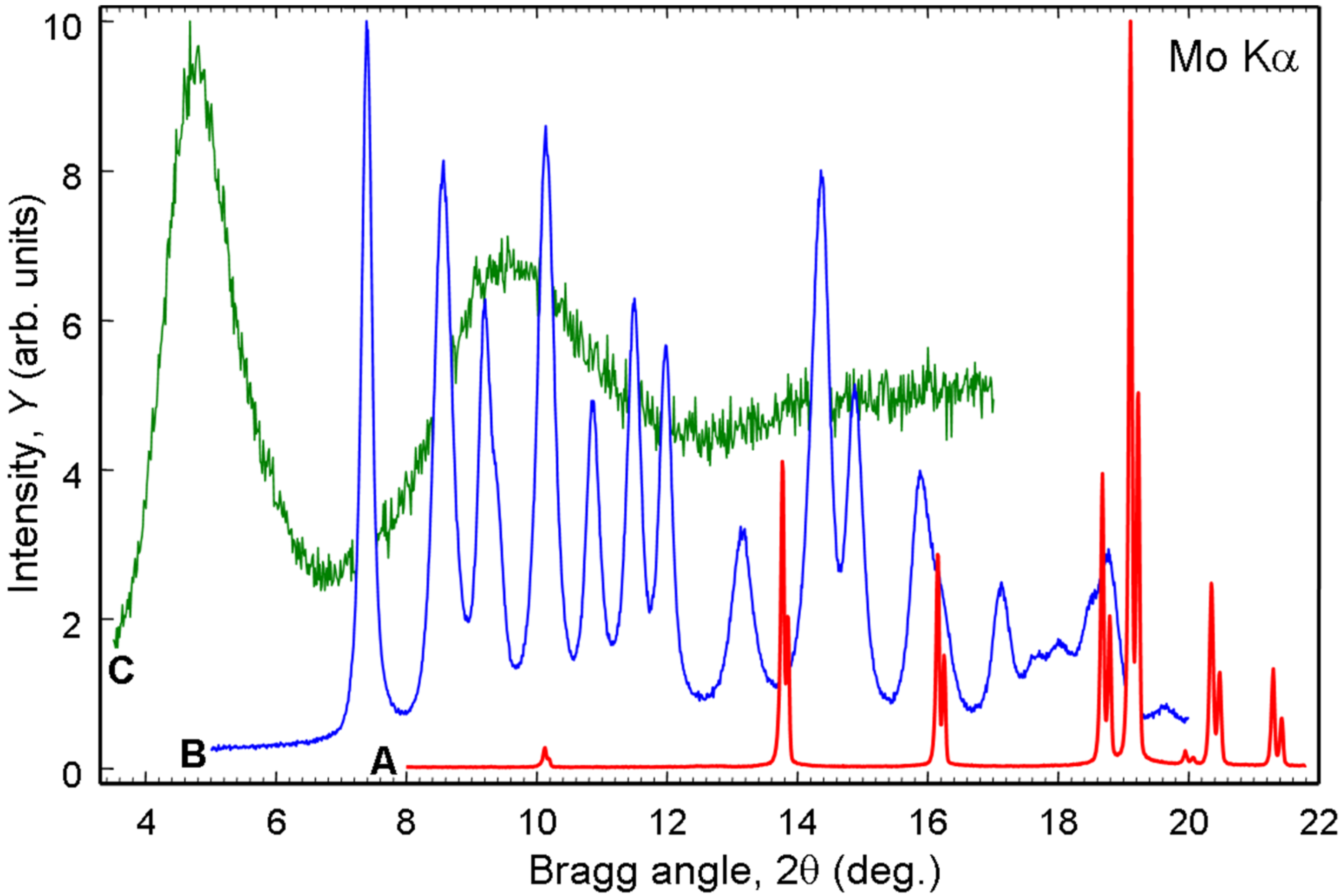
Crystal / powder requirements:

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

Instrument requirements:

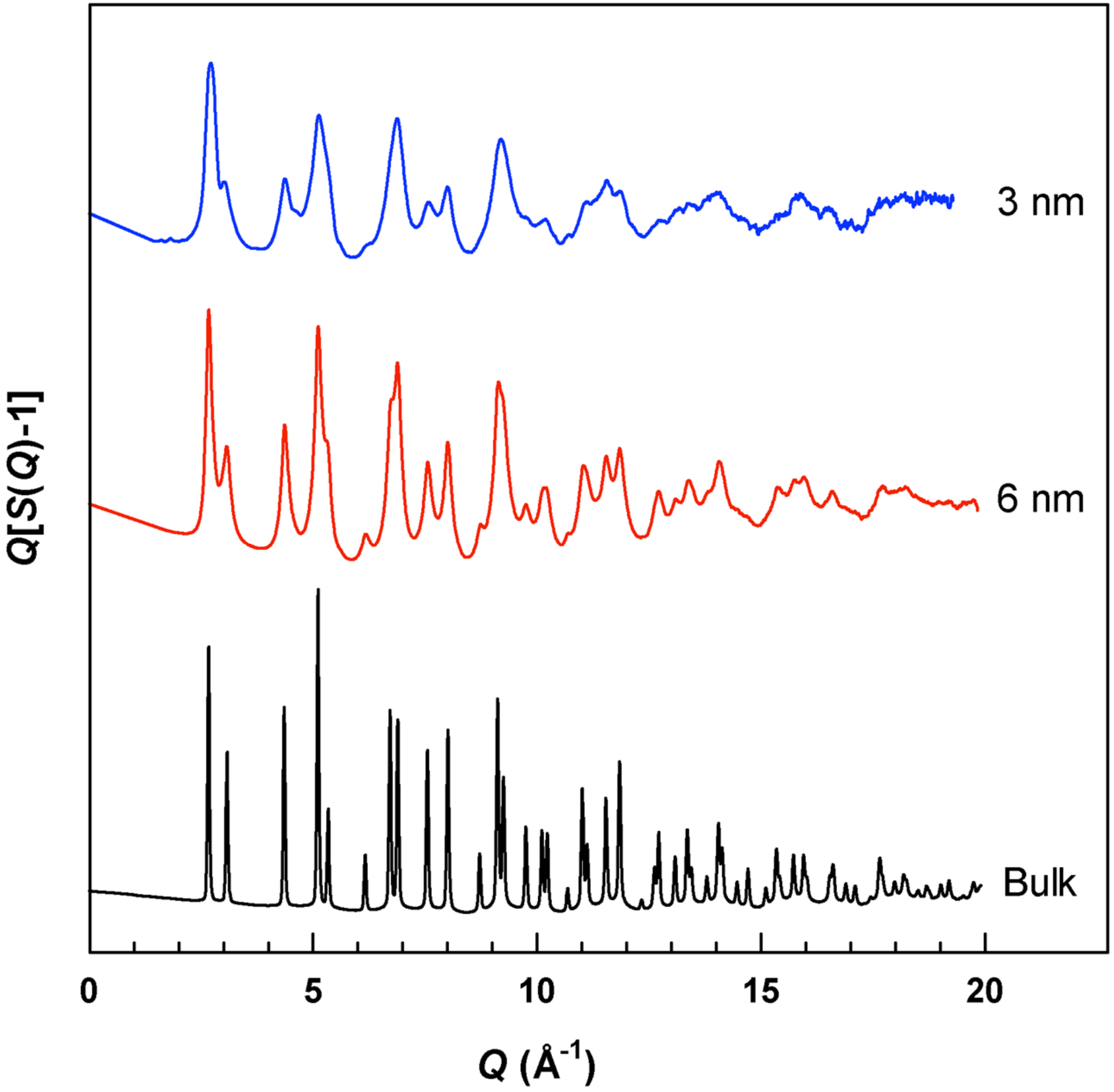
- Access a Q_{max} such that ratio of accessible Bragg reflections to crystallographically independent atoms is met
- Have a Q-resolution to resolve these Bragg reflections
- Be able to accurately measure the Bragg reflection intensity above the background

Diffraction limit

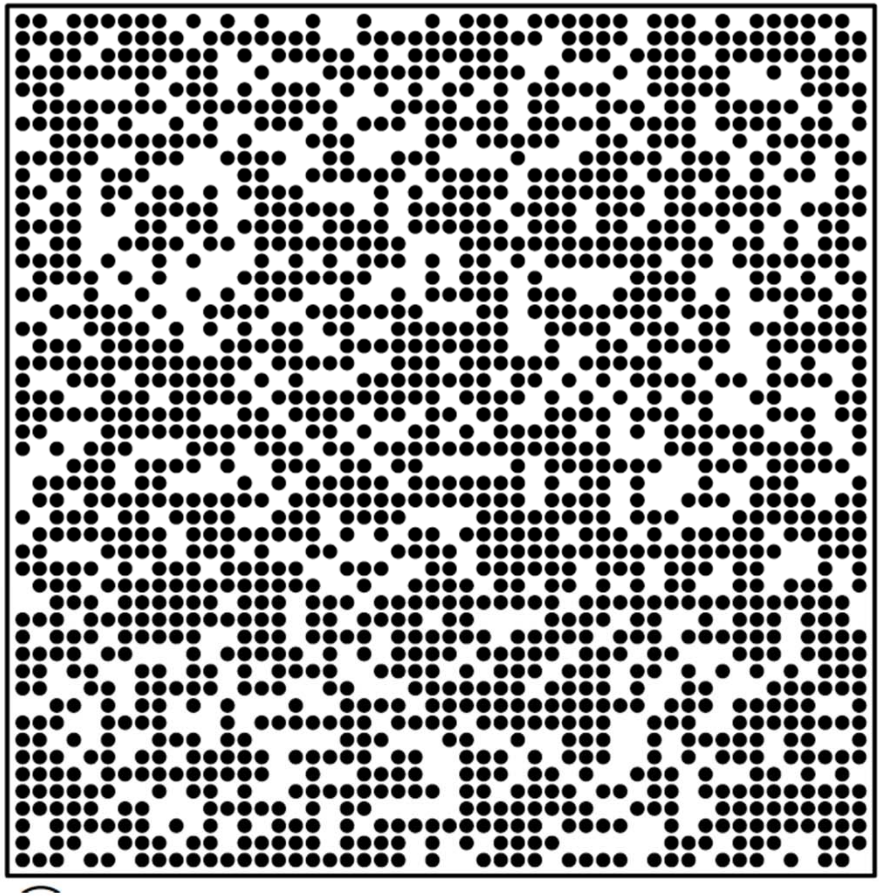
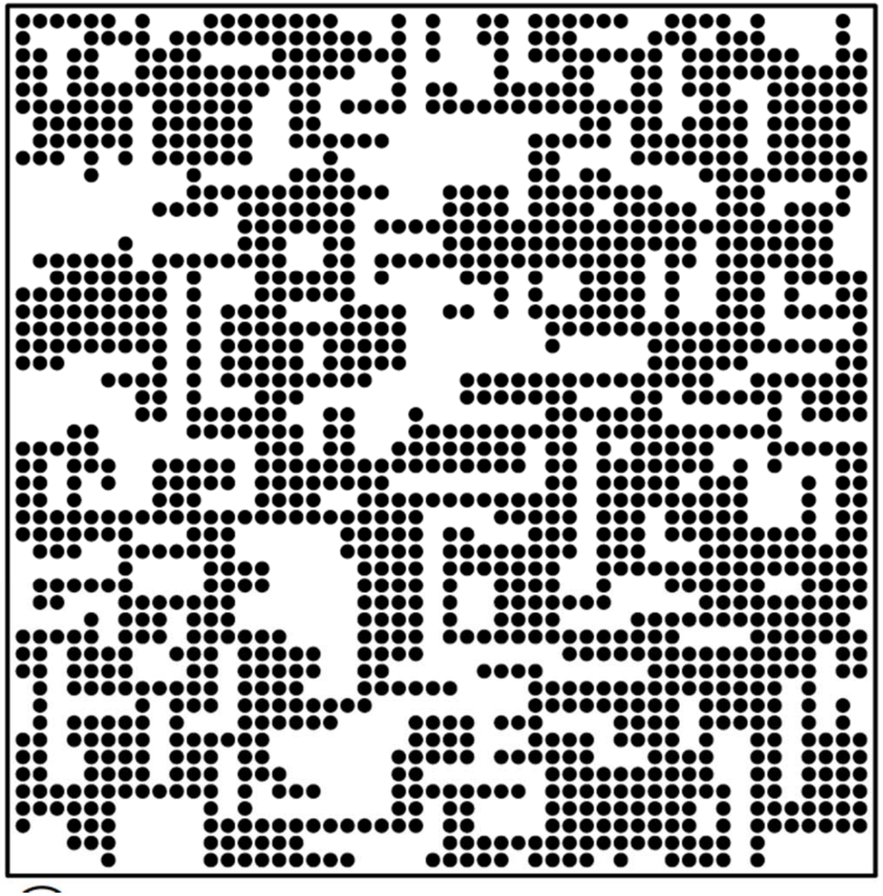


- A. Material with excellent crystallinity with low and nearly linear background
- B. Poorly crystalline material - causes for this can include small grain size, strained material, presence of an amorphous component, etc
- C. Non-crystalline material in the conventional sense - long-range order and periodicity are absent as no Bragg reflections. However, info on short range structure can be extracted

