SINGLE CRYSTAL AND POWDER DIFFRACTOMETERS

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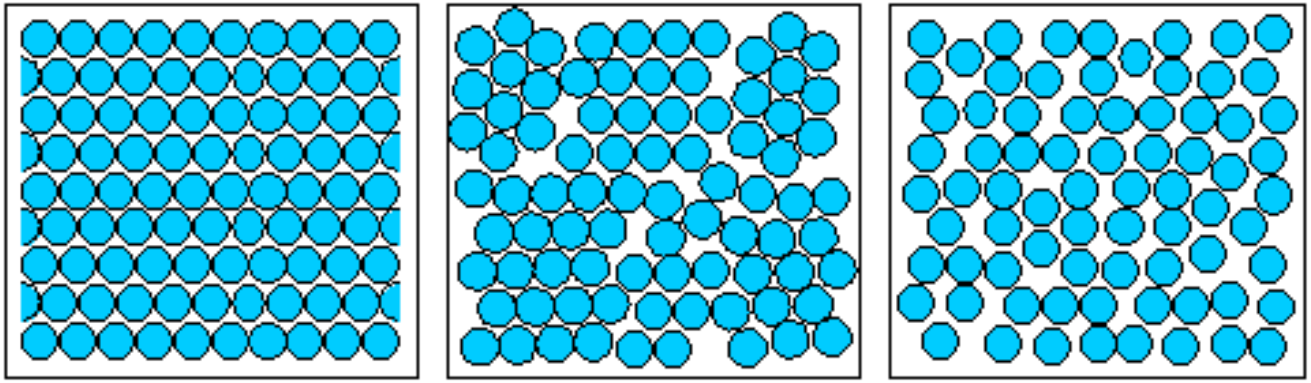
ISIS

OUTLINE OF TALK

- The Diffraction Technique.
- Neutrons versus X-rays.
- Design Criteria for a Neutron Diffractometer.
- Single Crystal Diffraction (Steady State Source).
- Single Crystal Diffraction (Pulsed Source).
- Powder Diffraction (Steady State Source).
- Powder Diffraction (Pulsed Source).
- Case Study : Polaris at ISIS.
- Closing Remarks.

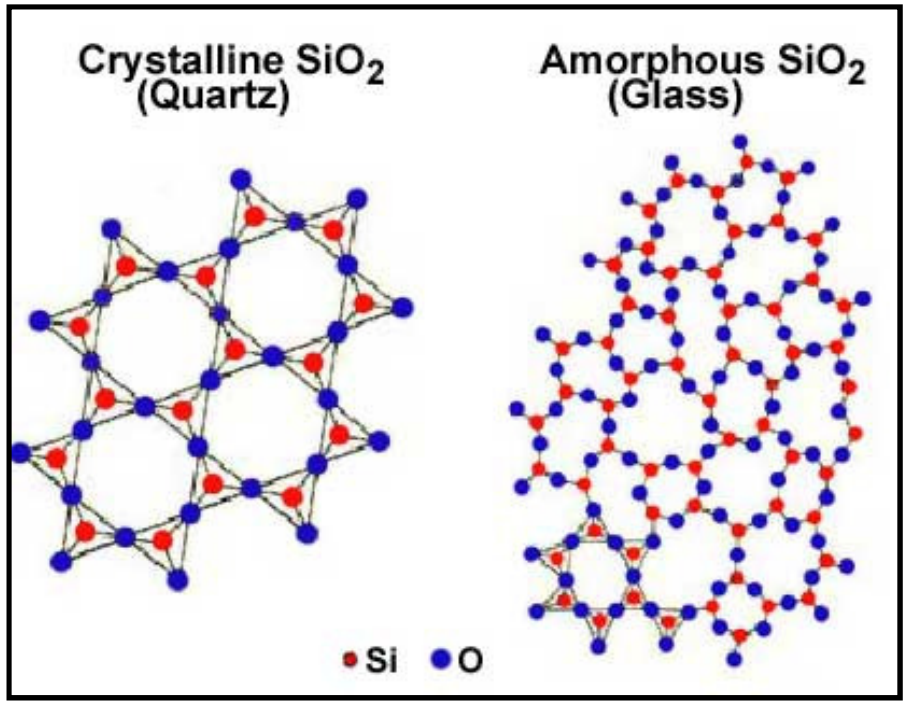
THE DIFFRACTION TECHNIQUE

Perfect crystal - long range order.



Perfect crystal Polycrystal Amorphous

Amorphous materials show no long-range atomic order, but do have short-range order, *i.e.* SiO_4 tetrahedra in silica glass.

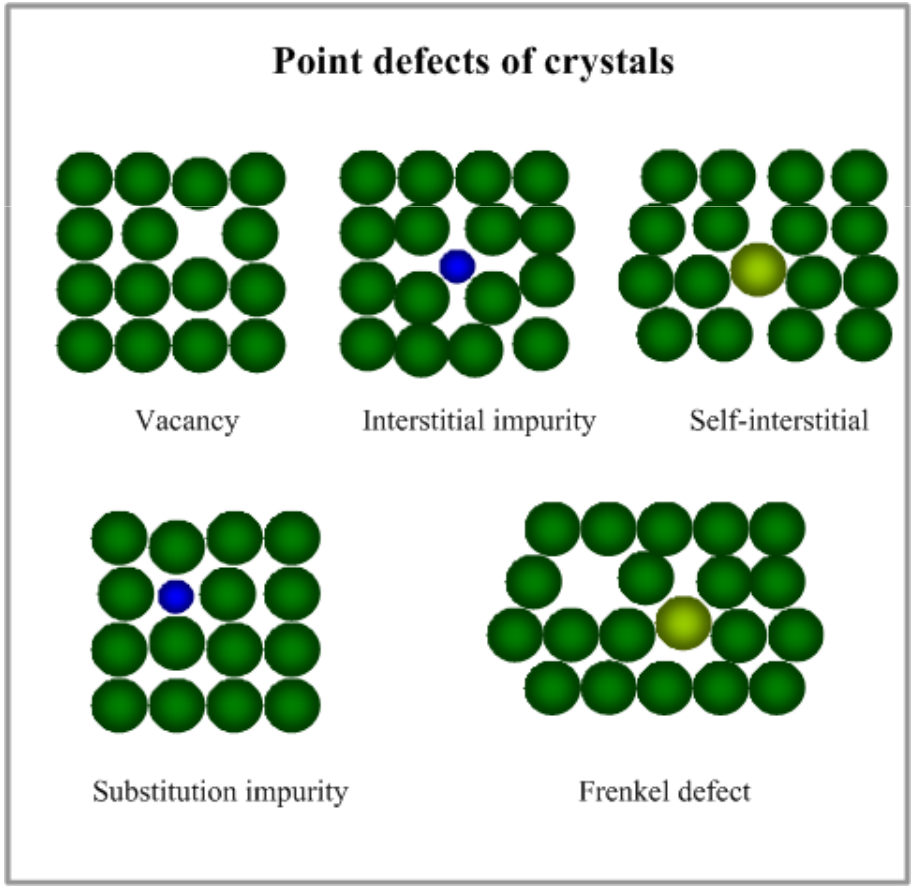


THE DIFFRACTION TECHNIQUE

Strictly, for crystalline materials, diffraction studies give the scattering density within the unit cell, averaged over time and all the unit cells in the sample.

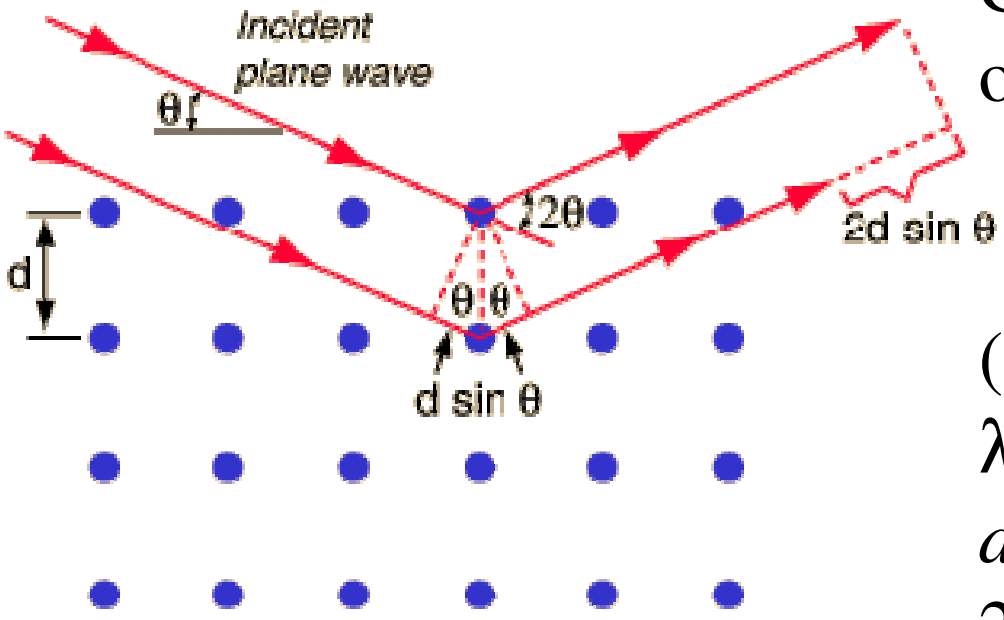
"*Crystals are like people, it is the defects in them that make them interesting.*"

(Sir Charles Frank).



Defects are responsible for many important properties in bulk materials - optical, electrical, mechanical.....

BRAGG DIFFRACTION



Constructive interference of waves occurs when

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

(Bragg's Law)
λ=wavelength of radiation
d=interplanar spacing
2θ=scattering angle

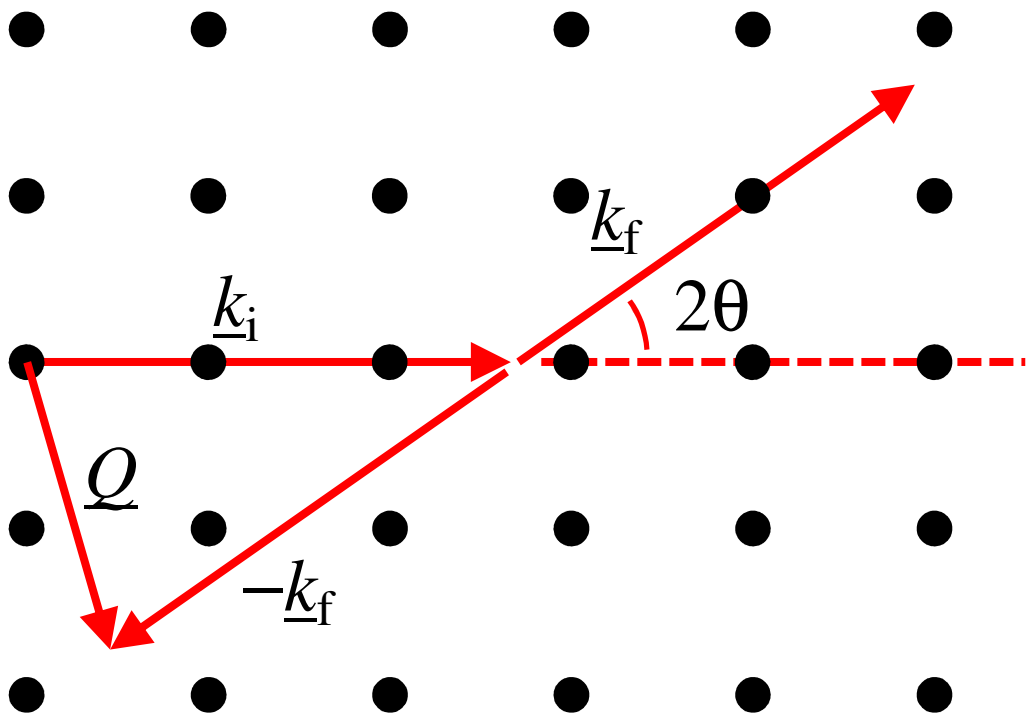
Historically, diffraction data (X-ray or neutron) collected by scanning detector through 2θ at fixed λ.