Particle size effect

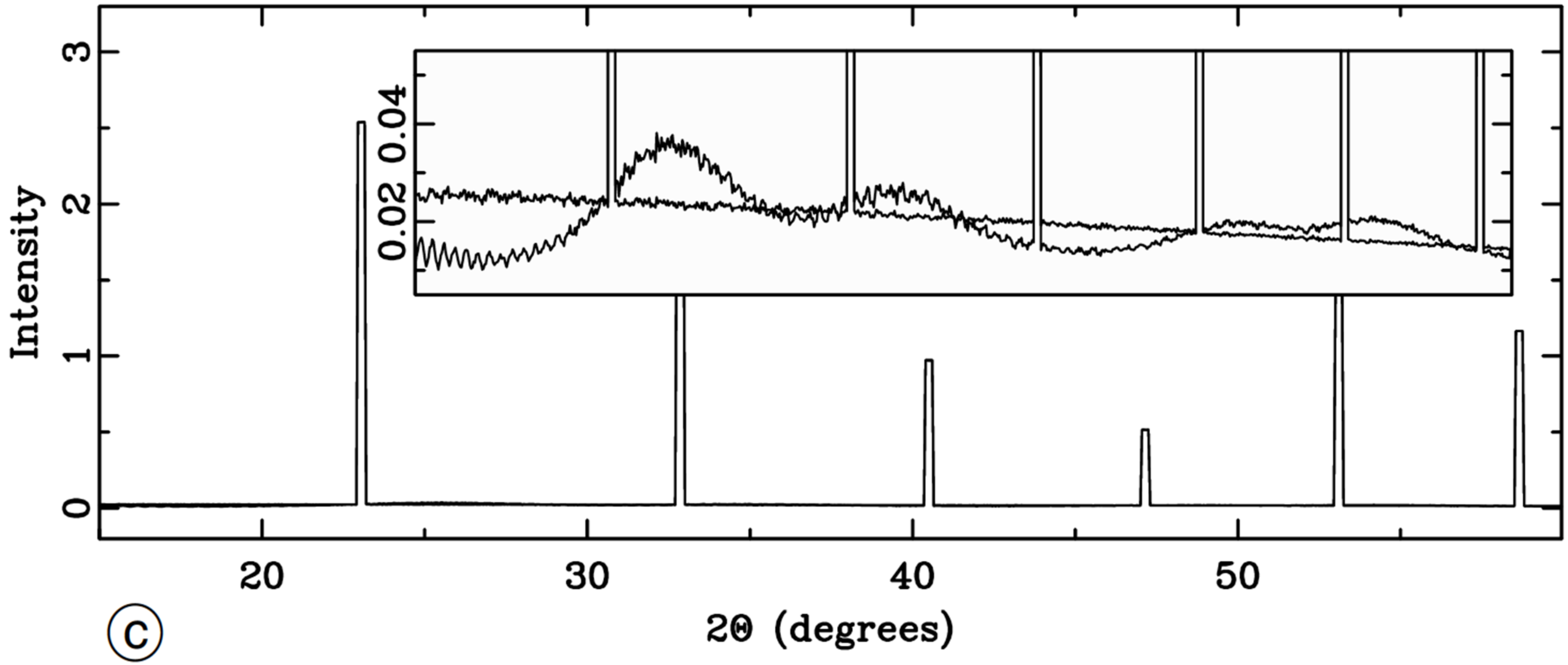


Local Order

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

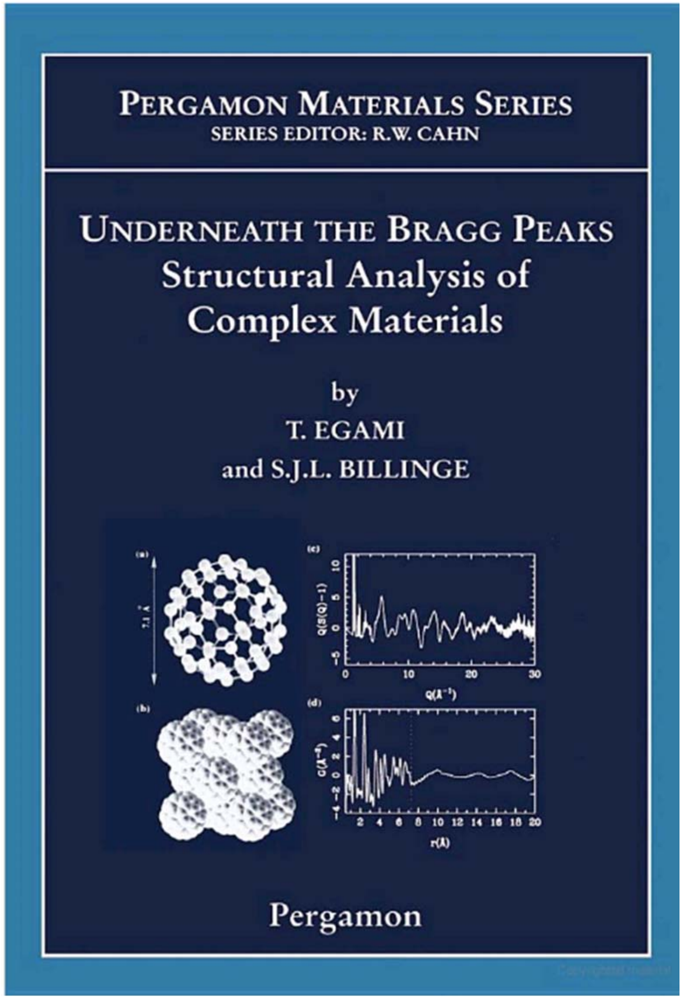
Local order



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



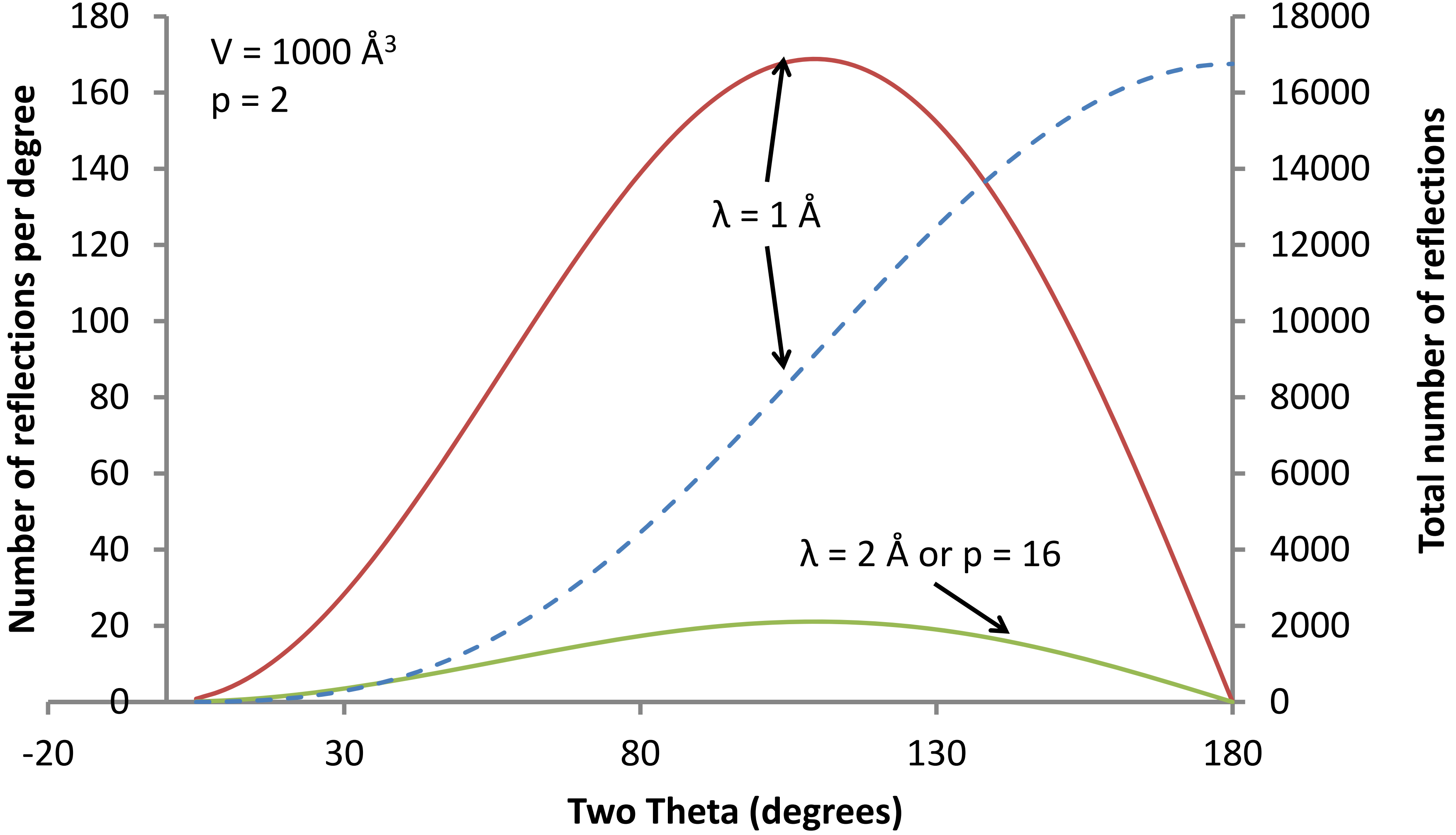
The PDF is obtained from the powder diffraction data via a sine Fourier transform of the normalized scattering intensity $S(Q)$:

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

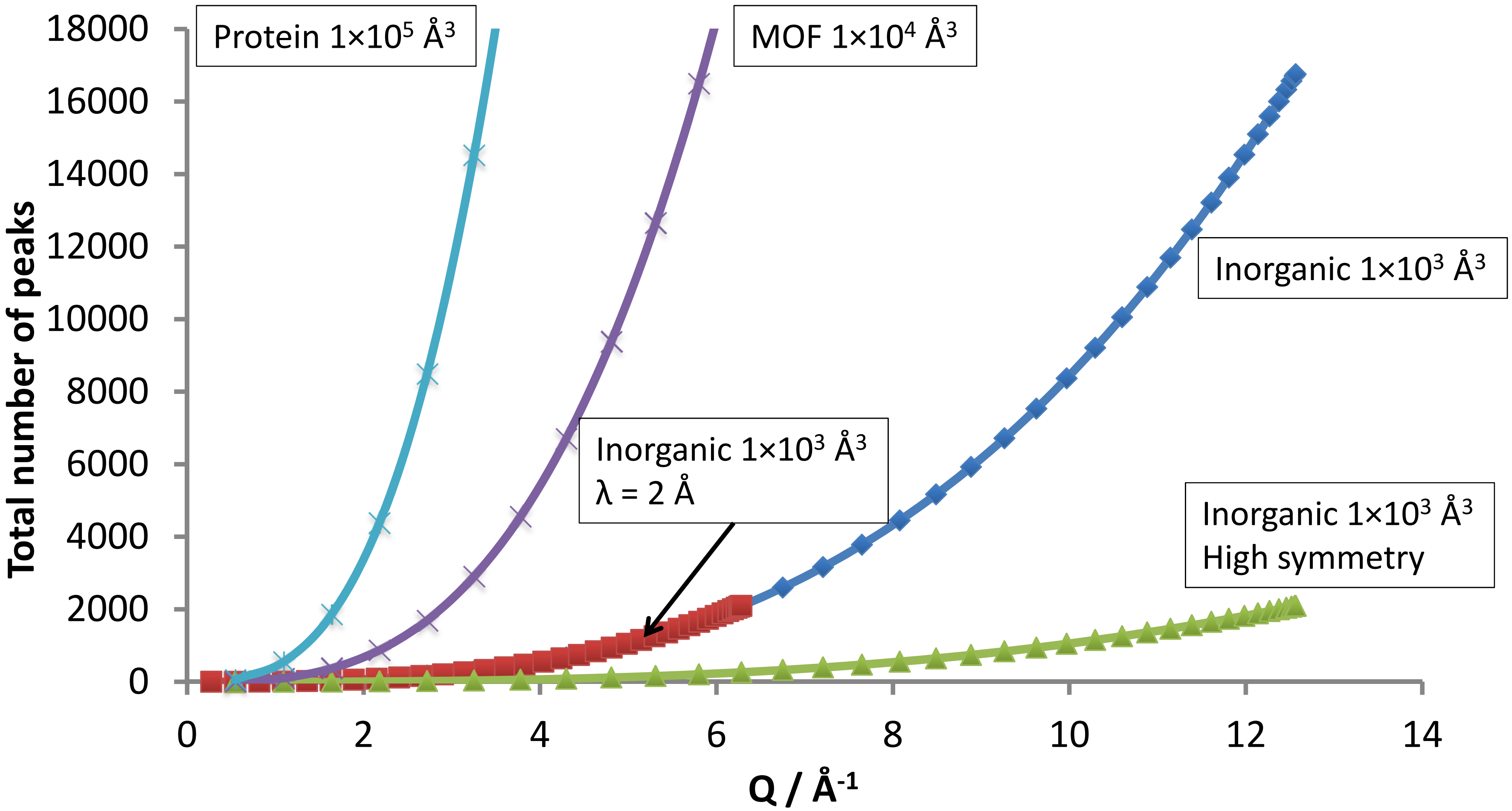
where $\rho(r)$ is the microscopic pair density, ρ_0 is the average number density and Q is the magnitude of the scattering vector. For elastic scattering $Q = 4\pi\,\sin\,(\theta)/\lambda$ with 2θ being the scattering angle and λ the wavelength of the radiation used.

http://www.totalscattering.org

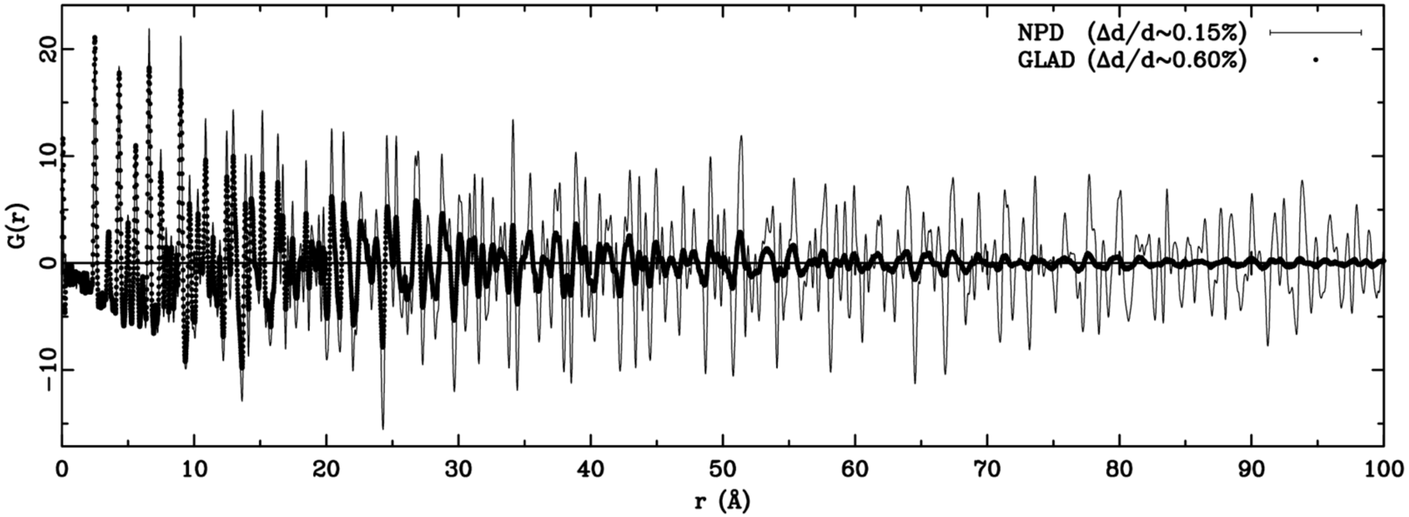
The effect of wavelength and symmetry on number and density of allowed reflections



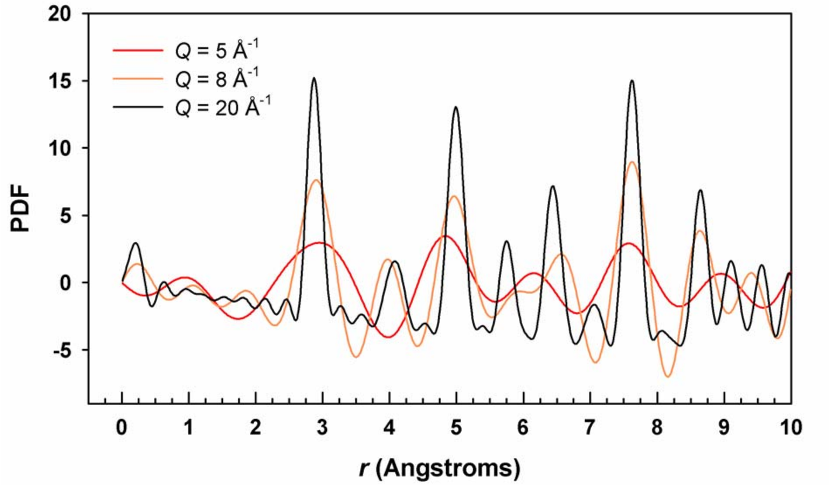
Total Number of Reflections using 1 Å wavelength in reciprocal space



PDF/Total scattering instrument requirements



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

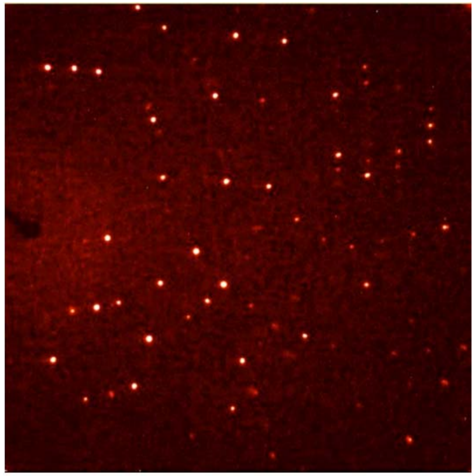


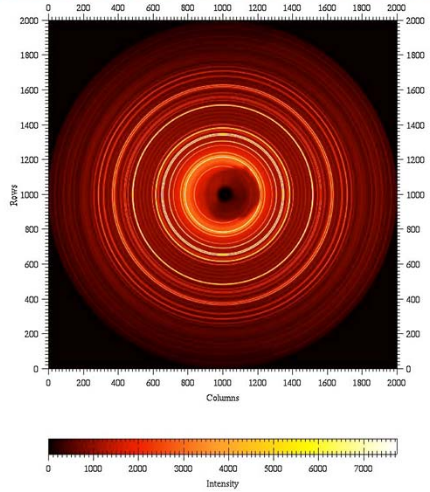
Reproduced from Michel, SSRL workshop (2010)

- Good Δd/d resolution at low d (ΔQ/Q resolution at high Q)
- Access to as low d (high Q) as possible

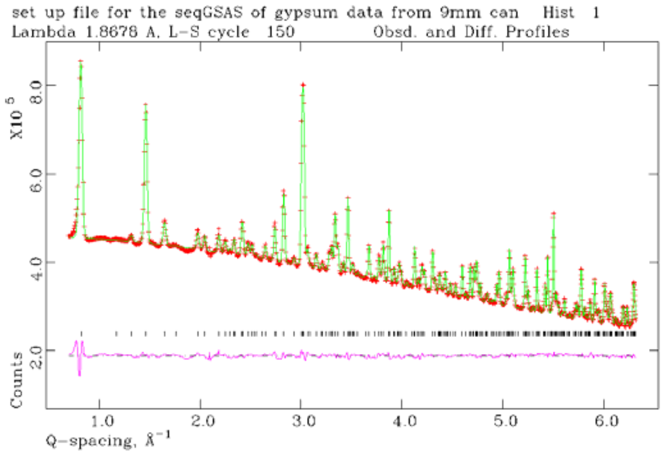
Instrument choice

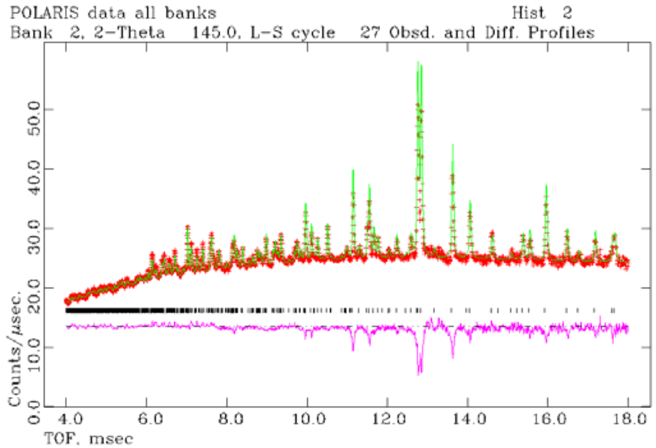
- Single crystal or powder?





- Monochromatic or TOF?





Single Crystal or Powder? Examples

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

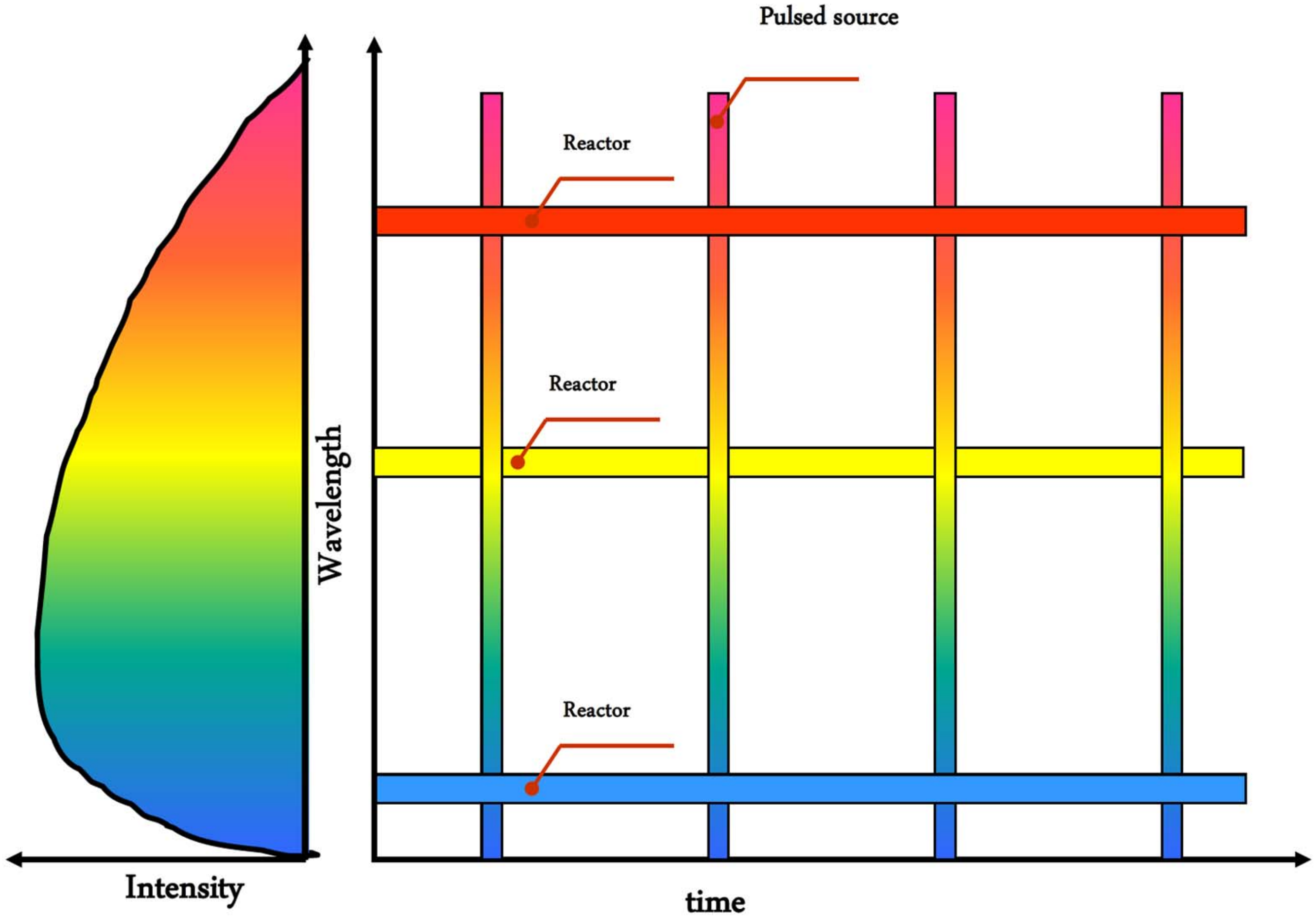
Neutron Diffractometers: Monochromatic or time-of-flight?