Single crystal : must be correctly oriented for diffraction.
Powder : collection of single crystals - no need to orient.

BRAGG DIFFRACTION

Can also define the scattering vector, $\underline{Q}$, in terms of the incident and scattered wavevectors, $\underline{k}_i$ and $\underline{k}_f$:

$$\underline{Q}=\underline{k}_i-\underline{k}_f$$



$$k = |\underline{k}| = 2\pi / \lambda$$

Elastic scattering :

$$k_i = k_f$$

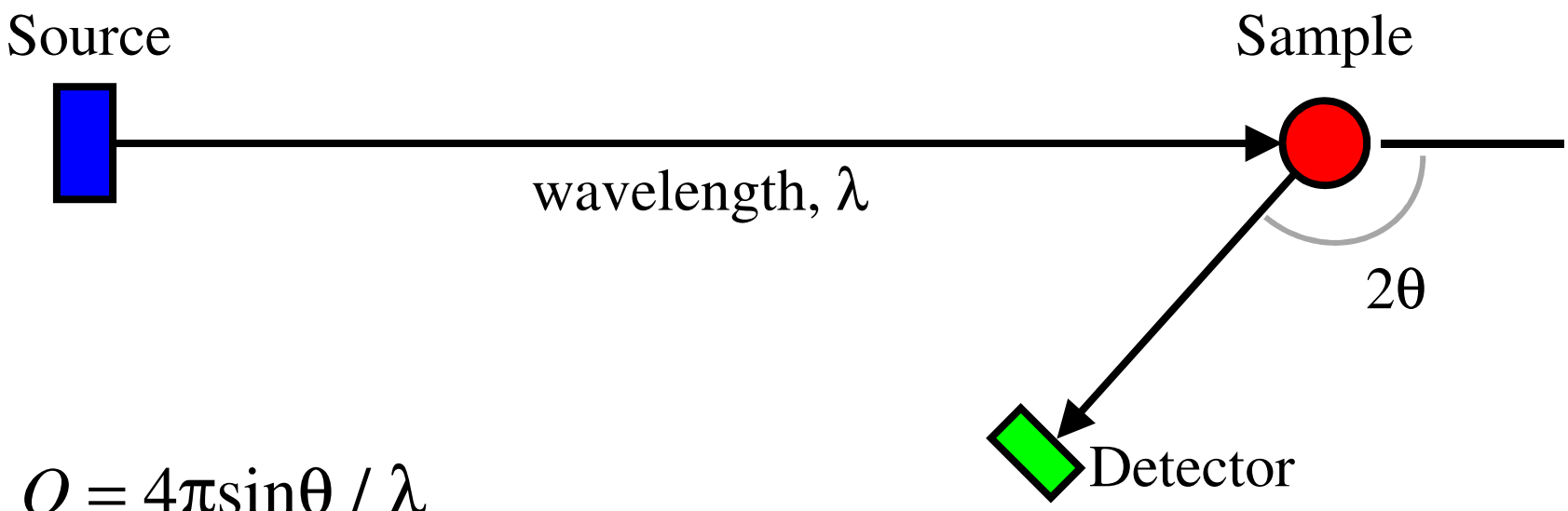
Geometry :

$$Q = 2k\sin\theta$$

$$\Rightarrow Q = 4\pi\sin\theta / \lambda$$

BRAGG DIFFRACTION

Basic features of a diffractometer are very simple!



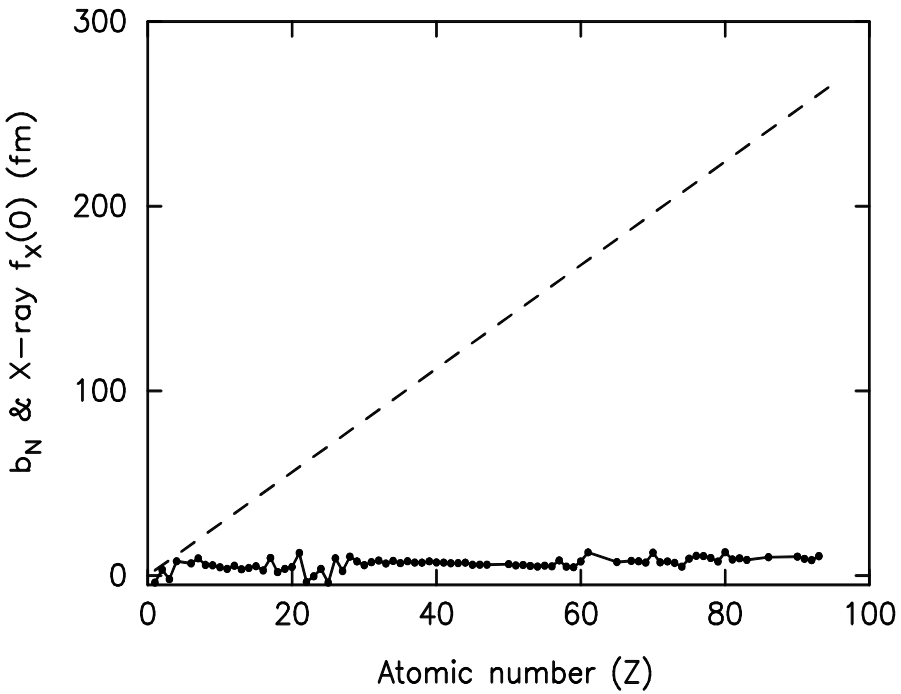
$$Q = 4\pi\sin\theta / \lambda$$

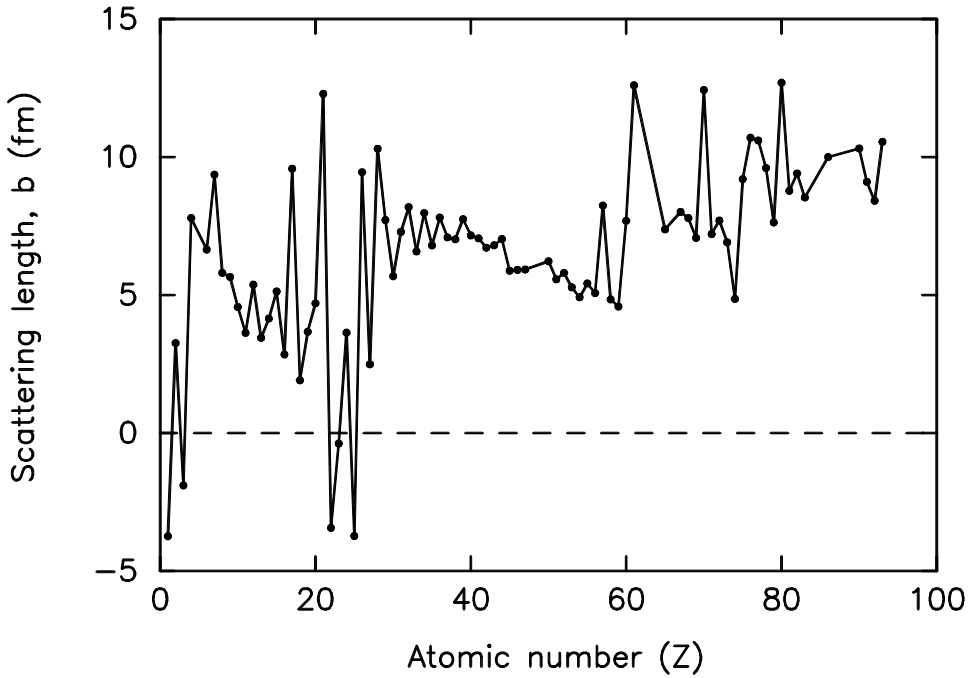
Measure Bragg peaks over a wide range of $\underline{Q}$ (for single crystal) or Q (for powder) by scanning scattering angle 2θ (and θ) or wavelength λ.

Neutrons or X-rays?

X-RAYS AND NEUTRONS

Flux. Smaller samples with X-rays.
Light atoms.
Neighbouring elements.
Magnetism.





BRAGG DIFFRACTION

Expression for the scattering intensity, $I(\underline{Q})$, is

$$I\left(\underline{Q}\right)=\frac{\mathrm{N_U}\left(2\pi\right)^3}{V_\mathrm{U}}\sum_{\underline{\tau}}\delta\left(\underline{Q}-\underline{\tau}\right)\left|F\left(\underline{Q}\right)\right|^2$$

$\Rightarrow$ only have scattering at Bragg positions, $\underline{Q}=\underline{\tau}$.

The structure factor, $F(\underline{Q})$, can be written as

$$F_{hkl}=\sum_{j=1}^{\mathrm{n_U}}b_j m_j e^{2\pi i\left(hx_j+ky_j+lz_j\right)}e^{-W_j(Q)}$$

sum over all atoms in unit cell

scattering length

site occupancy

h,k,l Miller indices
x,y,z atomic positions

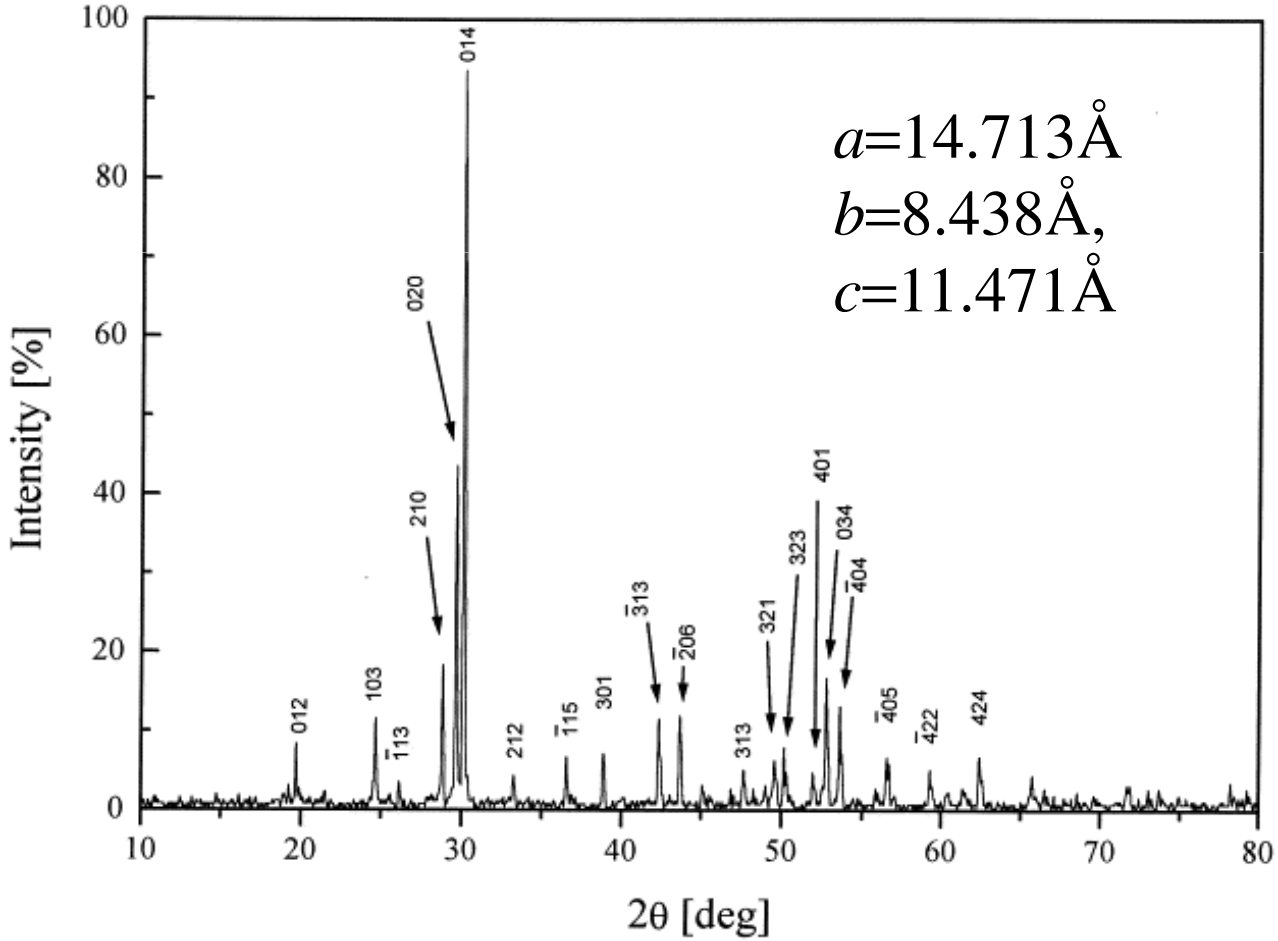
temperature factor

STRUCTURE SOLUTION

A (very) brief summary of route from diffraction data to the crystal structure.....

Indexing.

Using the Bragg peak positions (in Q, Q, 2θ, d, *etc.*) determine the size and shape of the unit cell.

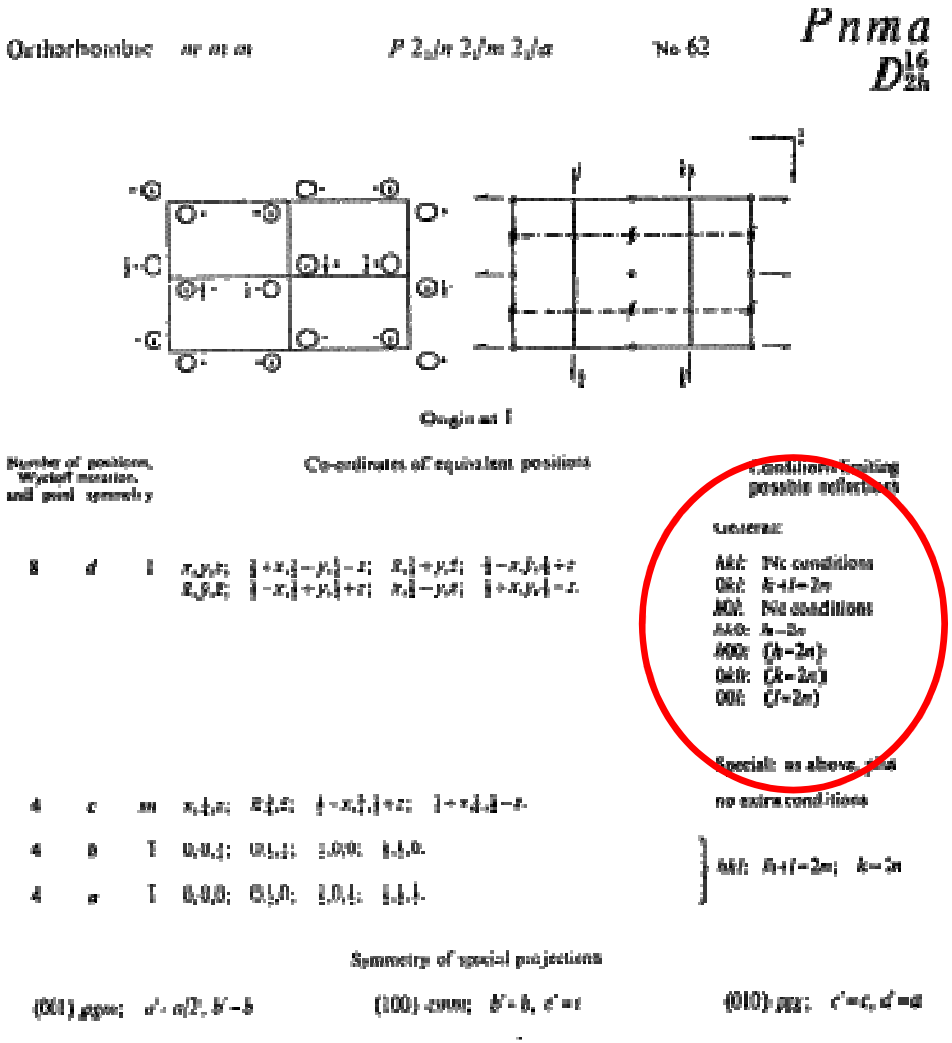


STRUCTURE SOLUTION

A (very) brief summary of route from diffraction data to the crystal structure.....

Determine the space group.

Using the systematic absences of certain classes of reflections to give the space group (or, at least, a small number of candidate possibilities).



Orthorhombic $mm\,m$ $P\,2_1/n\,2_1/m\,2_1/a$ No. 62 $Pnma$ D_{2h}^{16}

Origin at 1

Number of positions, Wyckoff notation, and point symmetry			Co-ordinates of equivalent positions	Conditions limiting possible reflections
				General:
8	d	1	x,y,z; $\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}-z$; $\bar{x},\frac{1}{2}+y,\bar{z}$; $\frac{1}{2}-x,\bar{y},\frac{1}{2}+z$; $\bar{x},\bar{y},\bar{z}$; $\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}+z$; $x,\frac{1}{2}-y,z$; $\frac{1}{2}+x,y,\frac{1}{2}-z$.	hkl: No conditions $0kl$: $k+l=2n$ $h0l$: No conditions $hk0$: $h=2n$ $h00$: $(h=2n)$ $0k0$: $(k=2n)$ $00l$: $(l=2n)$
				Special: as above, plus
4	c	m	$x,\frac{1}{4},z$; $\bar{x},\frac{3}{4},\bar{z}$; $\frac{1}{2}-x,\frac{3}{4},\frac{1}{2}+z$; $\frac{1}{2}+x,\frac{1}{4},\frac{1}{2}-z$.	no extra conditions
4	b	$\bar{1}$	$0,0,\frac{1}{2}$; $0,\frac{1}{2},\frac{1}{2}$; $\frac{1}{2},0,0$; $\frac{1}{2},\frac{1}{2},0$.	hkl: $h+l=2n$; $k=2n$
4	a	$\bar{1}$	$0,0,0$; $0,\frac{1}{2},0$; $\frac{1}{2},0,\frac{1}{2}$; $\frac{1}{2},\frac{1}{2},\frac{1}{2}$.	

Symmetry of special projections

(001) pgm; $a'=a/2$, $b'=b$ (100) cmm; $b'=b$, $c'=c$ (010) pgg; $c'=c$, $a'=a$

STRUCTURE SOLUTION

It is, in principle, possible to determine the scattering density within the unit cell, $\rho(x,y,z)$, directly from the structure factors, F_{hkl}, using

$$\rho(x, y, z) = \frac{1}{V_{\mathrm{U}}} \sum_h \sum_k \sum_l F_{hkl} e^{2\pi i(hx+ky+lz)}$$

However, experimentally we get $|F_{hkl}|$ rather than F_{hkl}.

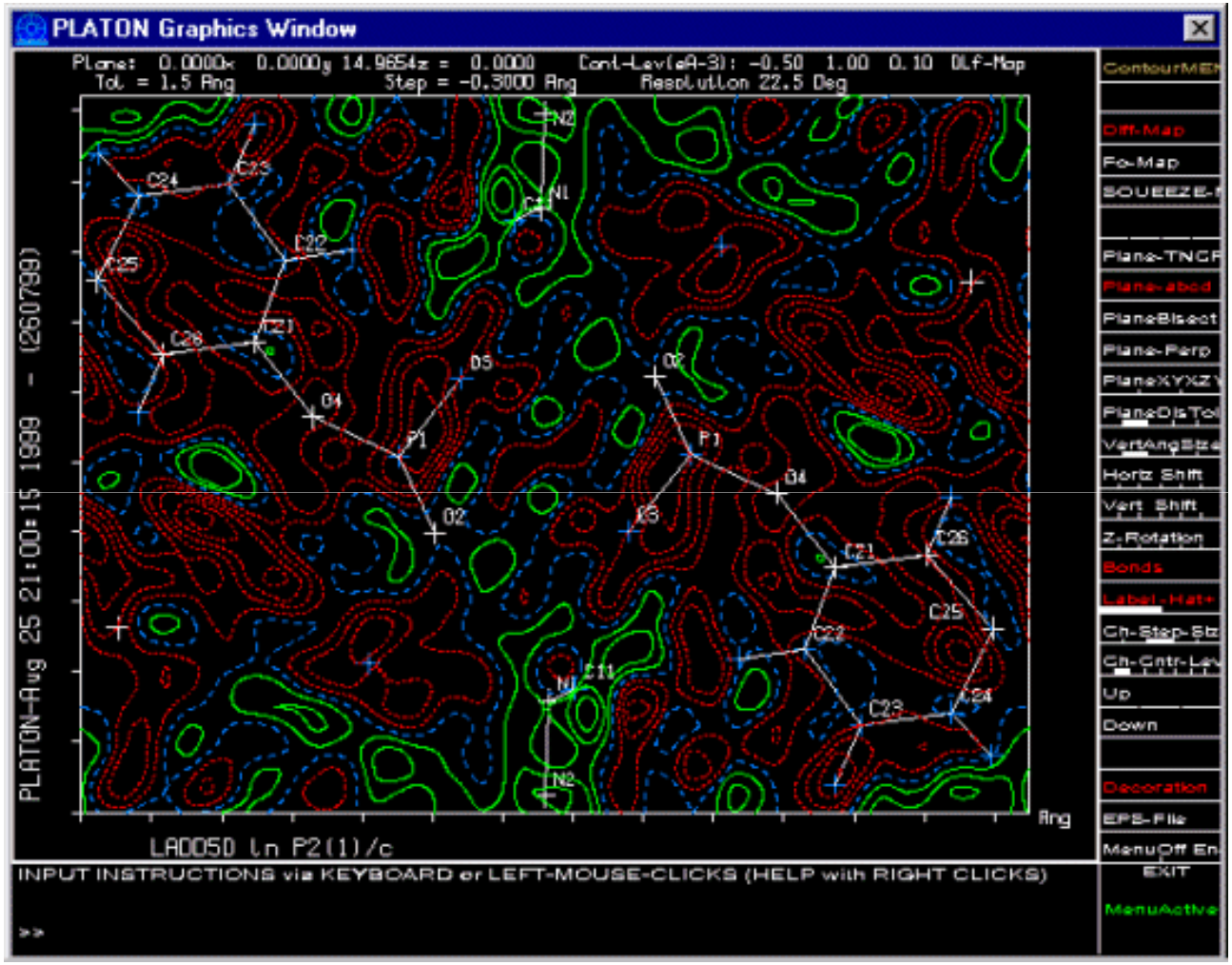
Various methods are used to overcome this 'phase problem'.