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

- Monochromatic
  - Fix wavelength and scan detector angle
  - Multiple 2θ required to cover Q(d) spacing range
  - Q(d) spacing limit $4\pi/\lambda$ ($2\pi/d$)

- 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

Monochromatic or time-of-flight? :Wavelength / energy selection



Monochromatic or time-of-flight: Accessible Q(d) range

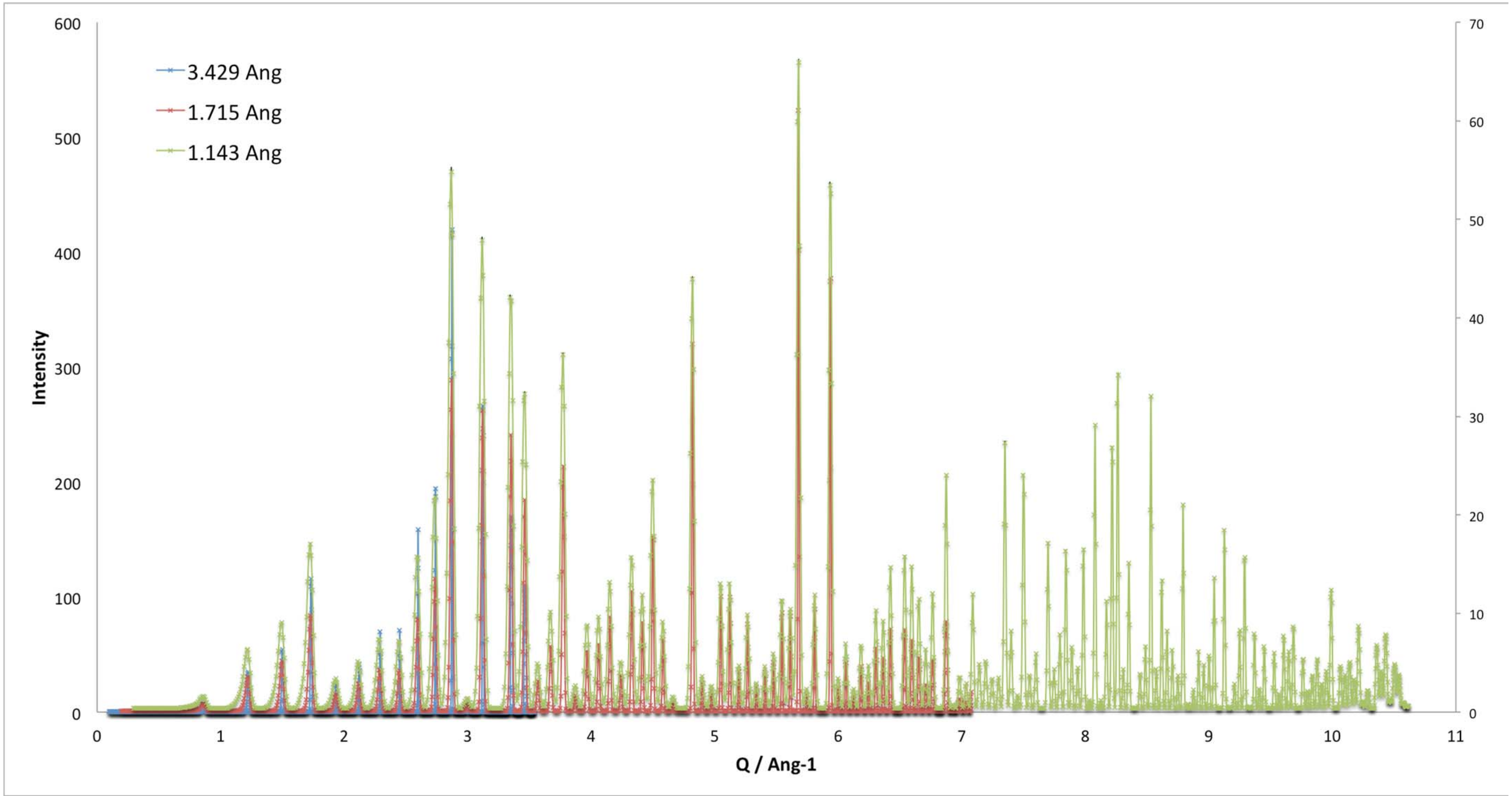
Monochromatic

- 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 $Å^{-1}$

Time-of-flight

- Q_{max} depends on λ_{min} and θ.
- λ_{min} can be much lower than for the monochromatic 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

Q coverage with different wavelengths



Monochromatic or time-of-flight? :Resolution

EUROPEAN SPALLATION SOURCE

Monochromatic

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

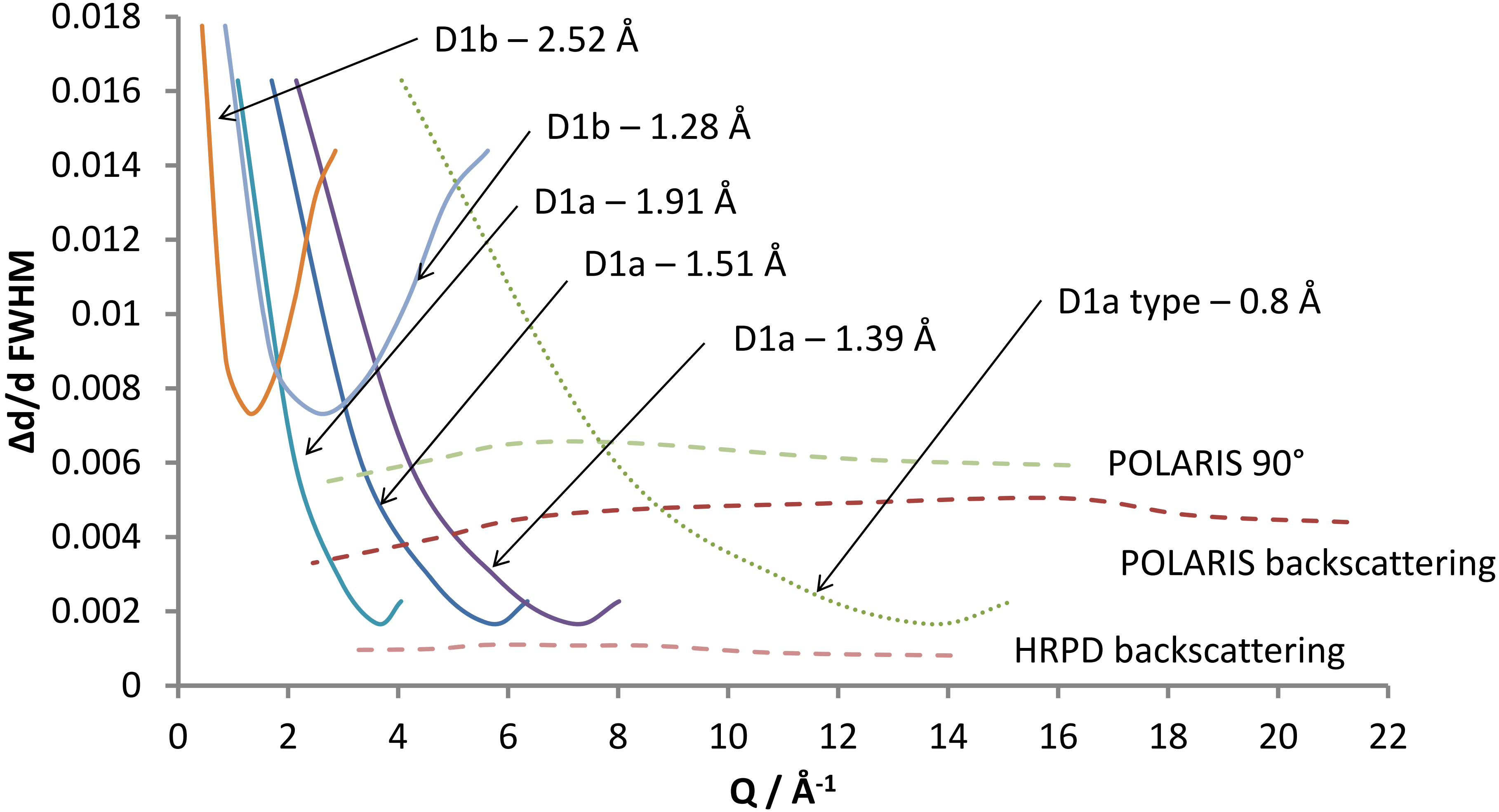
- U, V and W are functions of the collimation and U, V also takeoff angle to the monochromator
- Resolution minimum found near the takeoff angle of the monochromator $2\theta_M$
- Higher takeoff angle gives higher resolution for identical wavelength
- Wavelength produced by monochromator is takeoff angle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

Time-of-flight

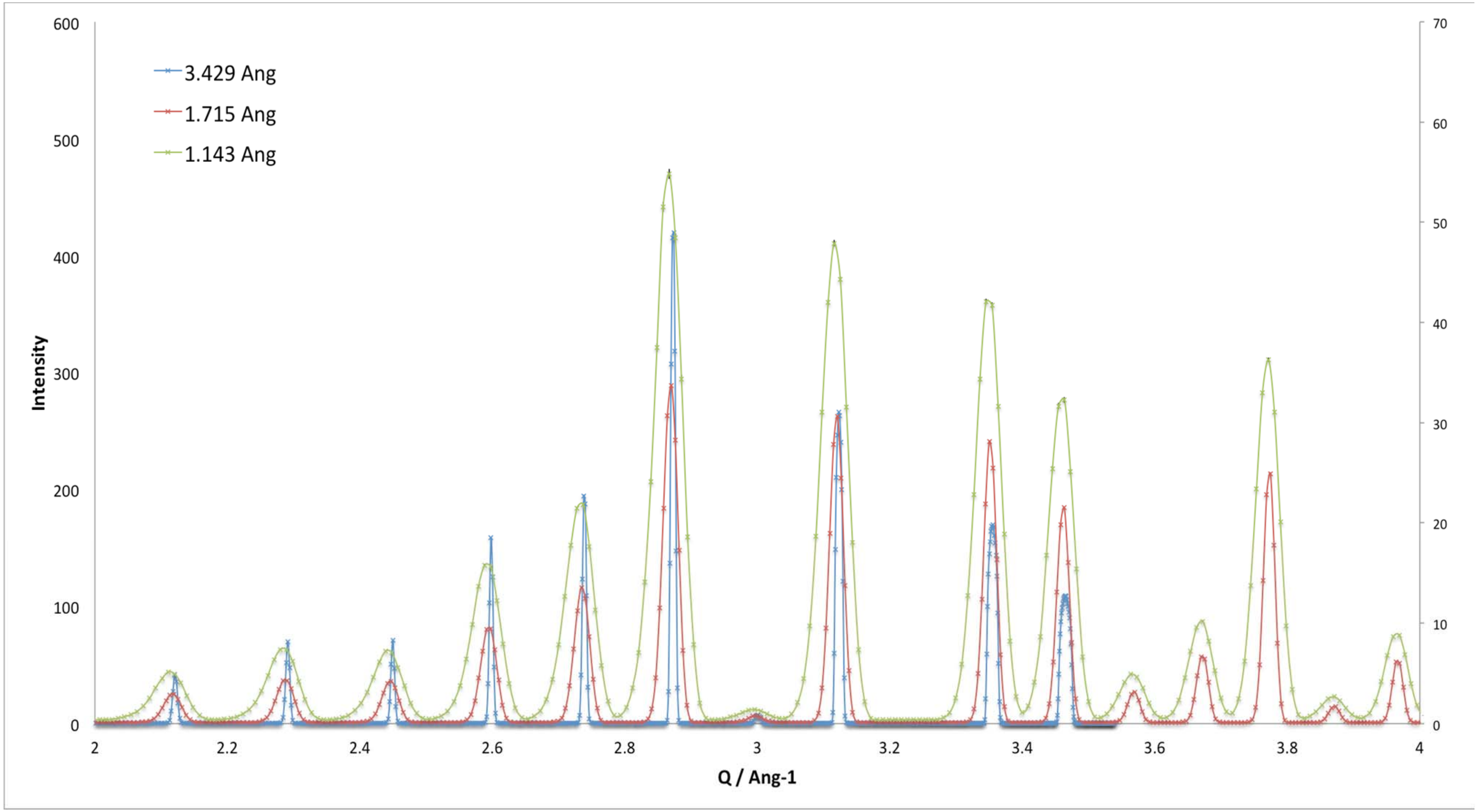
$$\Delta d/d = \left[\Delta\theta^2 \cot^2\theta + \left(\Delta t/t\right)^2 + \left(\Delta L/L\right)^2\right]^{1/2}$$

- Δθ 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

Resolution functions



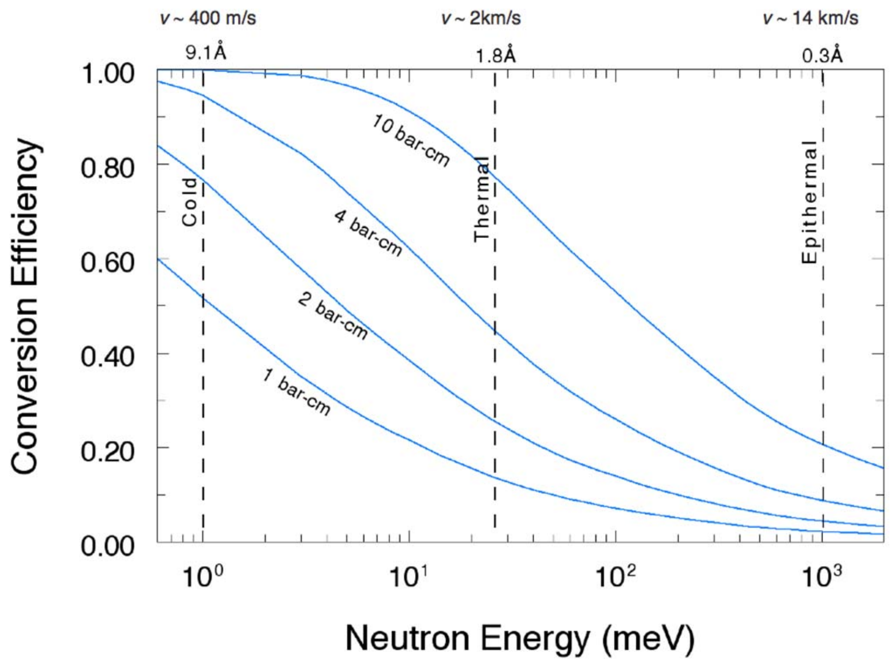
Q Resolution with different wavelengths



Monochromatic or time-of-flight? Resolution

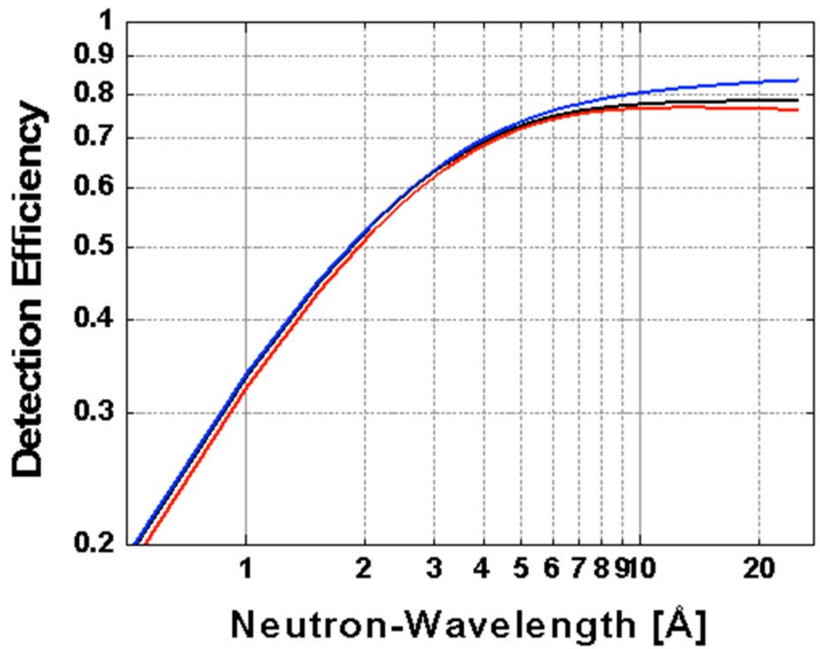
- Monochromatic
  - Simple, symmetric peakshape function
  - Resolution where it is needed
  - Best resolution where diffraction peak density is highest (see slides 62 and 52, which show minimum in resolution function around 120° 2θ)
  - Different wavelength can be used to give resolution in Q-space where required
  - Different takeoff angle can be used to change resolution function
- Time-of-flight
  - Complex asymmetric peakshape related to moderator characteristics
  - Resolution almost constant for a given detector bank so increasing peak density with Q can be an issue
  - Resolution improved by moving to higher scattering angle detector bank

Detection Efficiency



^{3}He detection efficiency as a function of detection depth. (from Radeka, Neutrons & photon detector workshop, 2012)

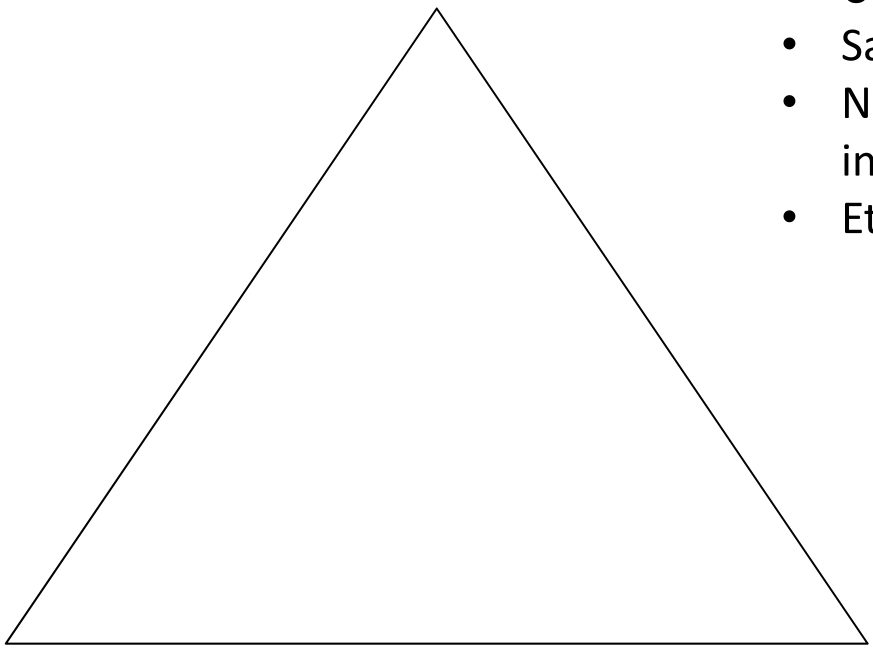
https://portal.slac.stanford.edu/sites/conf_public/nxd2012/presentations/VR_Neutron%20gas%20dets_Aug1_2012.pdf



Predicted detector efficiency CASCADE-detector for 20 ^{10}B layers

http://www.physi.uni-heidelberg.de/Forschung/ANP/Cascade/Projekt/results.php?lang=en

Why so many diffractometers?