- Patterson maps.
- Direct methods.
- Chemical intuition.

Most crystal structures solved using X-ray diffraction.

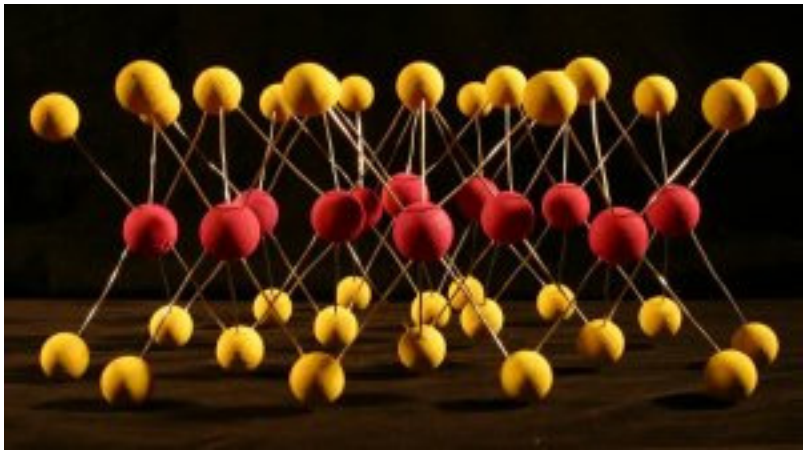
STRUCTURE SOLUTION

If the majority of the structure has been correctly determined, it is possible to find remaining atoms using Fourier difference methods



$$\Delta\rho(x,y,z) = \frac{1}{V_{\mathrm{U}}} \sum_h \sum_k \sum_l \left(|F_{obs}| - |F_{calc}| \right) e^{2\pi i(hx+ky+lz)}$$

STRUCTURE SOLUTION



Final stage is to perform least-squares fit to the experimental data using the structural model.

- Single crystal. Fit to the measured squared structure factors, $F^2_{obs}(hkl)$.

h	k	l	F^2_{calc}	F^2_{obs}
0	2	0	8177.16	8360.52
1	2	0	0.00	0.00
2	2	0	8361.77	8897.75
1	3	0	385.96	402.84
2	3	0	1.01	0.98
3	3	0	1006.42	1038.81
4	3	0	1.42	1.44
5	3	0	8.40	8.15
0	4	0	1386.12	1595.49
1	4	0	7.50	7.74
2	4	0	190.03	195.00
3	4	0	1.75	1.78
4	4	0	469.48	475.29
5	4	0	0.15	0.16
1	5	0	181.10	187.38
2	5	0	3.41	3.53
3	5	0	58.33	59.70
4	5	0	1.77	1.78
5	5	0	46.00	46.56
0	6	0	380.12	398.37
1	6	0	28.49	29.14
2	6	0	5461.81	5568.37
3	6	0	0.00	0.00
4	6	0	1554.40	1579.61
5	6	0	0.00	0.00

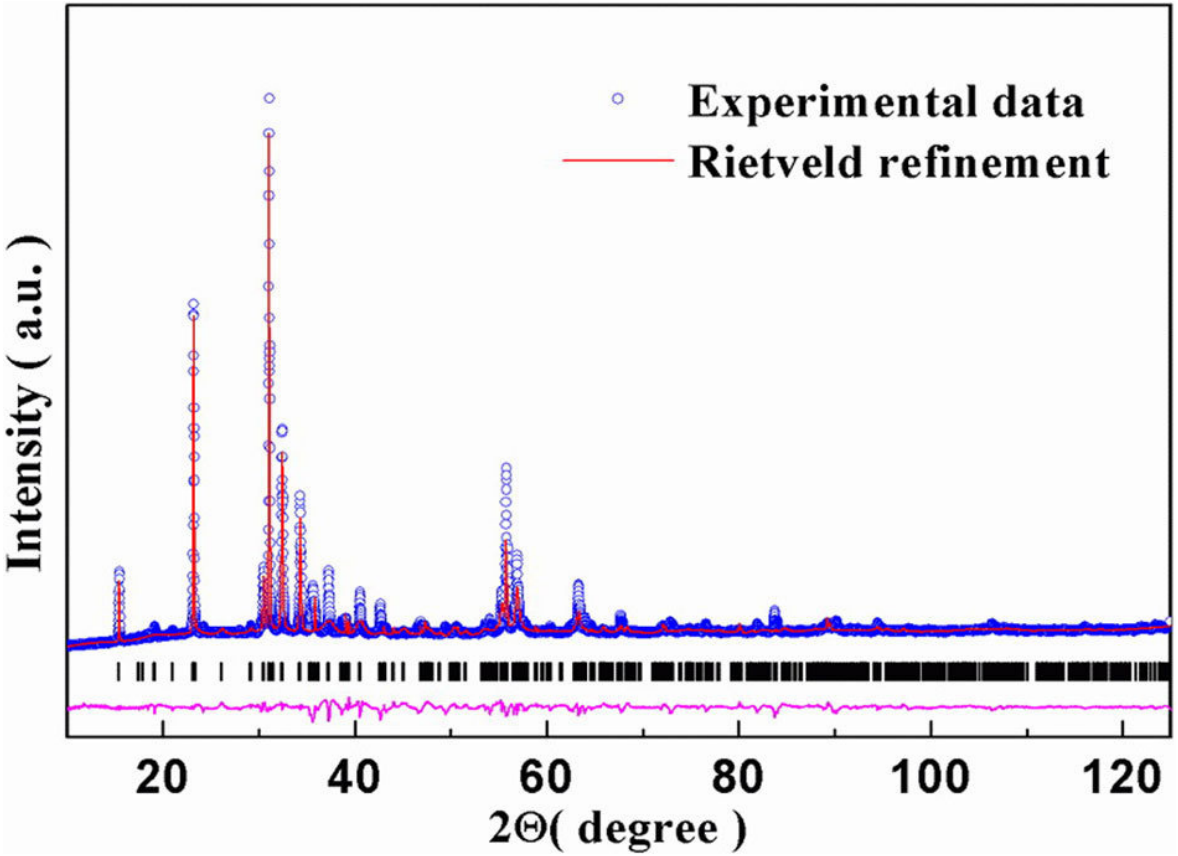
h	k	l	F^2_{calc}	F^2_{obs}
1	7	0	417.13	433.16
2	7	0	0.46	0.46
3	7	0	927.65	953.37
4	7	0	9.11	9.21
5	7	0	82.70	83.20
0	8	0	1611.91	1674.67
1	8	0	1.51	1.52
2	8	0	1706.40	1688.92
3	8	0	6.60	6.57
4	8	0	835.88	846.65
1	9	0	2381.82	2500.06
2	9	0	16.62	16.88
3	9	0	231.29	239.03
4	9	0	0.11	0.11
0	10	0	285.65	296.97
1	10	0	15.53	15.82
2	10	0	4.71	4.56
3	10	0	0.63	0.67
4	10	0	6.80	6.70
1	11	0	174.41	220.28
2	11	0	5.22	5.24
3	11	0	5.71	5.78
4	11	0	4.56	4.51
:	:	:	:	:
:	:	:	:	:

STRUCTURE SOLUTION

- Powder. Fit to the measured diffraction pattern (Rietveld method).

Requires parameters describing the peak shape, *etc*.

Provides.....
unit cell parameters,
thermal parameters,
site occupancies,
.....*etc*.



Average structure.

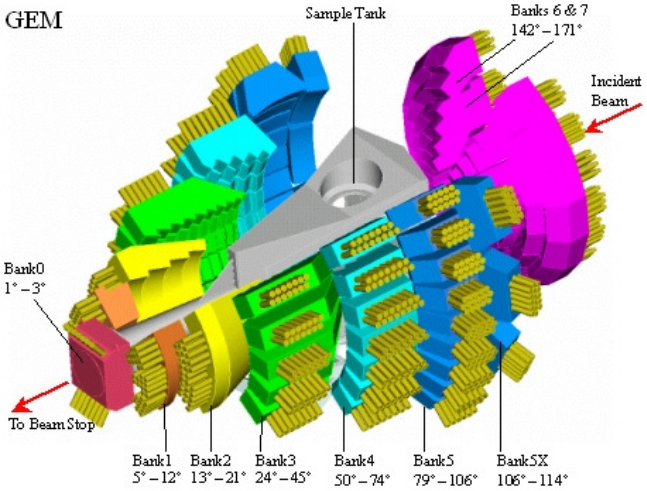
$$R_{\mathrm{W}}^{2} = \sum_{j=1}^{N_{\mathrm{D}}} \frac{\left(y_{obs,j} - y_{calc,j}\right)^{2}}{\left(\sigma y_{obs,j}\right)^{2}} \Bigg/ \sum_{j=1}^{N_{\mathrm{D}}} \frac{\left(y_{obs,j}\right)^{2}}{\left(\sigma y_{obs,j}\right)^{2}}$$

INSTRUMENT REQUIREMENTS

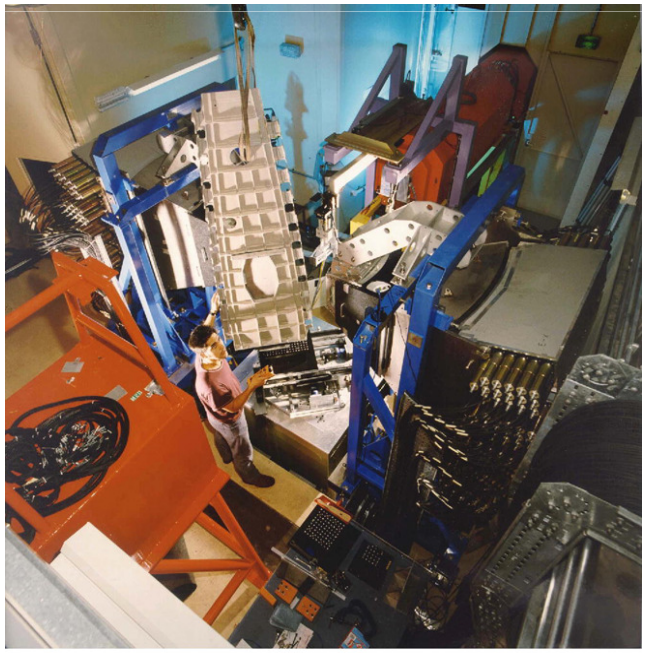
- Need a wide range of Q (single crystal) or Q (powder).
  - maximize number of measured Bragg peaks.
  - low Q important for indexing, magnetism, *etc*.
  - high Q good for thermal parameters, occupancies, *etc*.
- Need high countrate.
  - fast measurements (in-situ studies of kinetics, *etc*.).
  - small sample volumes (high pressure studies, *etc*.).
- Need good $\Delta Q/Q$ (or $\Delta d/d$) resolution.
  - observe subtle peak splittings.
  - accurate measurement of changes in unit cell parameters.
- Need low background.
  - see weak reflections (correct space group, superlattices).

INSTRUMENT REQUIREMENTS

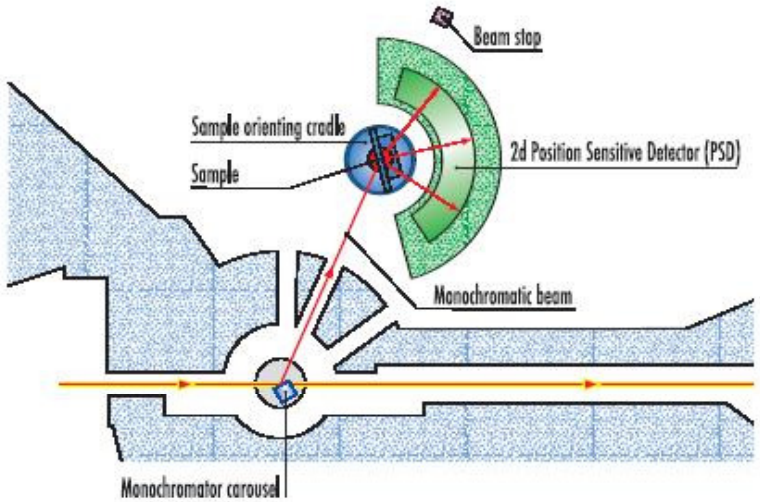
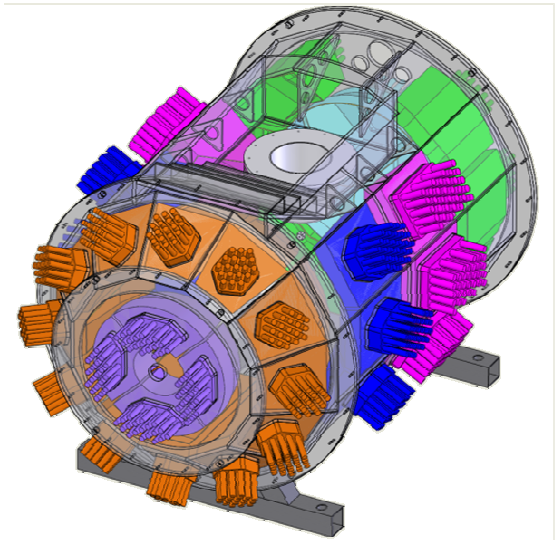
- General purpose diffractometers.
  - Suitable for a wide range of scientific applications.



- Specialised diffractometers.
  - Engineering.
  - High pressure.
  - Proteins.

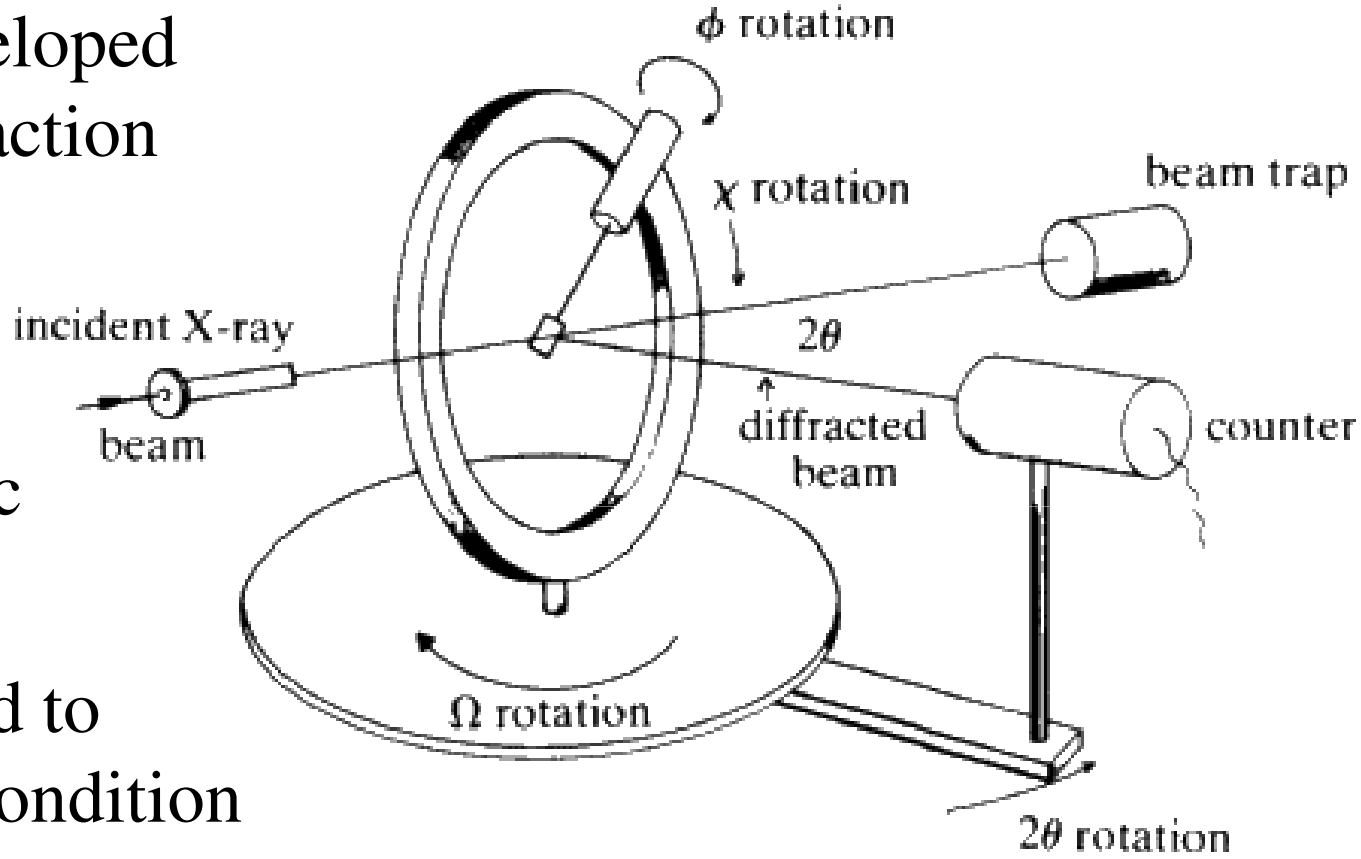


NEUTRON DIFFRACTOMETERS

	Steady State Source	Pulsed Source
Single Crystal		
Powder		

SINGLE CRYSTAL DIFFRACTION : STEADY STATE

Originally developed for X-ray diffraction studies of single crystals.



Monochromatic incident beam.

Crystal oriented to satisfy Bragg condition at the chosen 2θ value.

Typically perform a θ-2θ scan through Bragg peak to determine its intensity.

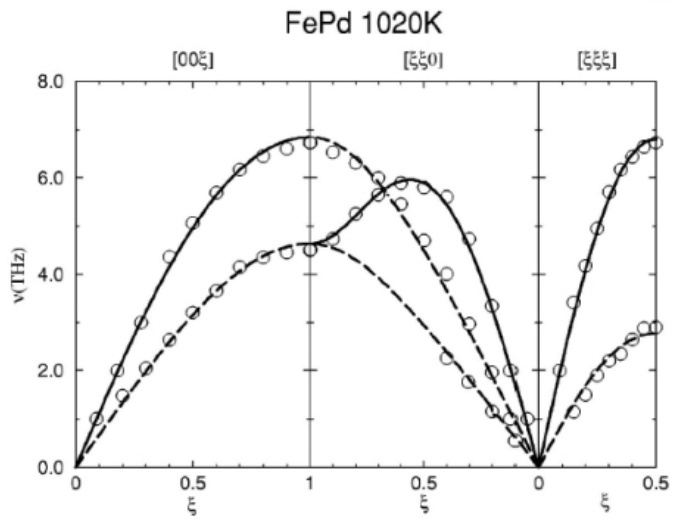
SINGLE CRYSTAL DIFFRACTION : STEADY STATE

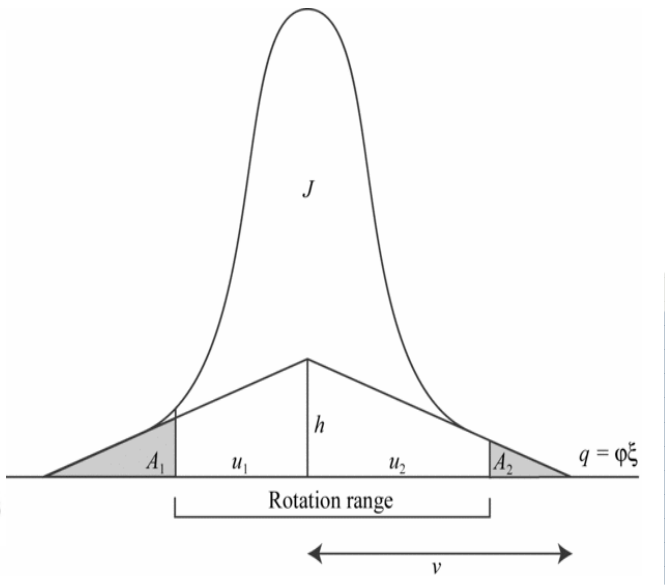
Corrections needed to make $I_{hkl} \propto F^2_{hkl}$.

Extinction. Loss of intensity due to multiple scattering events. Perfect crystal has $I_{hkl} \propto F_{hkl}$.

Absorption. Varies with scattering angle 2θ. Serious for large crystals with σ_{abs}. Corrections possible.

Thermal Diffuse Scattering (Phonons). Additional 'tails' under a Bragg peak. Effect tends to be strongest for intense peaks.

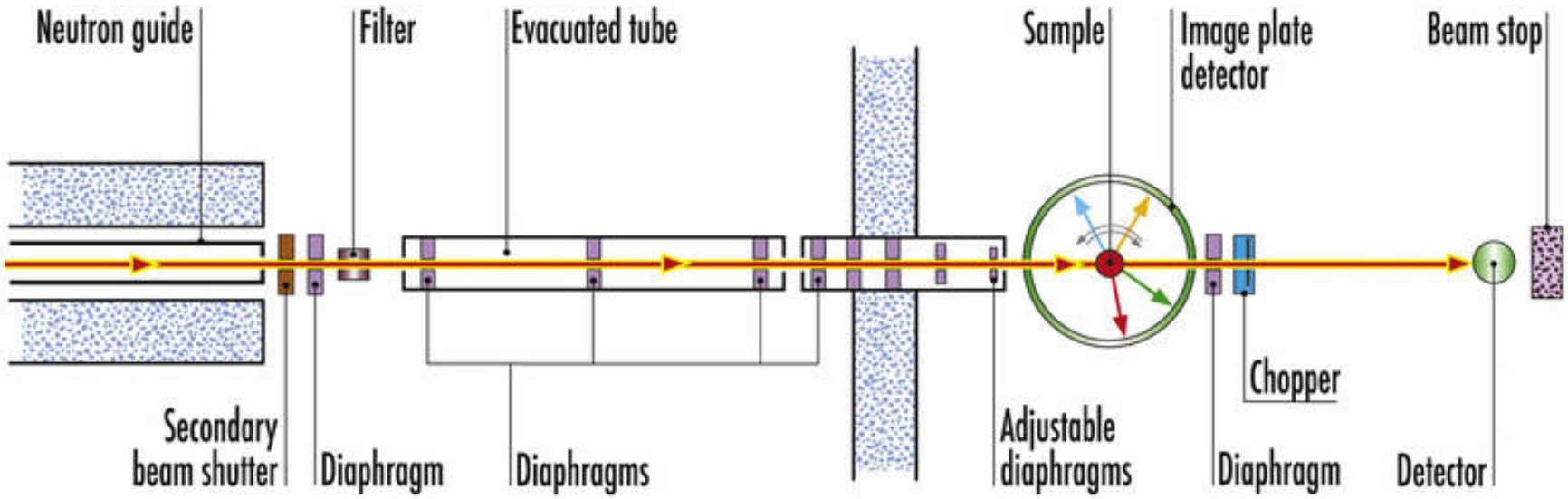




SINGLE CRYSTAL DIFFRACTION : STEADY STATE

VIVALDI (Very Intense Vertical Axis Laue Diffractometer) surveys large volumes of reciprocal space rapidly using the Laue technique with a cylindrical image-plate detector on a white neutron beam.