- Unit cell volume
- Sample environment restrictions
- Number of crystallographically independent atoms
- Etc…

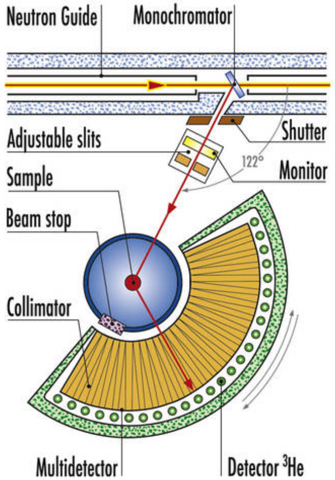
Examples of Neutron Diffractometer

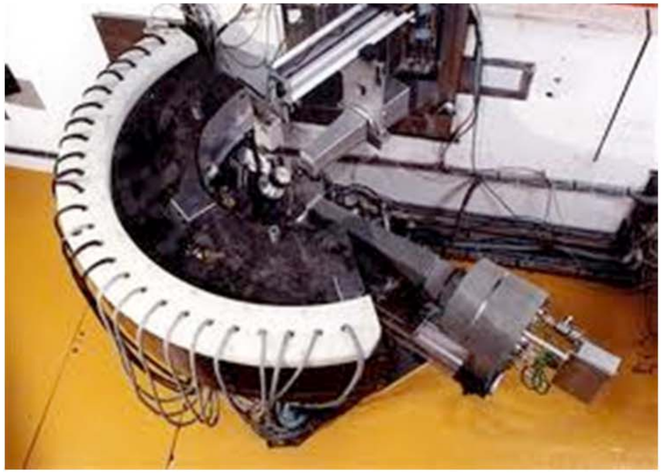
- Earliest diffractometers
- Continuous wavelength powder
  - High resolution powder
  - High flux powder
- Time-of-flight powder
  - High resolution powder
  - High flux powder
- Single crystal diffractometers

Evolution of Instruments: First monochromatic neutron instruments

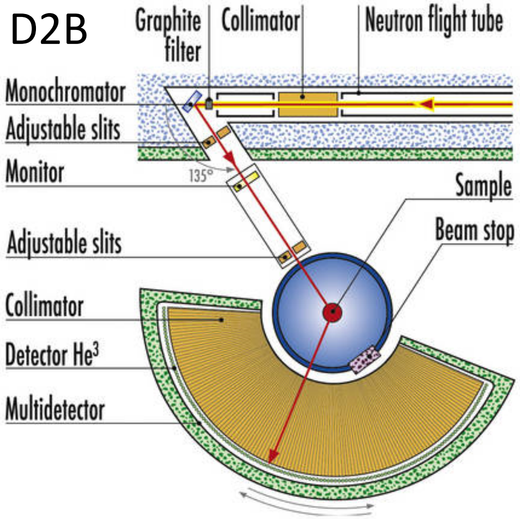
Continuous wavelength, high resolution powder – D1A and D2B at ILL

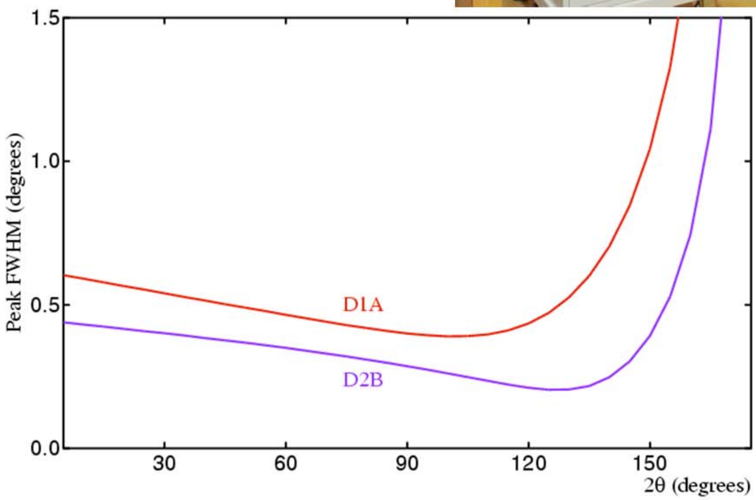
D1A





D2B





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

Continuous wavelength, high resolution powder – D1A and D2B at ILL

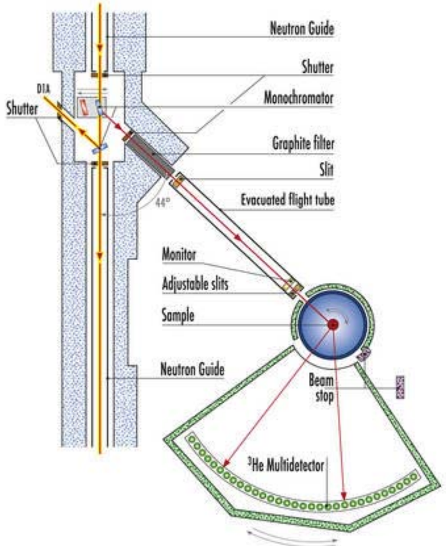
Instrument	D1A	D2B
Takeoff angle / °	122	135
Flux / n cm^{-2} s^{-1}	10^6	10^6 to 10^7
Beam (h × w) / mm	30 × 20	50 × 20
Detectors	25 ^3He × 10 cm h	128 ^3He × 30 cm h
Wavelengths	Ge(hhl)	Ge(hhl)
Δd/d Resolution	2-3 × 10^{-3}	Min 5 × 10^{-4}
Background	Very Low (60 m)	Low (15 m)
Average data collection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

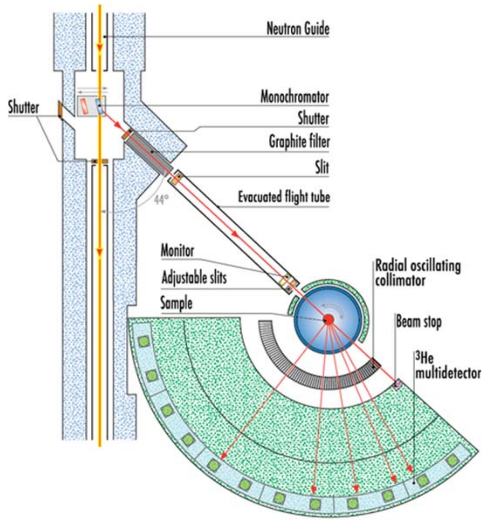
http://www.ill.eu/instruments-support/instruments-groups/

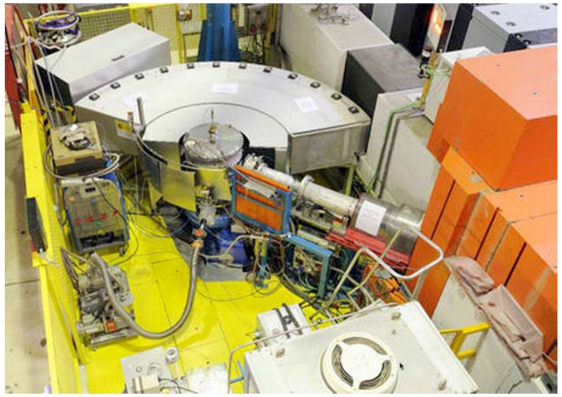
Continuous wavelength, high flux powder – D1B and D20 at ILL

D1B

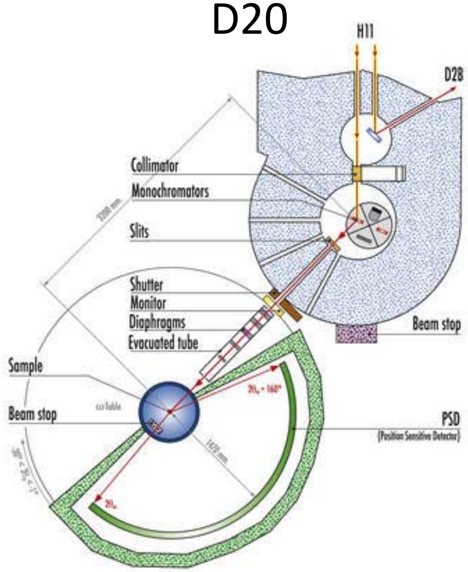


newD1B





D20



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

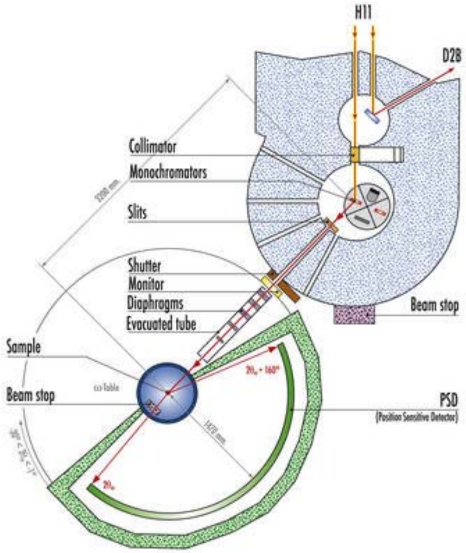
Continuous wavelength, high flux powder – D1B and D20 at ILL

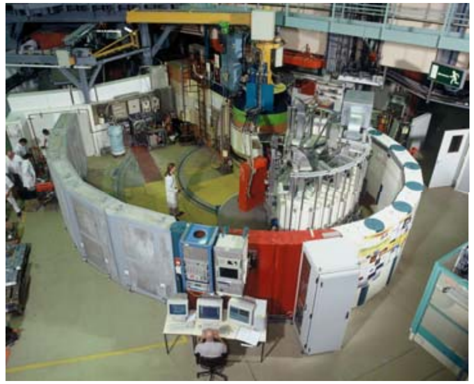
Instrument	D1B (old) / D1B (new)	D20
Takeoff angle / °	44	28, 42 (±2)
Flux / n cm^{-2} s^{-1}	6.5×10^6 HOPG(002) 0.4×10^6 Ge(311)	4.2×10^7 HOPG(002) 9.8×10^7 Cu(200) 42° 3.2×10^7 Cu(200) 28°
Beam (h × w) / mm	50 × 20	50 × 20
Detectors	80° multi-wire / 128° multi-wire 0.2° separation / 0.1° separation 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)

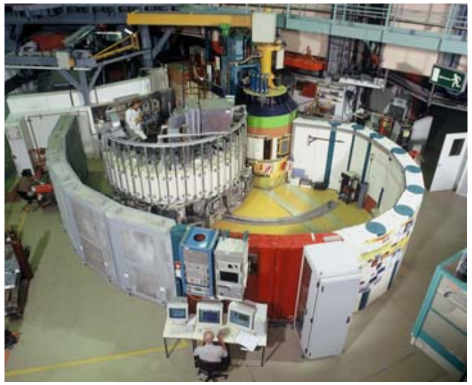
Continuous wavelength, variable resolution powder – D20 at ILL

120°

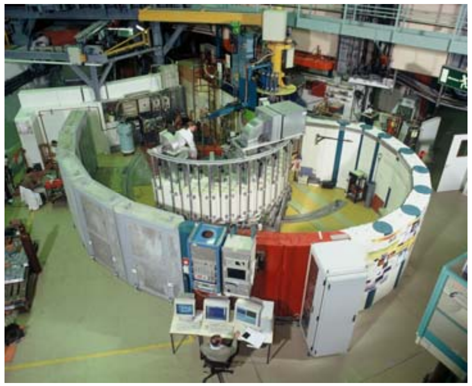




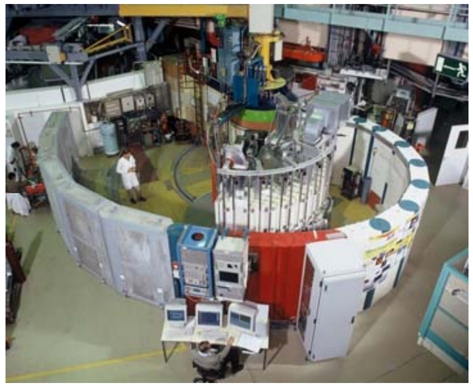
28°



90°



65°



42°

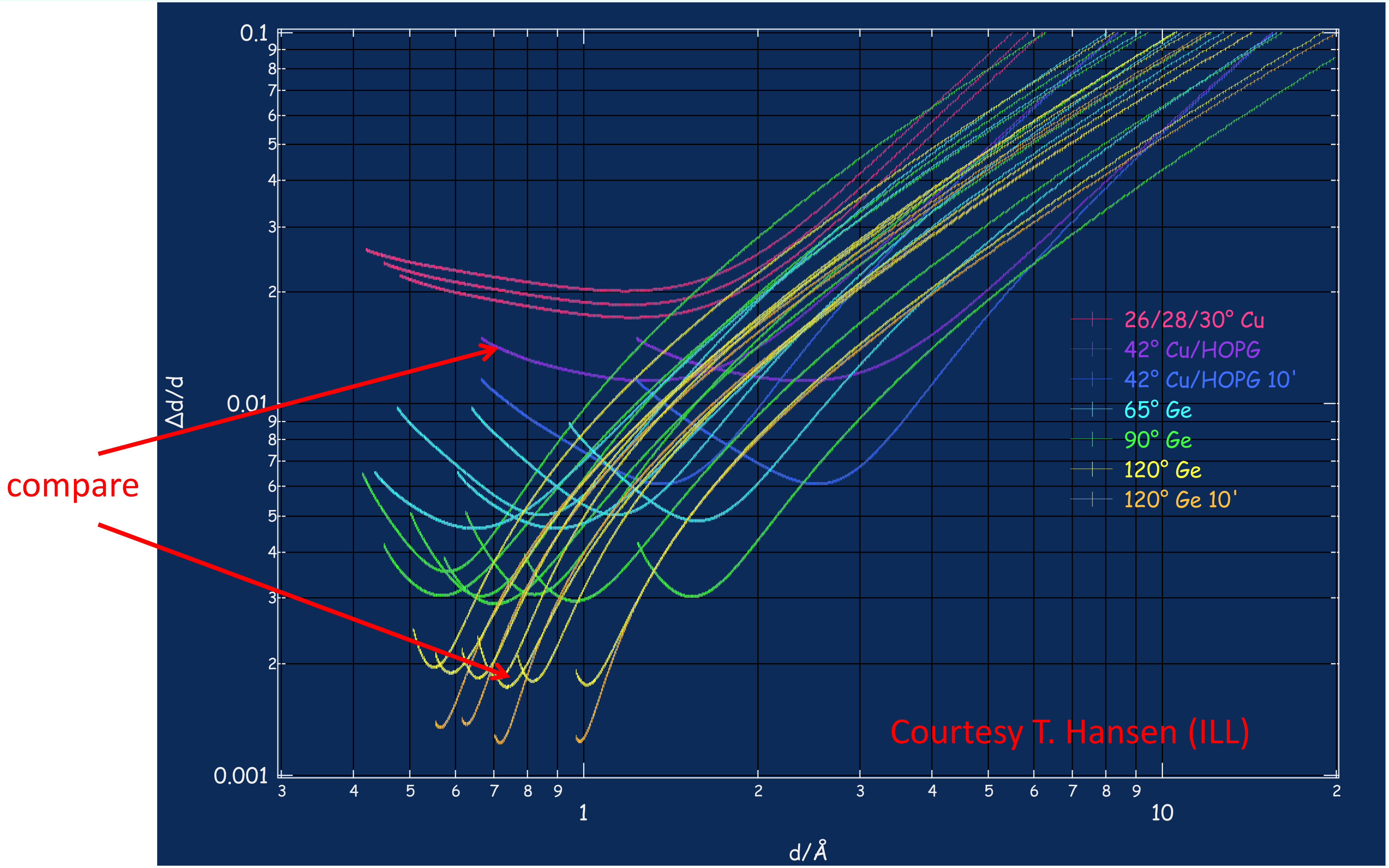
Photos courtesy T. Hansen ILL

Continuous wavelength, General Purpose powder – D20 at ILL

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)

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

Resolution as a function of θ_B

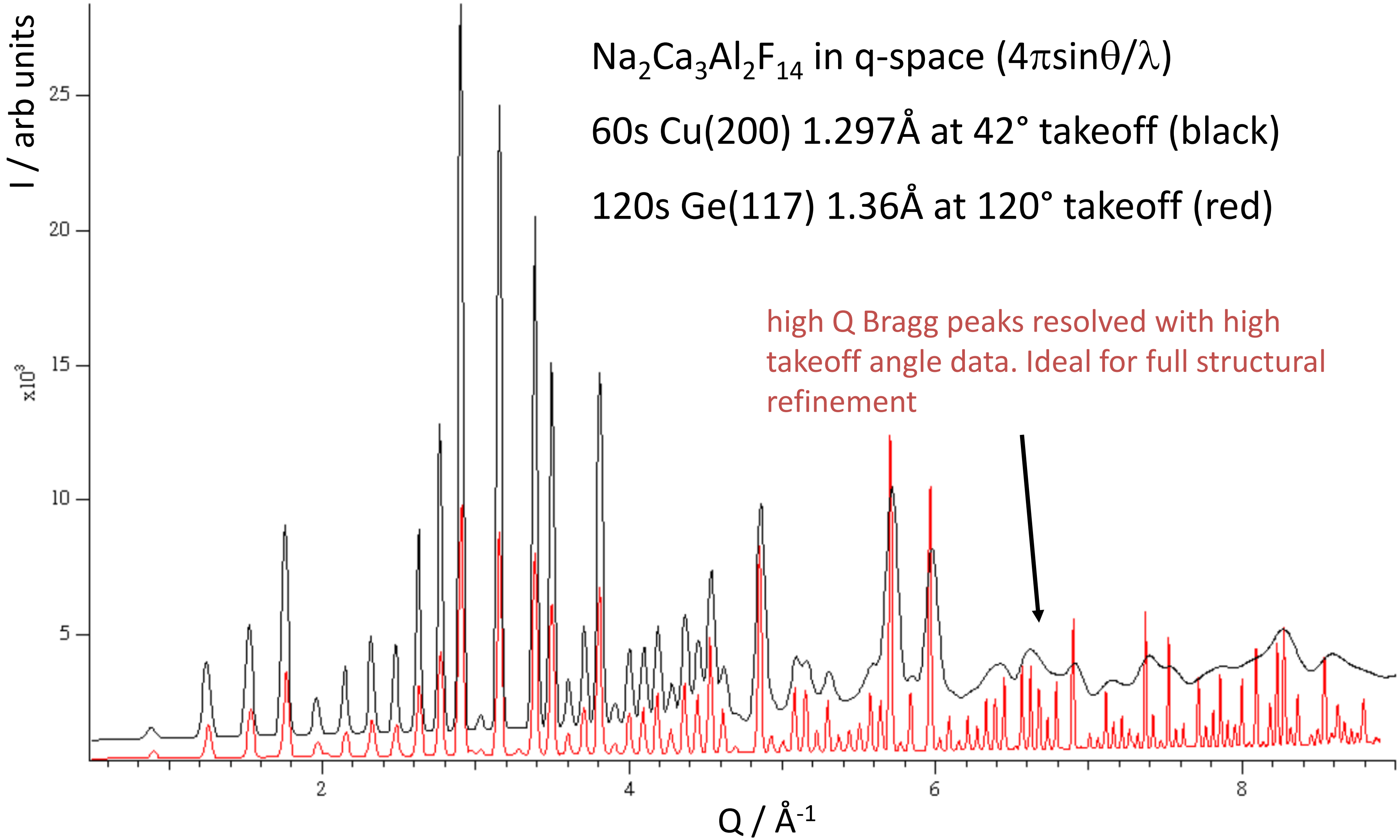


High flux v high takeoff-angle

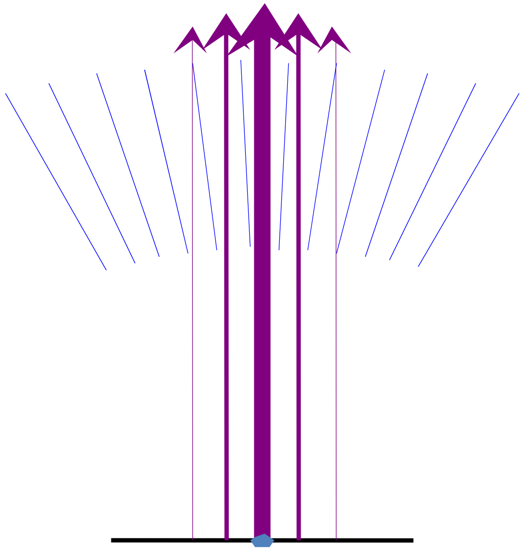
$Na_2Ca_3Al_2F_{14}$ in q-space ($4\pi\sin\theta/\lambda$)

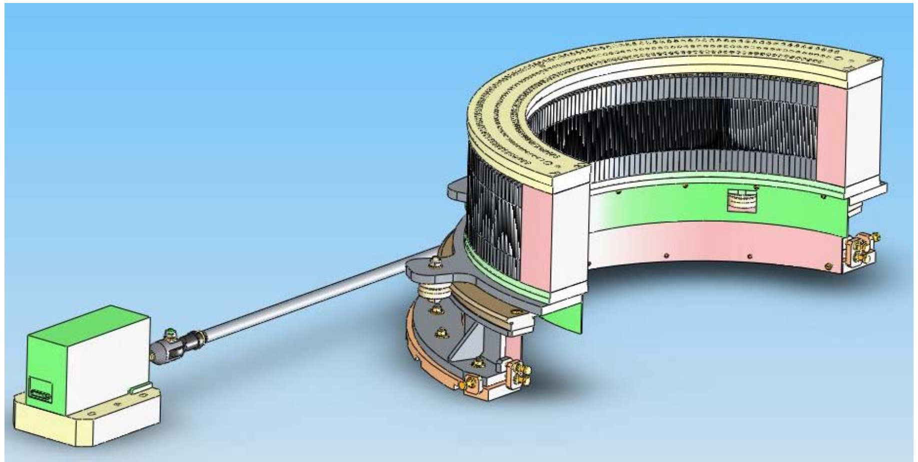
60s Cu(200) 1.297Å at 42° takeoff (black)

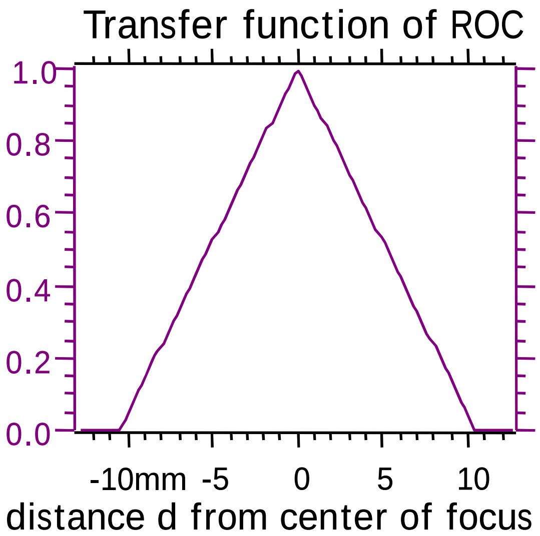
120s Ge(117) 1.36Å at 120° takeoff (red)

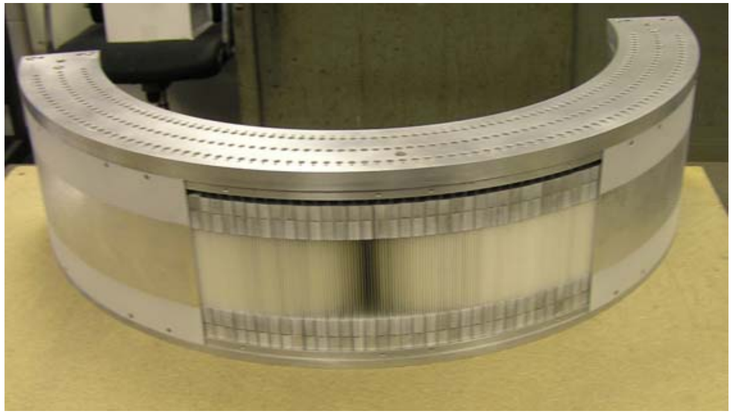


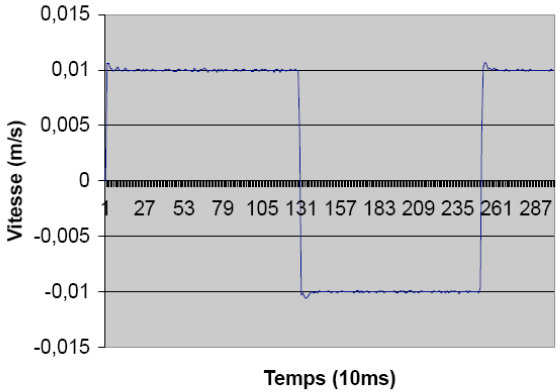
Parasitic Scattering with high flux instruments: Radial Oscillating Collimators (ROC)





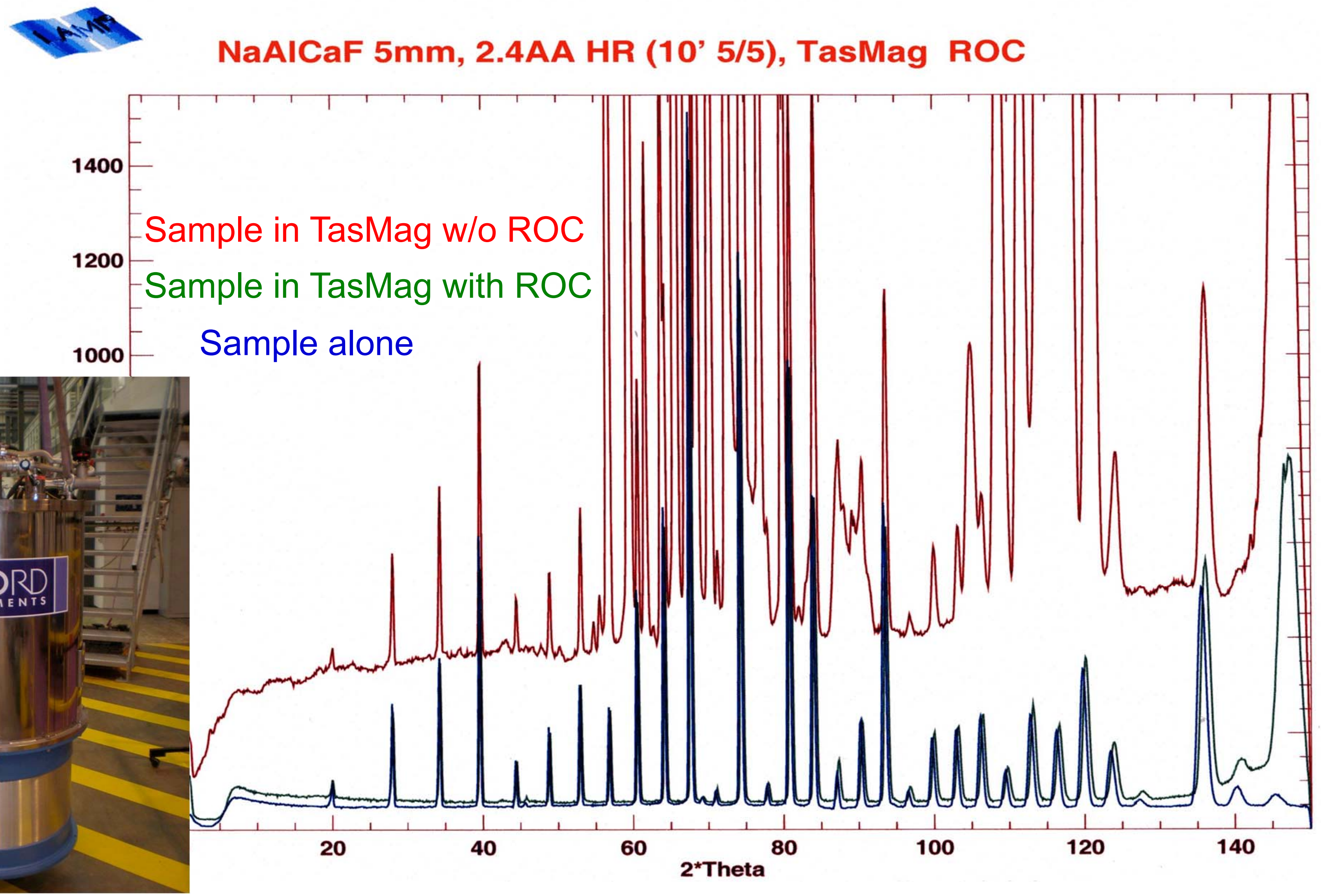






Photos Courtesy ILL

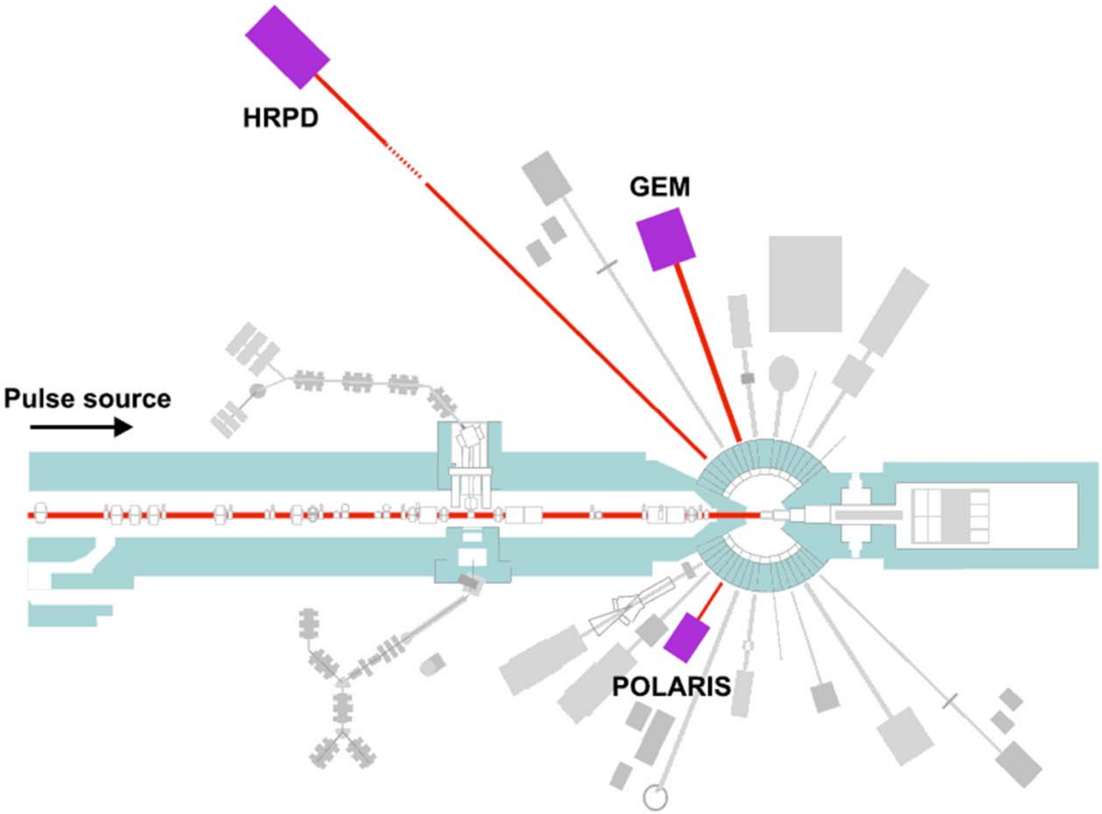
Parasitic scattering can ruin experiments: ROC example



Time-of-flight Powder Instruments

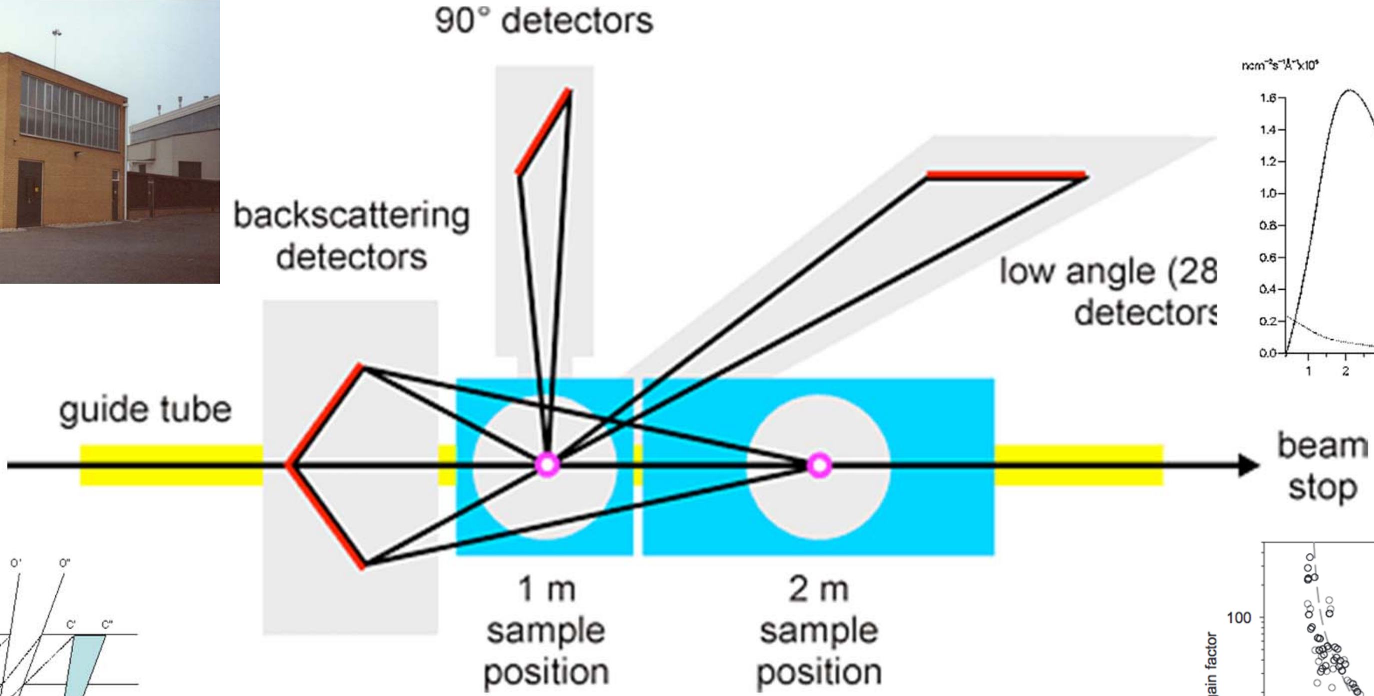
Highlight using 3 examples from ISIS TS-1

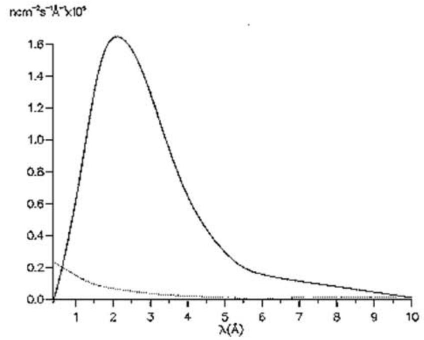
- HRPD – high resolution powder
- GEM – general purpose powder
- POLARIS – general purpose powder (old and new configuration)

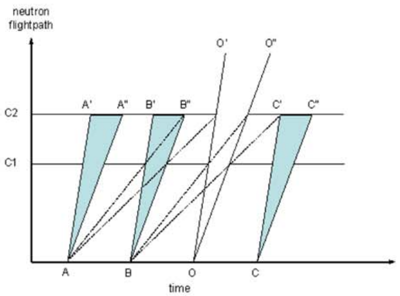


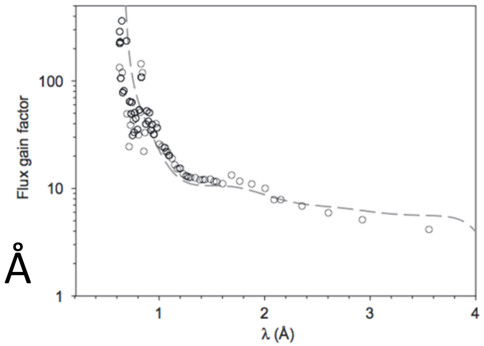
All photos on the following slides from instruments at ISIS are courtesy of STFC

Time-of-flight, high resolution powder: HRPD at ISIS









- 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
- Wavelength band 4 Å (5 Hz) or 2 Å (10 Hz)
- Supermirror guide upgraded in 2008 (36 km radius of curvature)

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

HRPD at ISIS

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° < 2θ < 176° (1m)	87° < 2θ < 93°	28° < 2θ < 32°
Solid Angle (Ω)	0.41 ster (1m)	0.08 ster	0.01 ster
Resolution (Δd/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

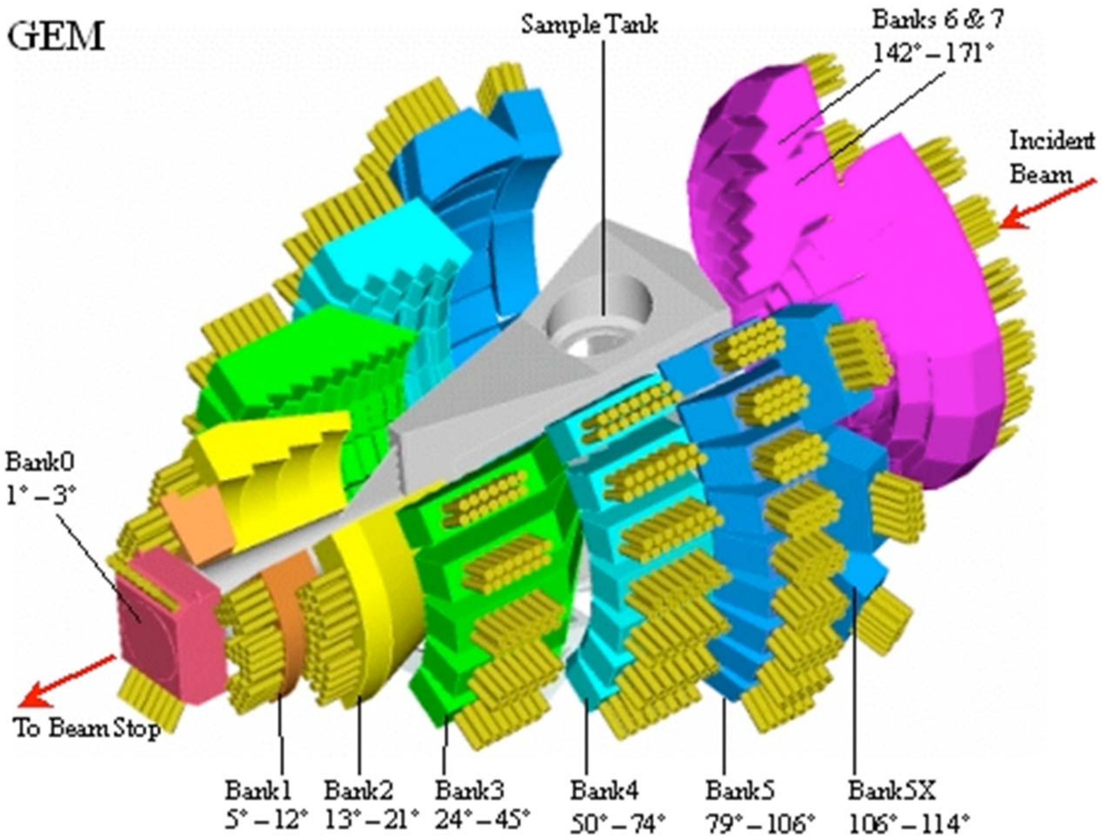
- Large backscattering detector to minimise $\cot^2\theta$ in resolution term
- High resolution at intermediate Q
- Long flight path to reduce Δt/t and ΔL/L uncertainties
- Pulse skipping to increase bandwidth (@50 Hz 0.4 Å)
- Good combination of parameters for a high resolution TOF diffractometer