Can provide a 10-100× gain in efficiency over conventional monochromatic diffractometer.

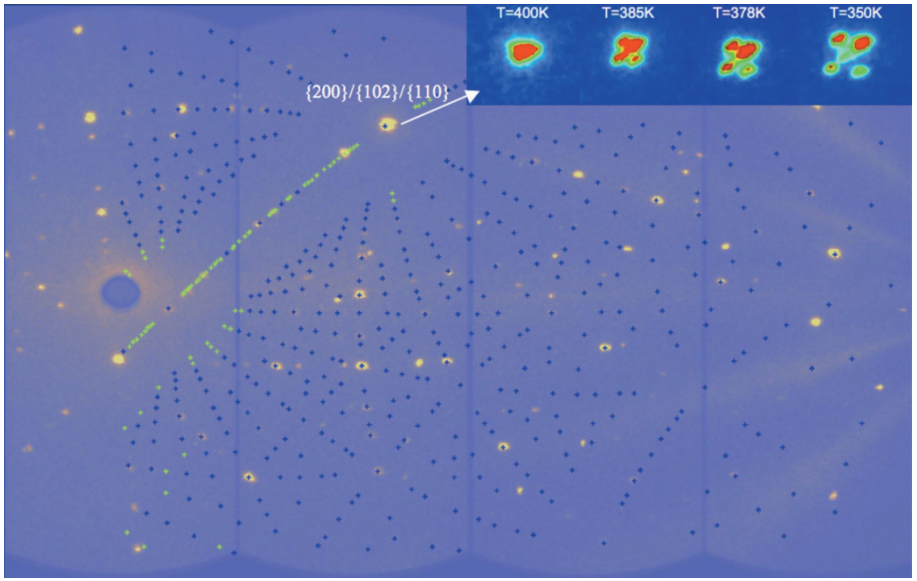


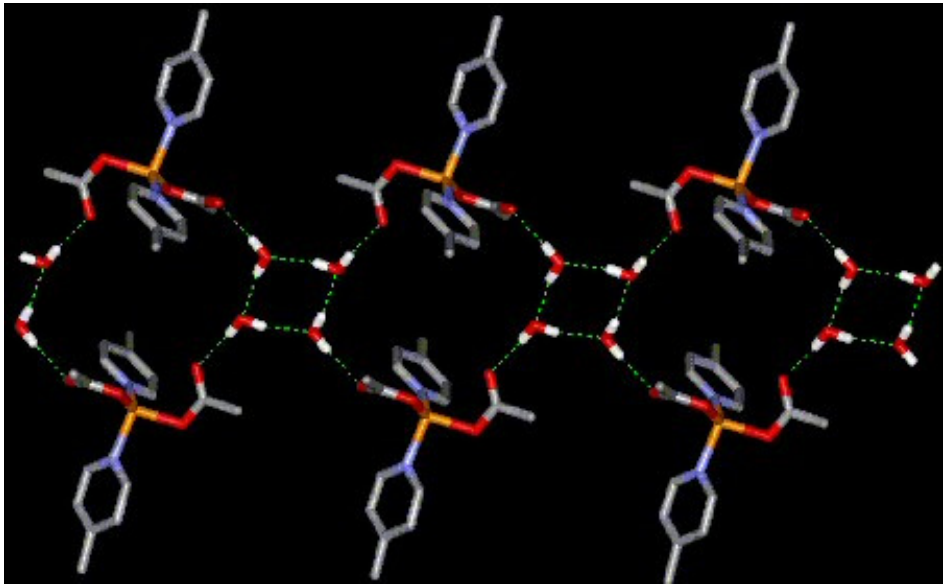
SINGLE CRYSTAL DIFFRACTION : STEADY STATE

Laue diffraction uses a ‘white’ incident beam with a range of wavelengths.

For each *d*-spacing, the wavelength to satisfy Bragg’s law is selected from the incident beam.

However, all orders (*nh*,*nk*,*nl*) of a given reflection (*h*,*k*,*l*) are superimposed.





SINGLE CRYSTAL DIFFRACTION : PULSED

SXD diffractometer at ISIS pulsed source.

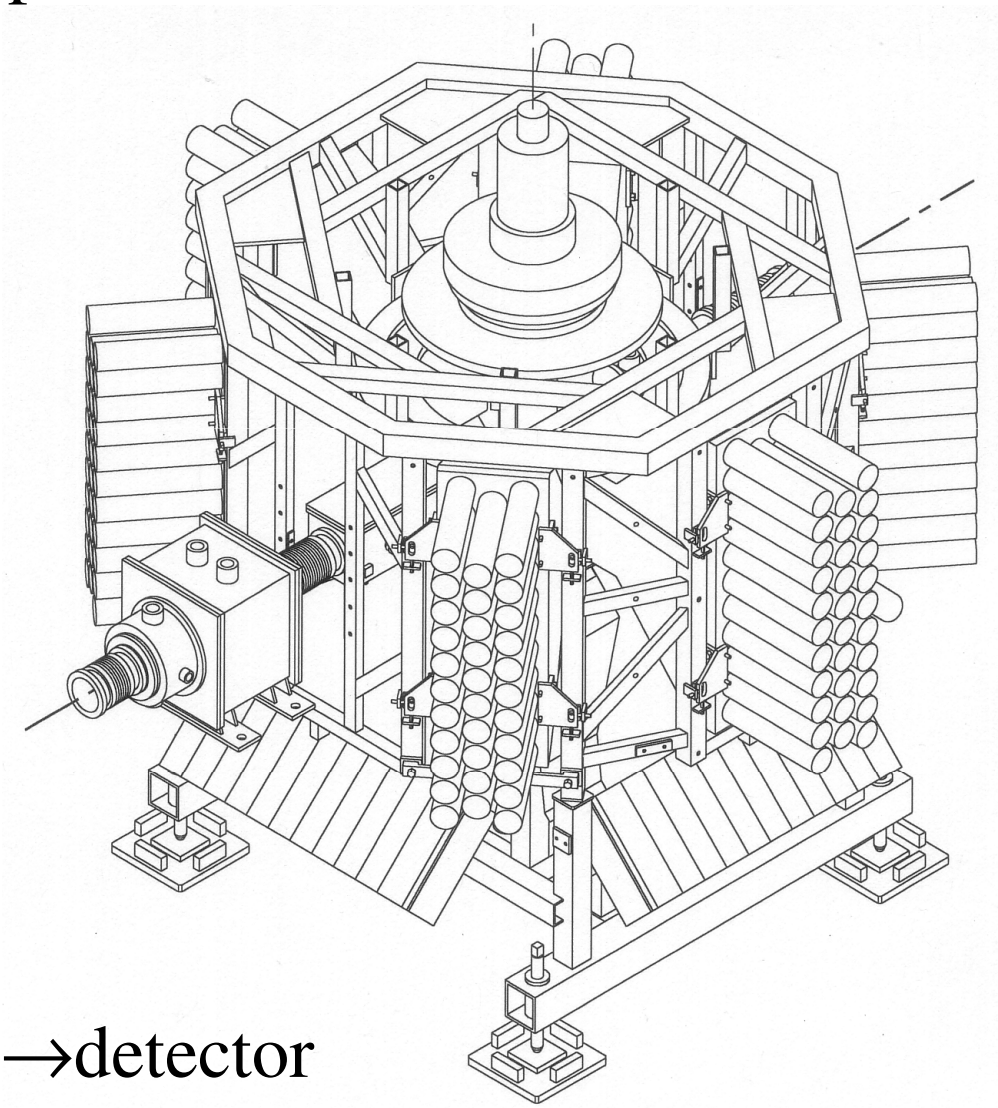
'Time-sorted Laue'.

Neutron time-of-flight technique used to separate different orders of reflections.

$$\lambda(\text{Å}) = 0.003956 \frac{t(\mu\text{sec})}{\text{L(m)}}$$

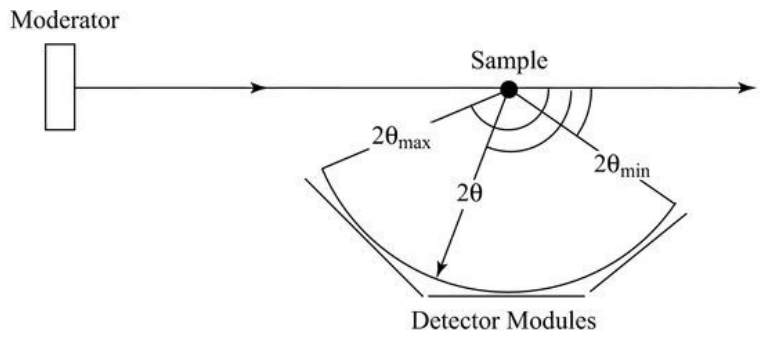
t=time taken for neutron to travel distance L