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

Time-of-flight, General Purpose Powder: GEM (General Materials) at ISIS

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

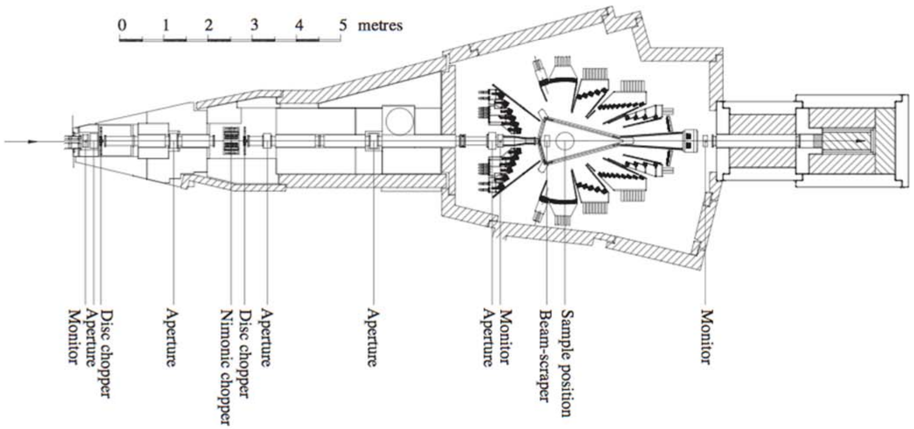
- Approximately 17 m primary flight path
- 100K methane moderator
- 50 Hz Operation
- Wavelength band 0.05 – 3.4 Å
- Large area detector array of 7.27 m^2
- ZnS detectors
- Radial oscillating collimator

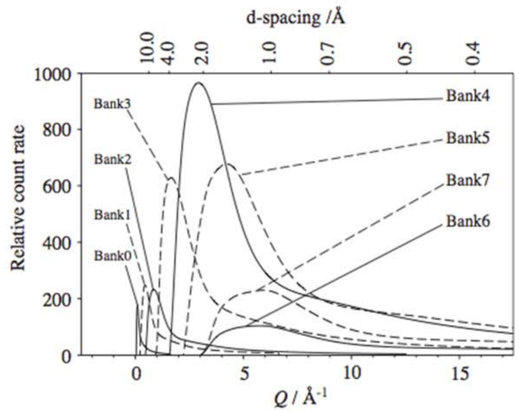


http://wwwisis2.isis.rl.ac.uk/disordered/gem/gem_home.htm

GEM at ISIS

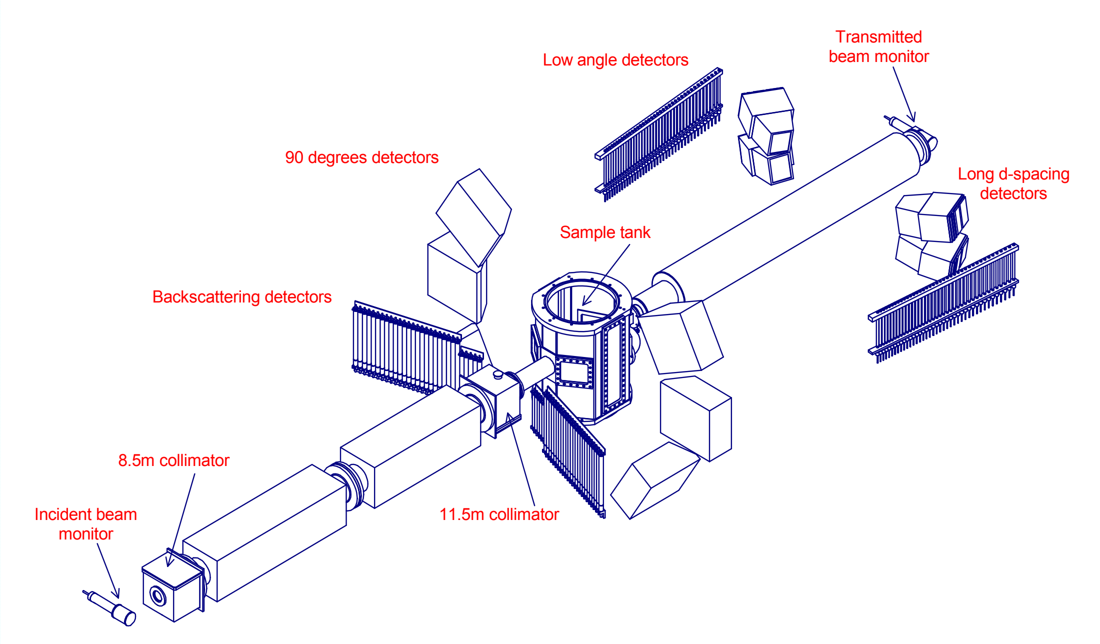
Detector Bank	Scattering angle 2θ (deg)	Range in azimuthal angle ϕ (deg)	Secondary flight path L_2 (m)	Number of detector elements/ modules	Solid angle Ω (sr)	Resolution $\Delta Q/Q$(%)	Minimum accessible momentum transfer Q_{min} (Å^{-1})
Bank0	1.21–3.18	±90.0	2.757–2.767	80/4	0.008	5–10	0.04
Bank1	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

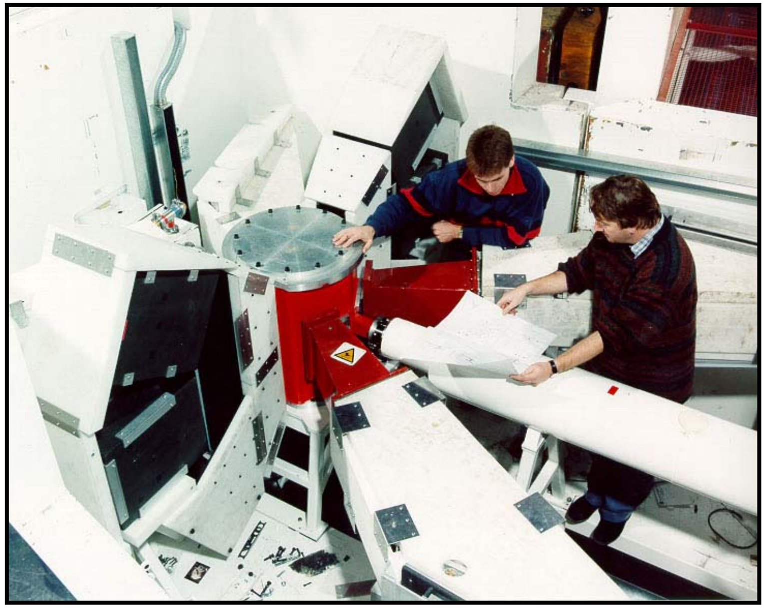




From Hannon, NIMA (2005), **551**, 88-107

Time-of-flight, General Purpose Powder: POLARIS (old configuration)





- 316K H_2O poisoned at 1.5 cm
- Primary flight path 12 m
- Wavelength band 0.1 – 6 Å
- 50 Hz operation
- Maximum sample dimensions 4 × 2 cm

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

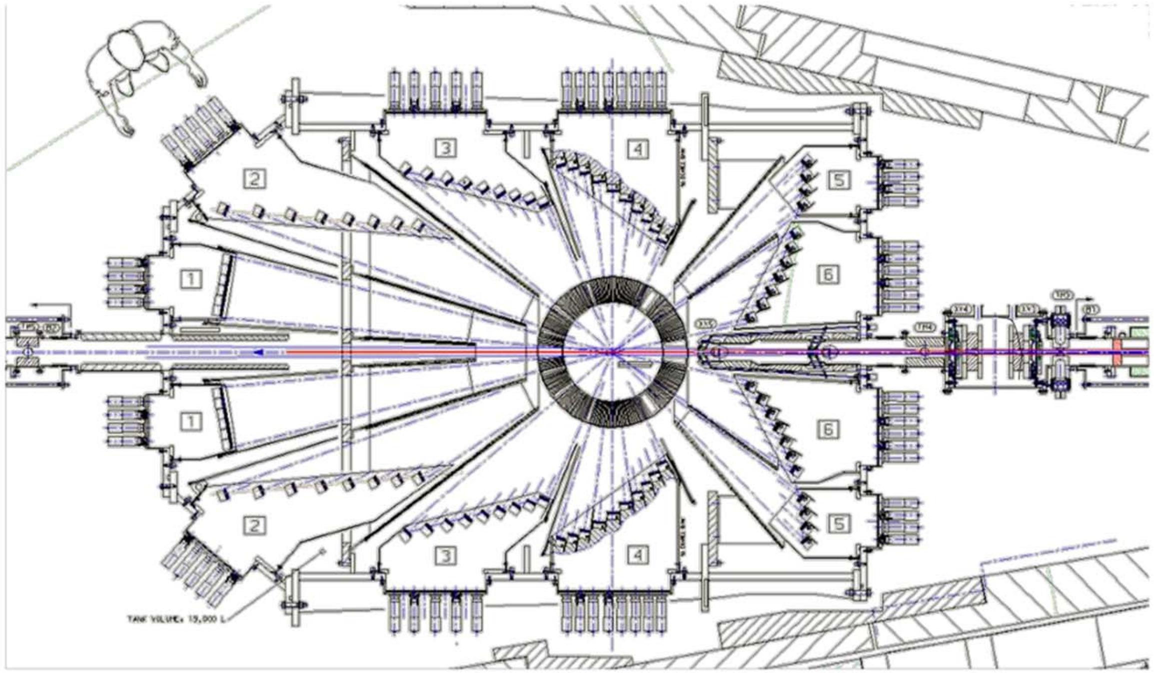
POLARIS (old configuration)

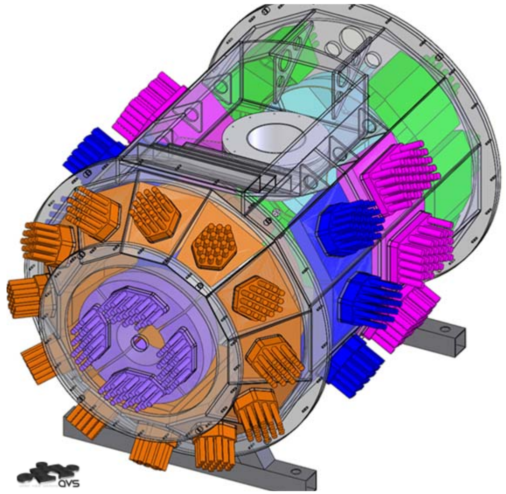
bank position (label)	low angle (A)	low angle (B)	backscattering (C)	90 degrees (E)
detector type	^{3}He	ZnS	^{3}He	ZnS
no. of elements	2 x 40 = 80	4 x 20 = 80	2 x 29 = 58	6 x 36 = 216
L_2 (m)	1.72 - 2.65	~2.2	0.65 - 1.35	~0.80
2θ range	28°< 2θ < 42°	13°< 2θ < 15°	130°< 2θ < 160°	83°< 2θ < 97°
Ω (ster)	0.046	0.009	0.29	0.48
Δd/d	$\sim 1 \times 10^{-2}$	$\sim 3 \times 10^{-2}$	$\sim 5 \times 10^{-3}$	$\sim 7 \times 10^{-3}$
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

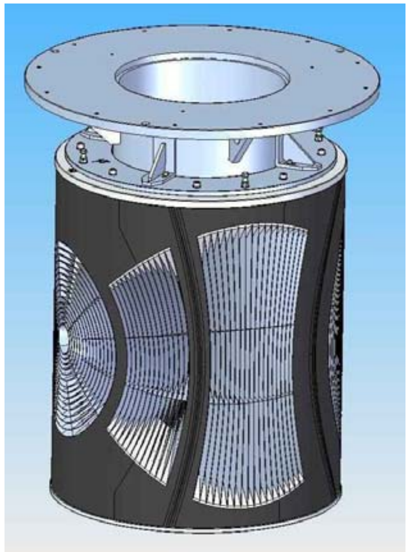
- Good workhorse instrument for powder diffraction
- High Q accessible for disordered materials investigation using the PDF method
- Some in situ capability but limited by count-rate
- Compatible with a wide range of restricted geometry sample environment

Once GEM detector array completed in 2005, ISIS started to look at how POLARIS might be upgraded. Huge growth in PDF studies and in situ processing communities. Need an instrument with extended Q-range, higher count-rate and similar resolution to POLARIS taking lessons learned from GEM instrument design and construction.

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

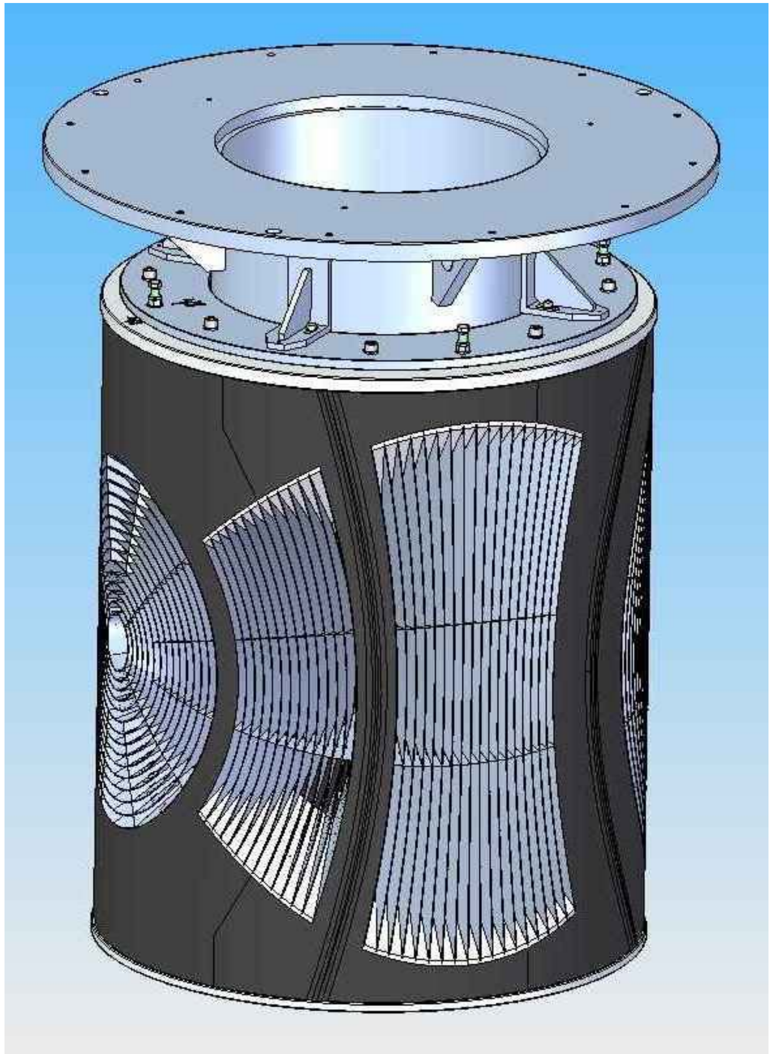




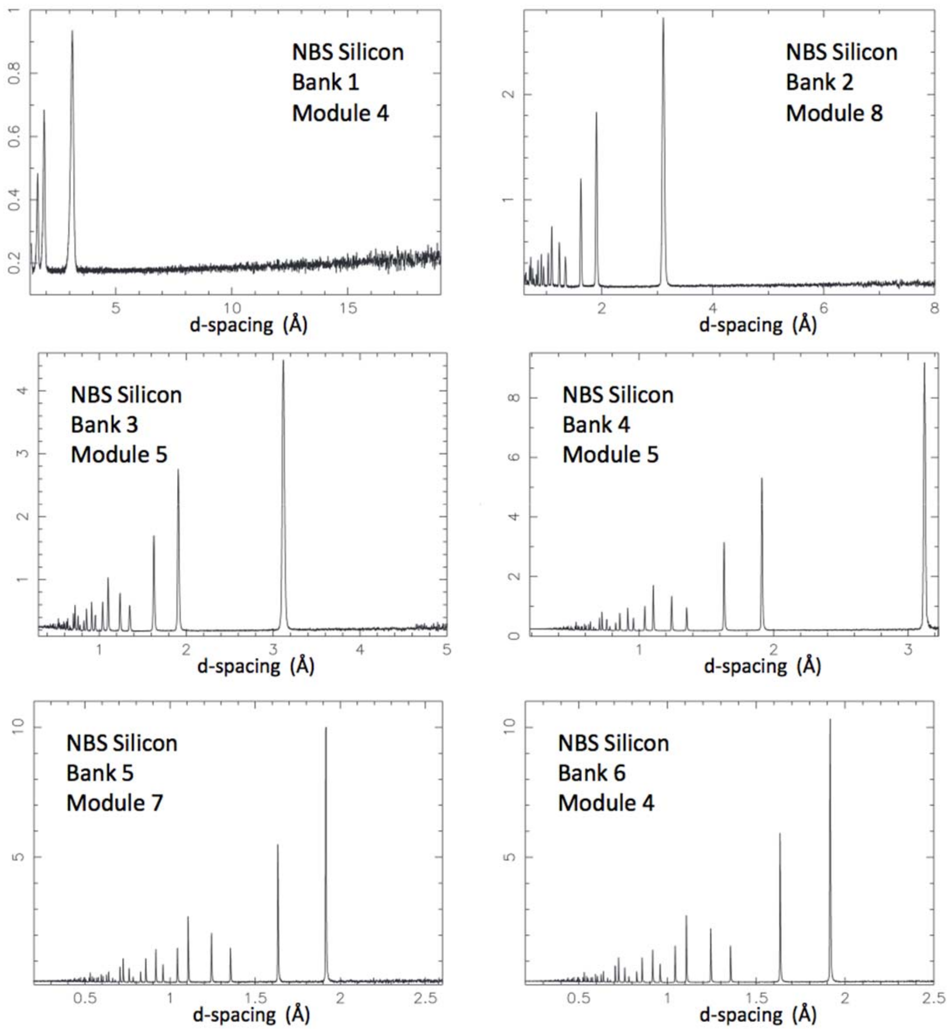
http://www.isis.stfc.ac.uk/instruments/polaris/polaris4643.html

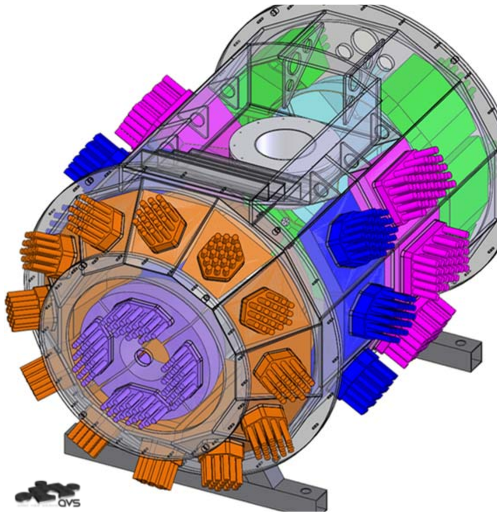

RLO39

POLARIS Upgrade



New POLARIS



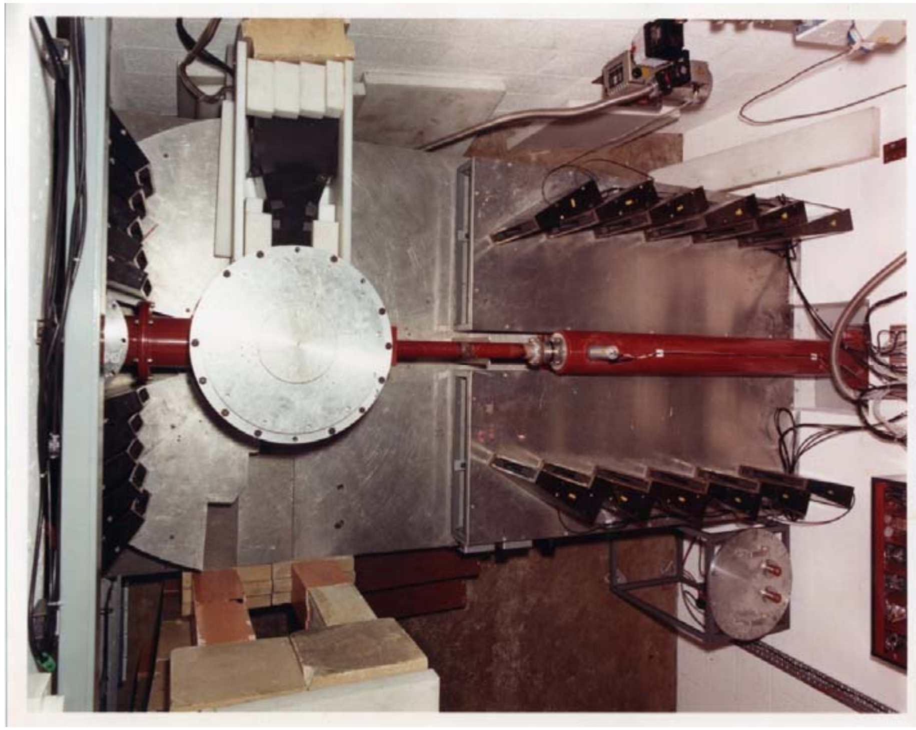


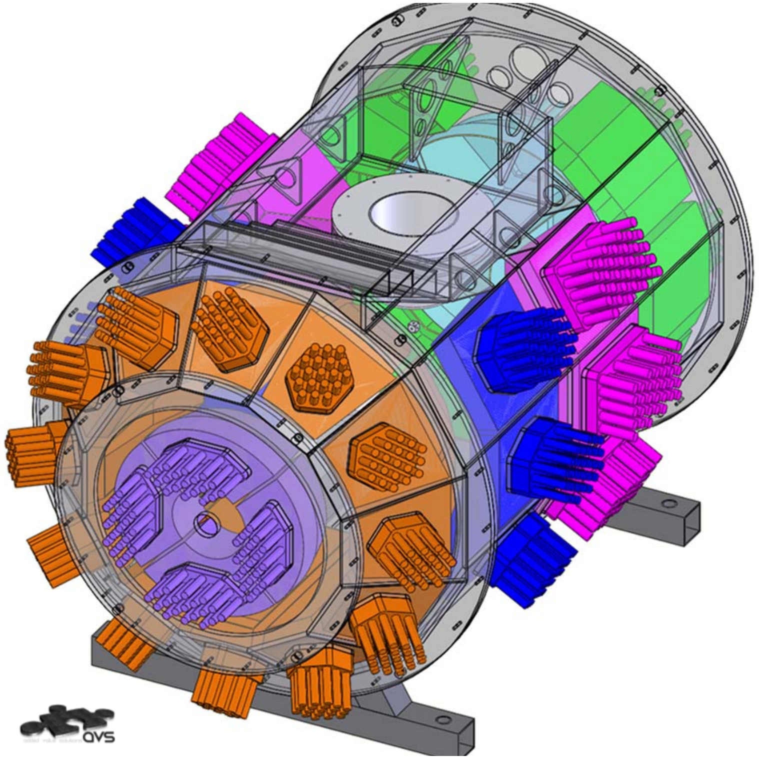
Bank 1 – cyan
Bank 2 – green
Bank 3 – pink
Bank 4 – blue
Bank 5 – orange
Bank 6 - purple

- Increased count rate factor from 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

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

POLARIS 1995 cf. 2013

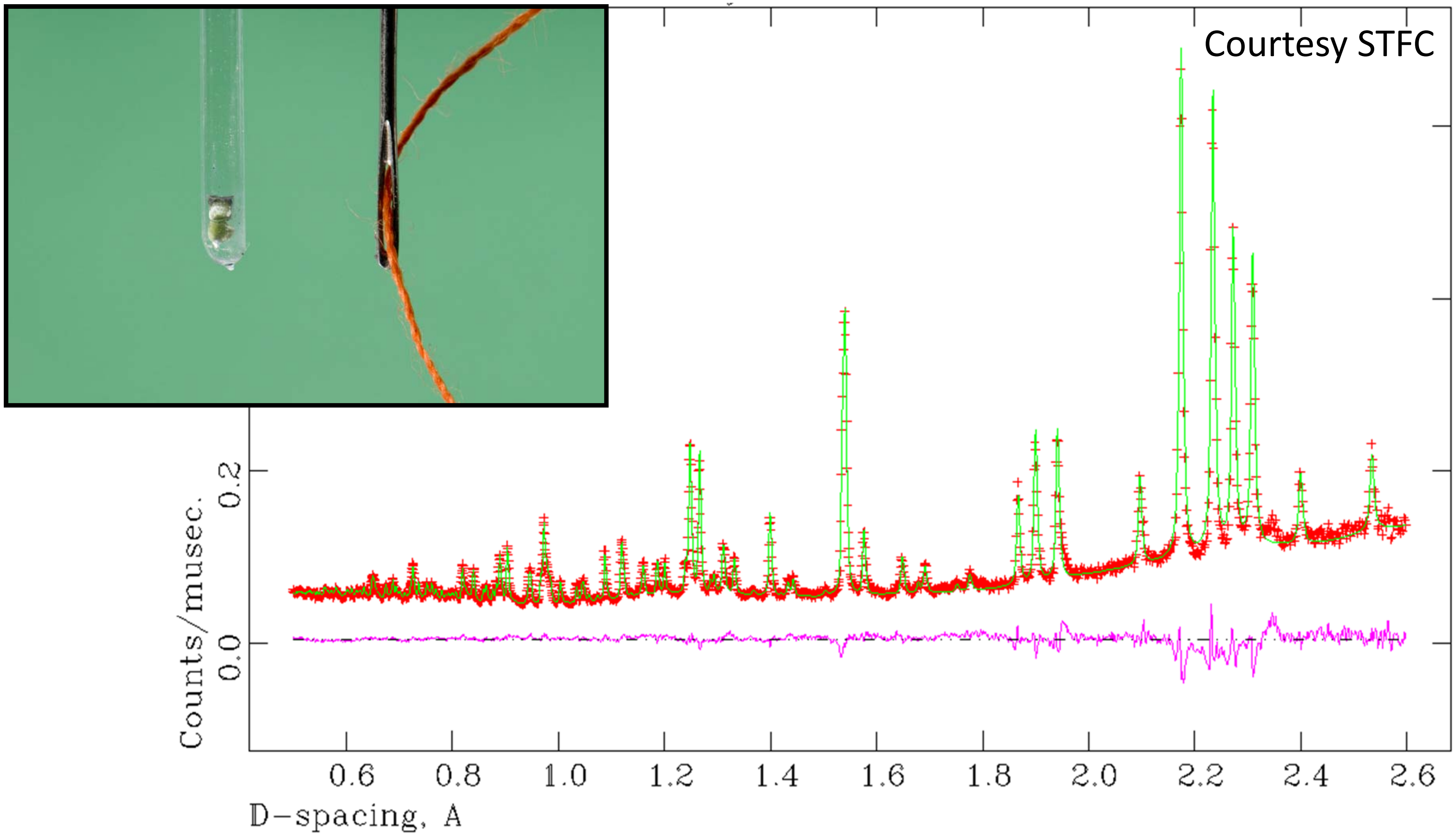




- 1995 500 mg 24+ hrs
- 2013 500 mg 15-20 minutes with increased Q-range

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

Pushing the boundaries in sample size

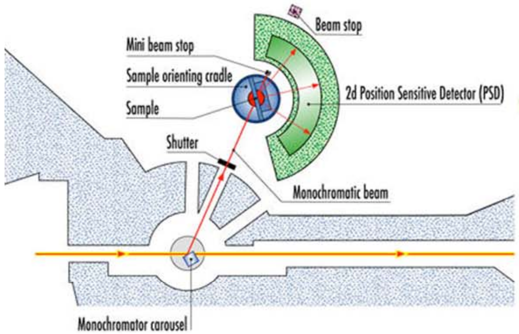


~1mm^3 sample of $NaNiF_3$ phase prepared at high *p* + high T

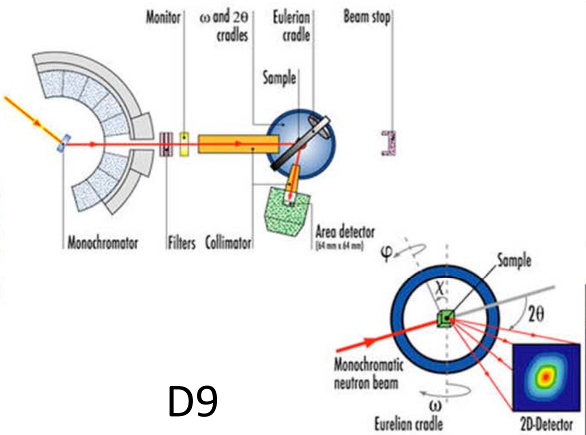
Lindsay-Scott *et al*, J. Appl. Cryst., **47**, 1939 (2014).

Single Crystal Instruments Continuous Source - ILL

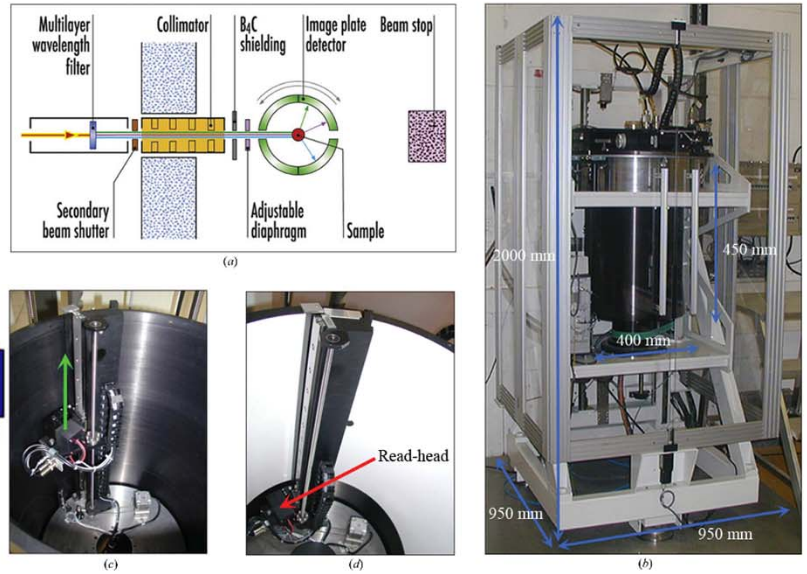
EUROPEAN SPALLATION SOURCE



D19

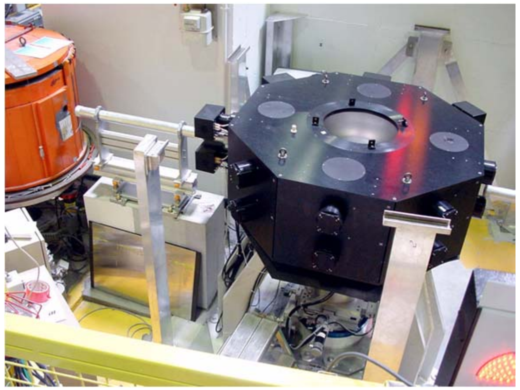


D9



↑

LADI-III



CYCLOPS

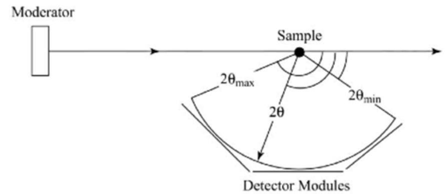
- Monochromatic and Laue type instruments are represented
- Q-range of interest and unit cell volume determine whether hot, thermal or cold neutron spectrum required for both instrument types

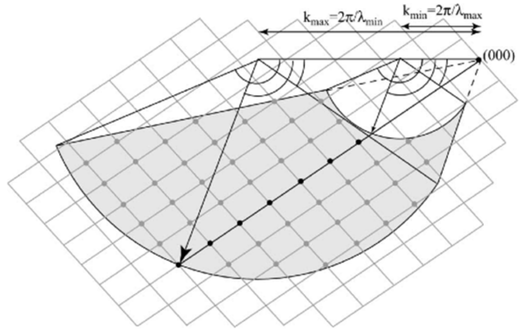
http://www.ill.eu/instruments-support/instruments-groups/

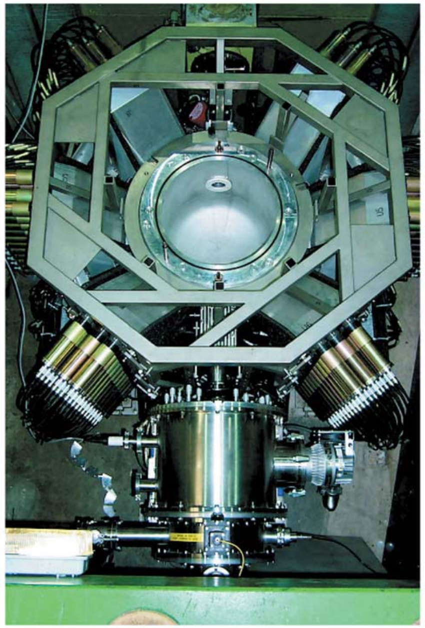
Single Crystal Instruments: Spallation Source – SXD at ISIS

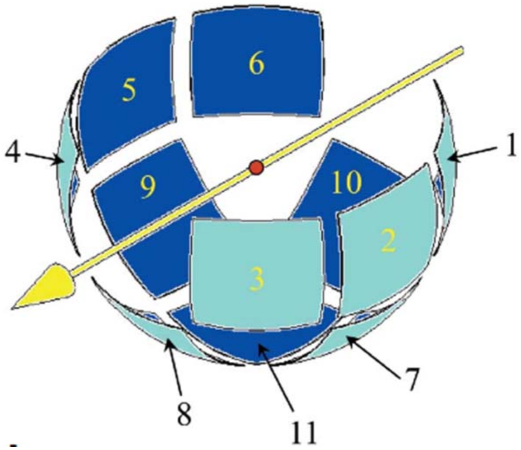
EUROPEAN SPALLATION SOURCE

- H_2O moderator poisoned at 2 cm
- 0.2 – 10 Å wavelength band
- Primary flight path 8.3 m
- Beam size < 15 mm
- 11 192 × 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 and minimising background

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

Designing diffractometers

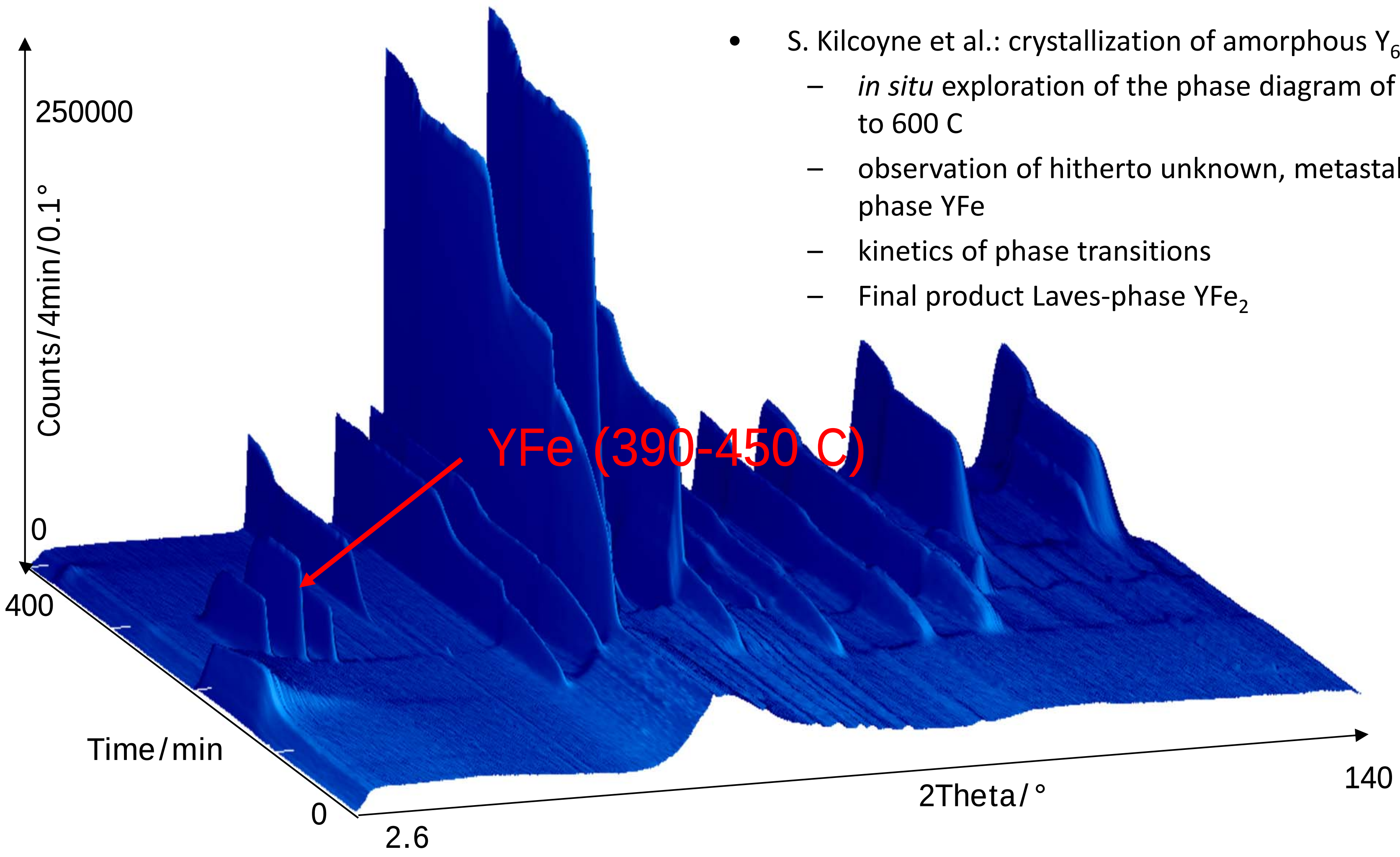
Define a science case

Instruments are designed and built to perform science

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 size
- Analyse residual stress within materials
- Process control
- Many other uses