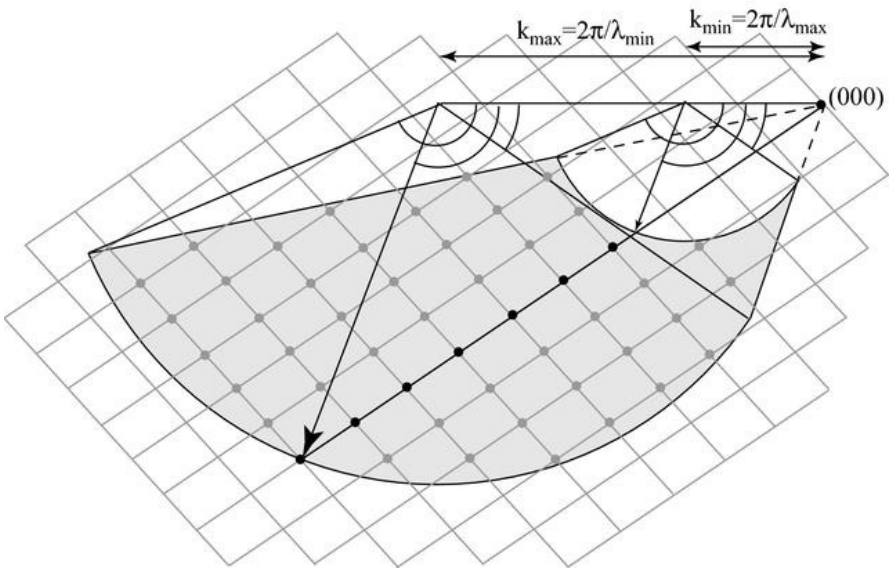
L=distance source→sample→detector

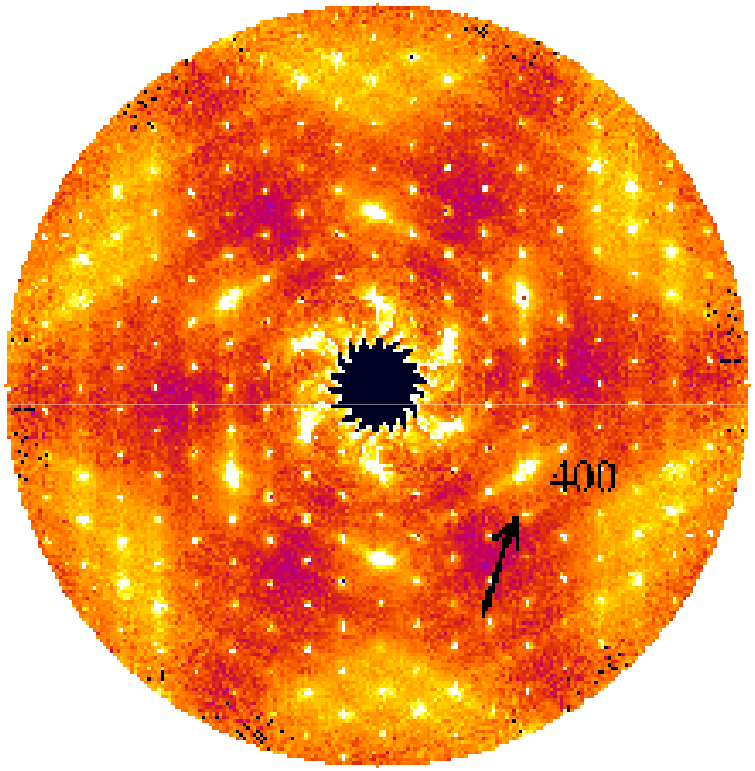


SINGLE CRYSTAL DIFFRACTION : PULSED

SXD scans a large volume of reciprocal space, $\underline{Q}$, at one orientation of the single crystal.



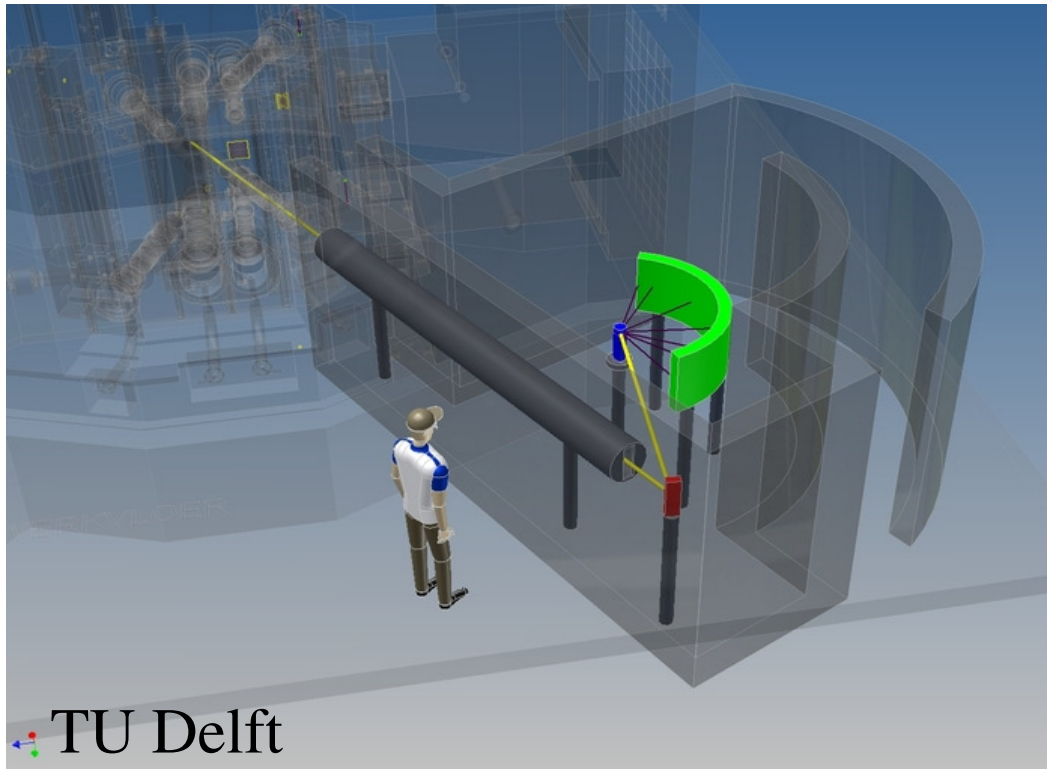


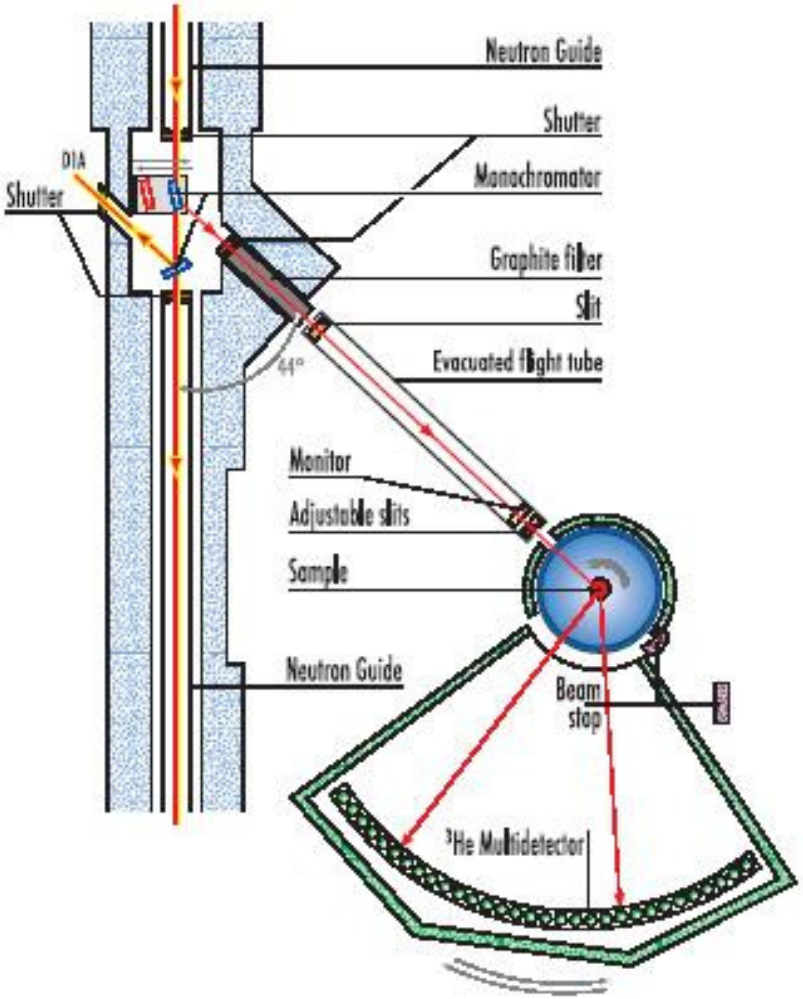


$\Rightarrow$ Good if $\underline{Q}$ space is full of interesting features, such as diffuse scattering!

POWDER DIFFRACTION : STEADY STATE SOURCE

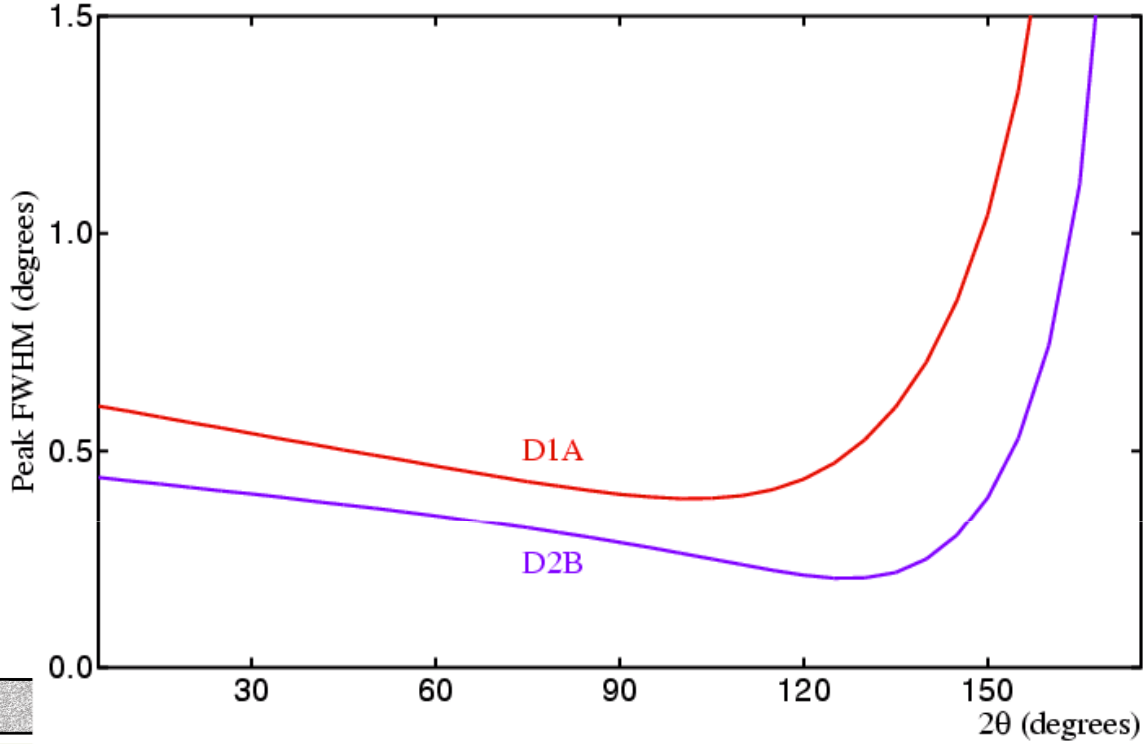
In the simplest terms, a powder diffractometer at a steady state source consists of an incident neutron guide, a monochromator, sample position and detector(s).

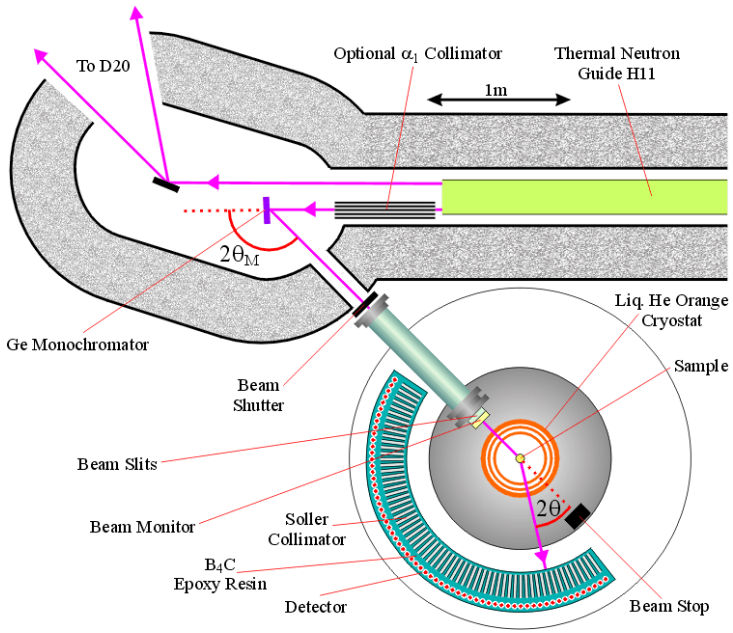




POWDER DIFFRACTION : STEADY STATE SOURCE

Resolution considerations.