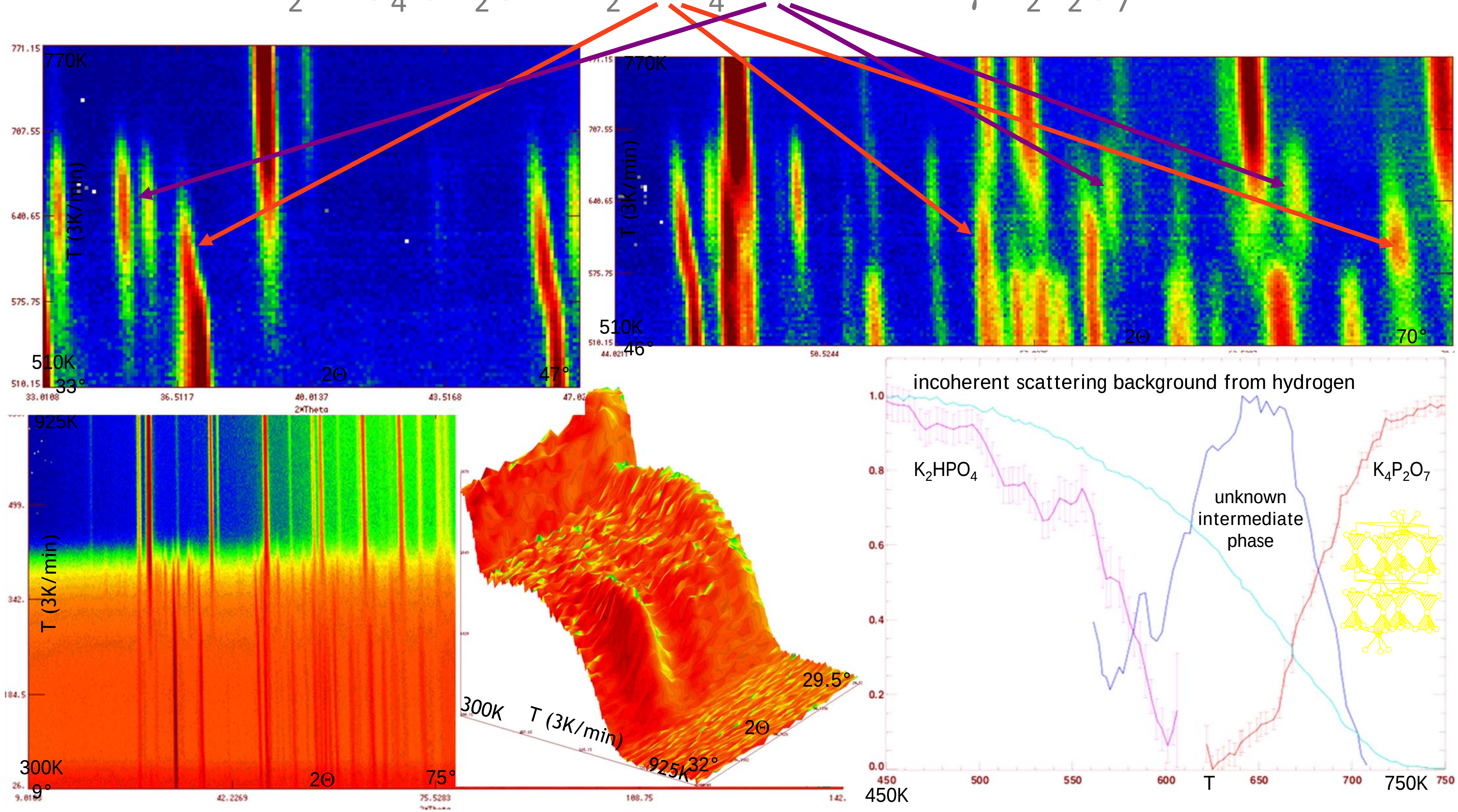
Crystallisation



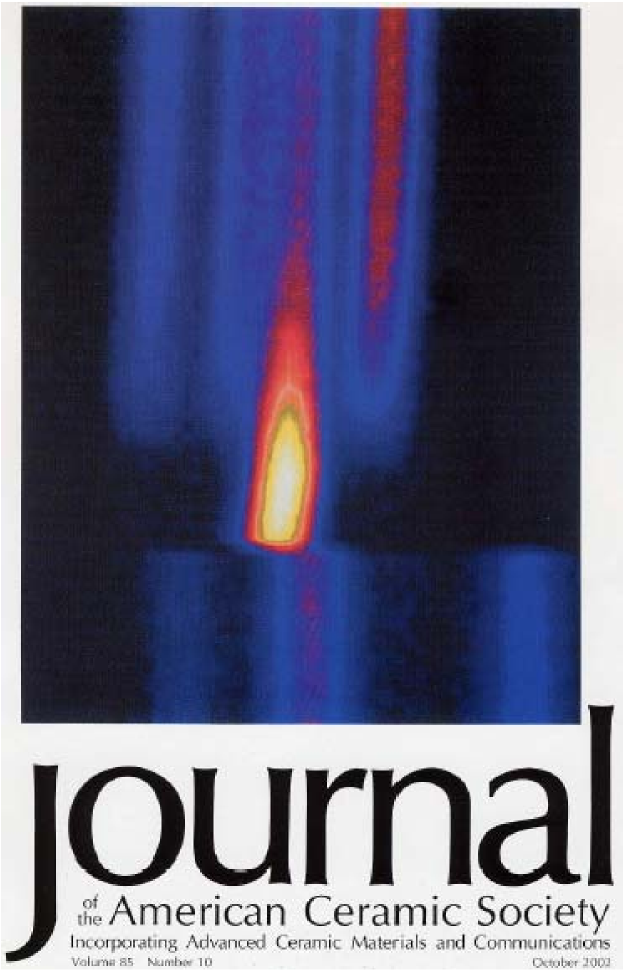
- S. Kilcoyne et al.: crystallization of amorphous $Y_{67}Fe_{33}$
  - *in situ* exploration of the phase diagram of Y-Fe RT to 600 C
  - observation of hitherto unknown, metastable phase YFe
  - kinetics of phase transitions
  - Final product Laves-phase YFe_2

In situ processing: dehydration

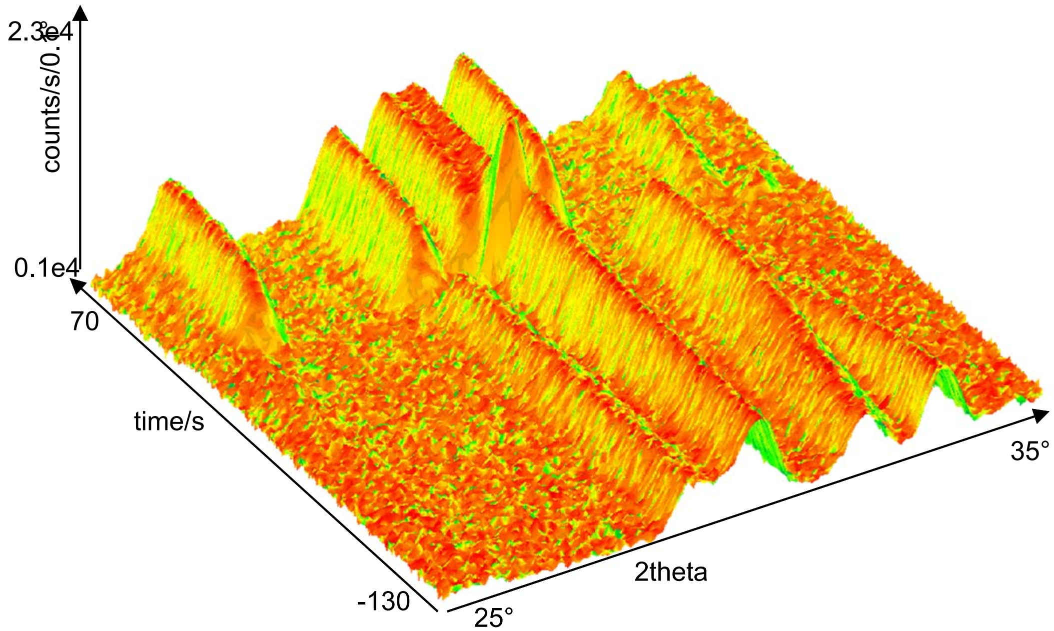
- $K_2HPO_4 \cdot 3H_2O$ □ K_2HPO_4 □ ?? □ ? □ γ-$K_2P_2O_7$



In situ processing: fast reactions

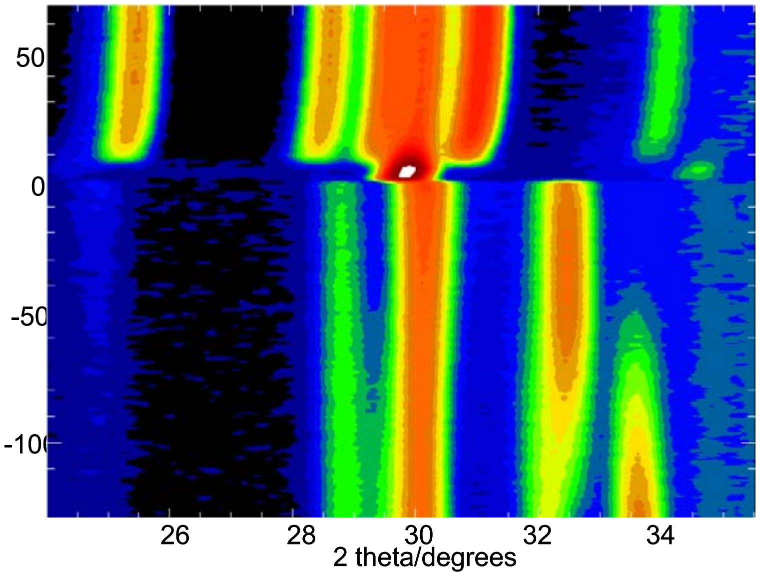


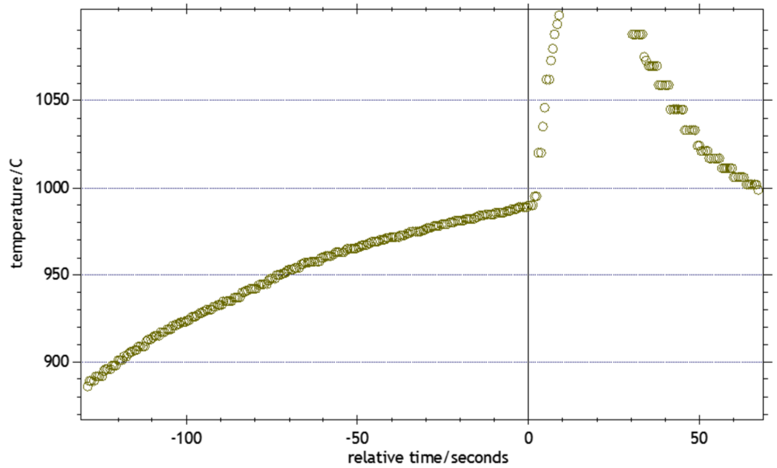
Ti_3SiC_2 made by hot isostatic pressing is expensive
In-situ investigation of thermal explosion synthesis (TES)
Initiate by heating from 850-1050 °C at 100 °C/min
Acquisition time 500 ms (300 ms deadtime)

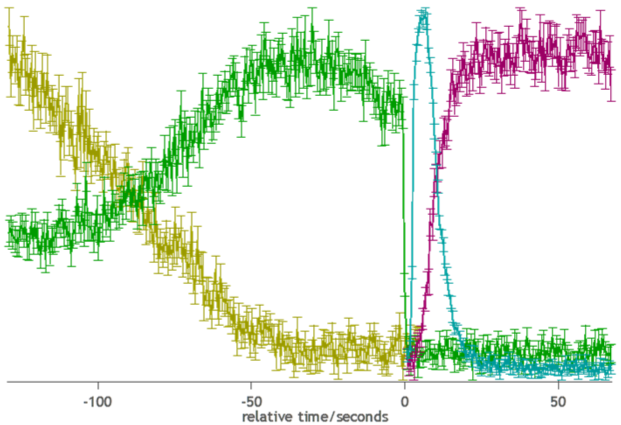


D.P.Riley et al. *J. Am. Ceramic. Soc.* 2002, 2417-2424.

In Situ Processing







α→βTi at 870°C
TiC_x growth
Ignition + melting T ↑<2000°C
Si substituted TiC formed
Ti_3SiC_2 precipitates after 5s
Complete after further 5s

Diffraction: residual stress

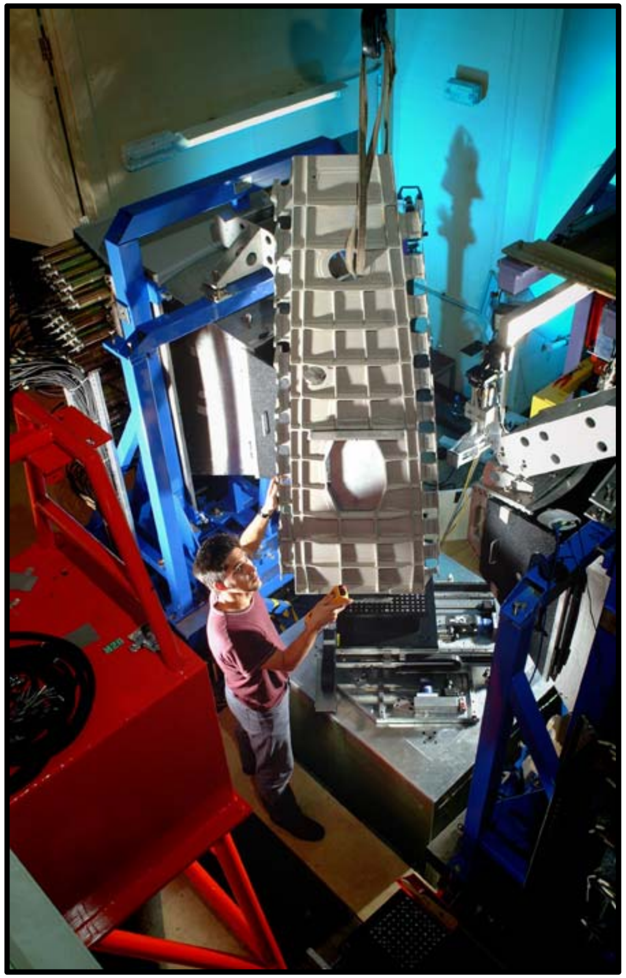
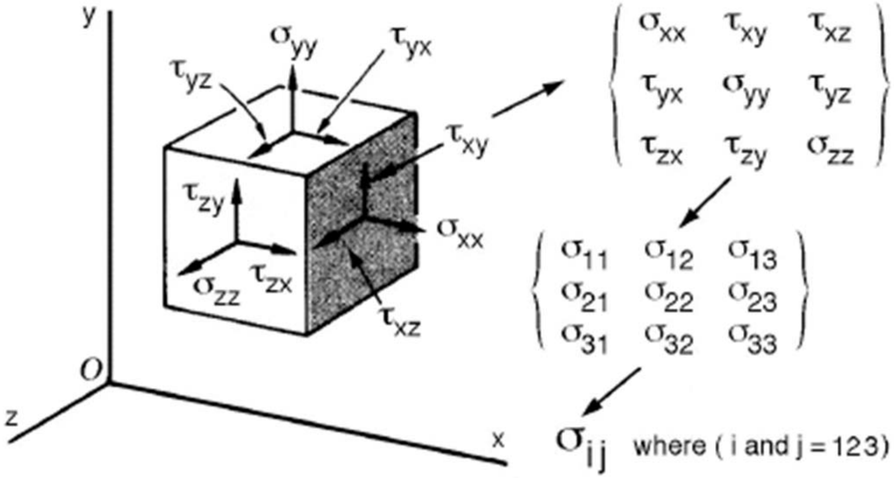


Photo courtesy STFC



Applications w.r.t. Residual stresses

Fatigue/Structural Integrity

Welds

Alloy development

Microstructure/Texture

Phase transformation

In-situ experiments

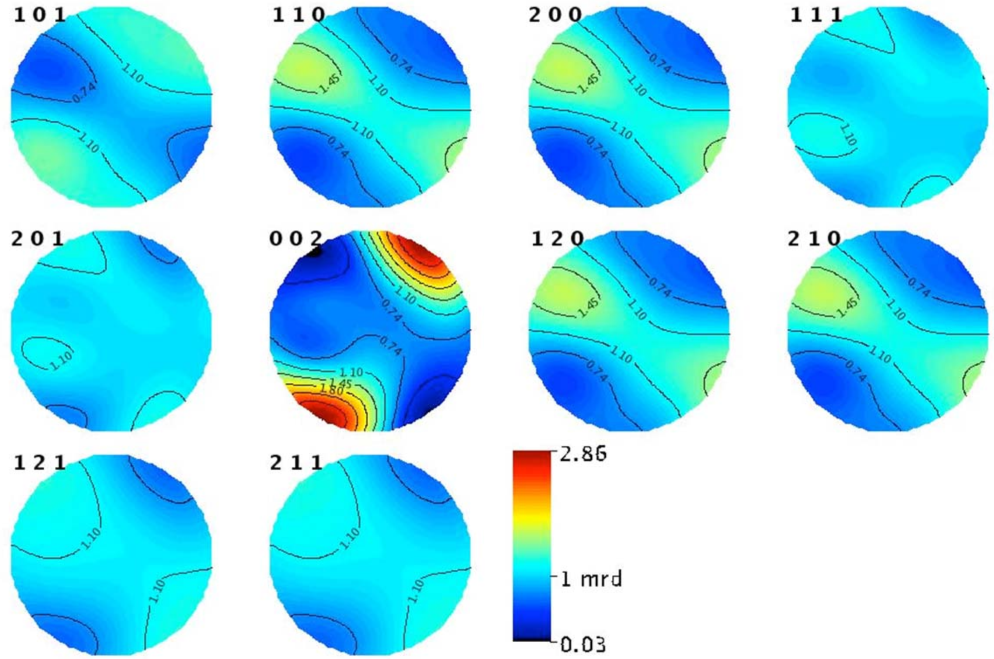
Texture analysis

- Peak intensity depending on sample orientation $I(2\theta,\chi,\varphi)$

  $\rightarrow$ transformed to pole figures (*PF*) $I(\alpha,\beta)/\langle I \rangle$

  $\rightarrow$ crystallite *orientation distribution function* (*ODF*)

- *Rietveld texture analysis* (*RITA*)
  - *ODF* as parameter set in least squares refinement of a whole data set (300-2000 patterns)
  - reconstruction of complete *pole figures* from *ODF*
  - program *MAUD* (Lutterotti)



Final comments

- Diffraction covers a very wide science case
- There are many diffractometers, each optimised to a particular region of parameter space that is determined by the science case
- New sources and instruments will offer new opportunities
- Instrument upgrades can give order of magnitude increases in performance

Wish list

- Detectors with high efficiency for short wavelength neutrons
- Improved beam transport for short wavelength neutrons