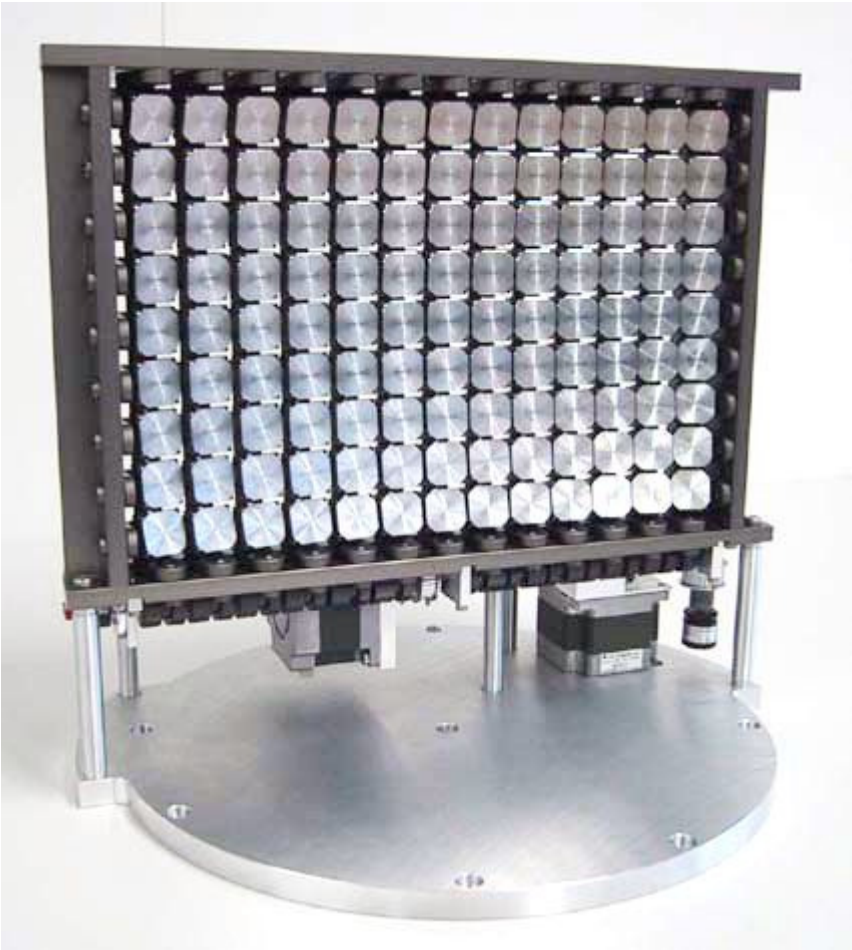




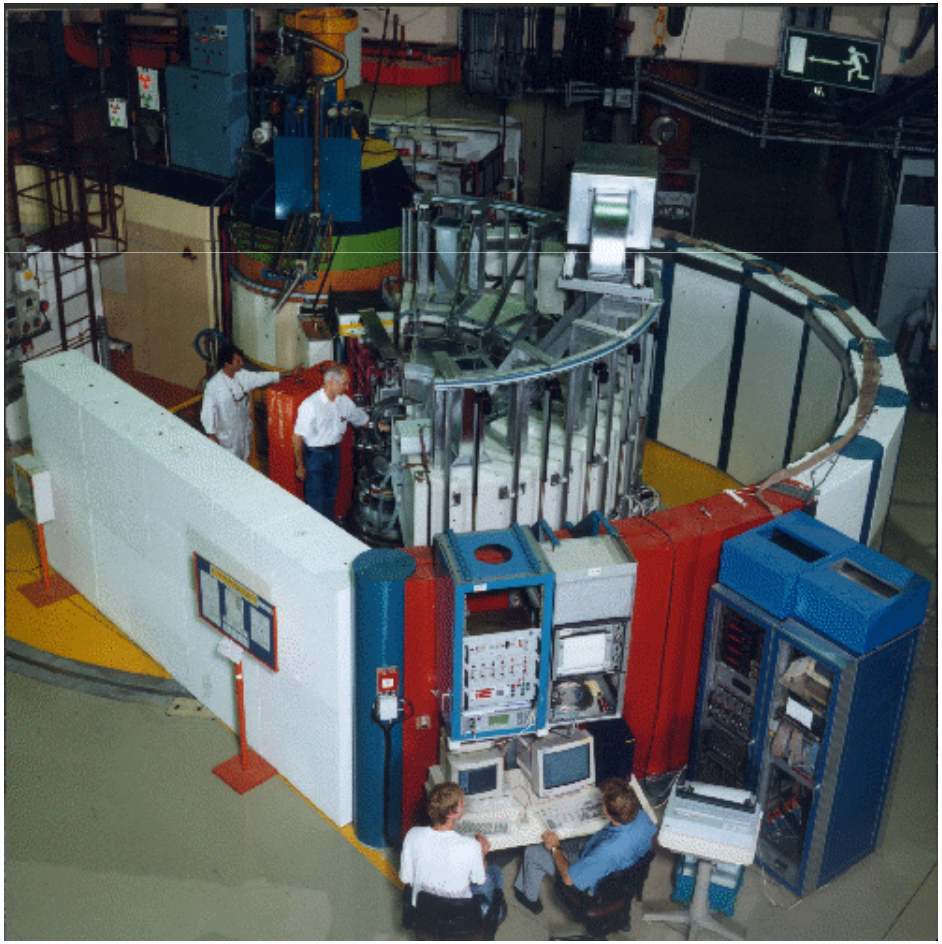
'Z' configuration of scattering from monochromator and sample gives better resolution.

Variation of peak width with 2θ.

POWDER DIFFRACTION : STEADY STATE SOURCE



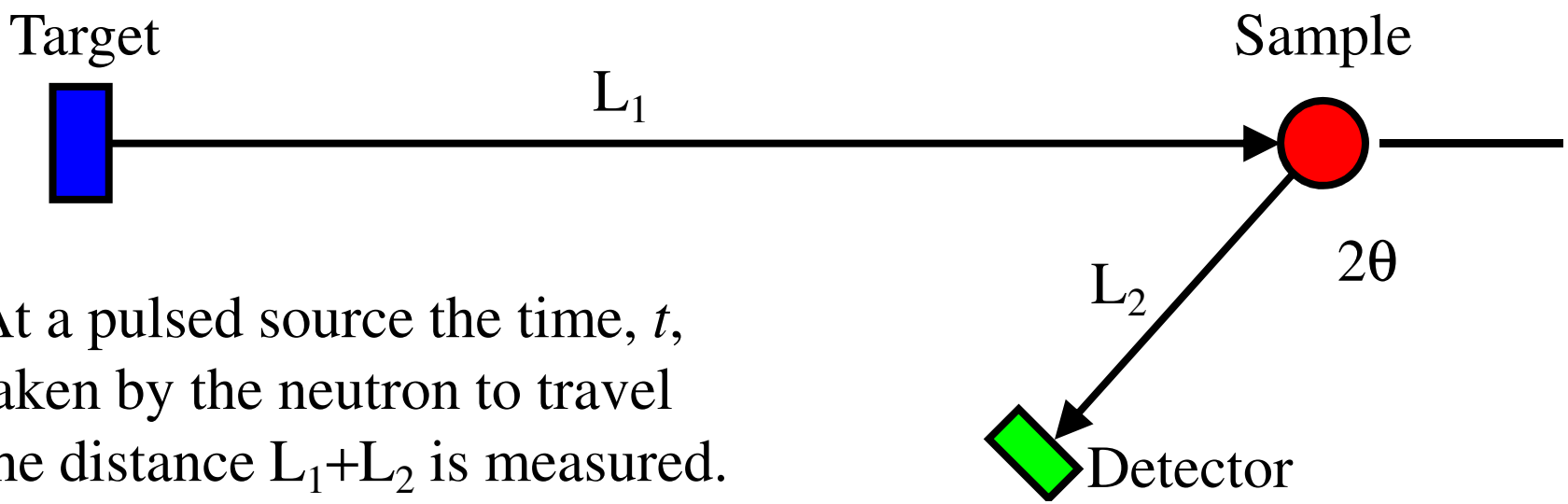
Intensity (countrate) considerations.



Focussing monochromator

Large area detectors

POWDER DIFFRACTION : PULSED SOURCE



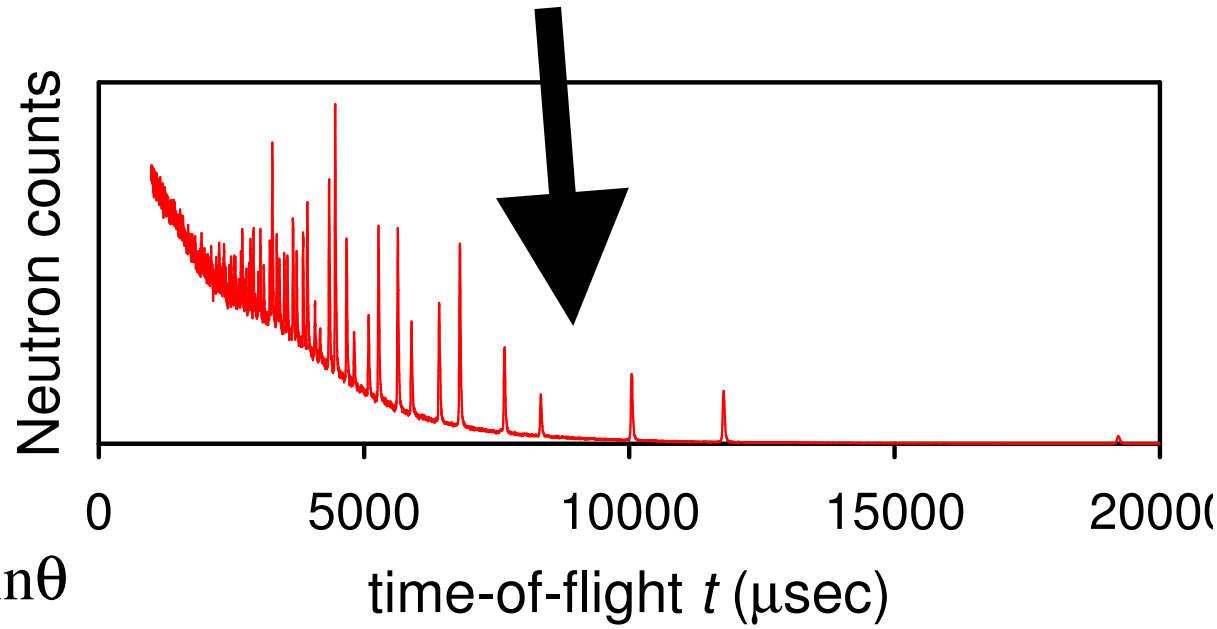
At a pulsed source the time, *t*, taken by the neutron to travel the distance L_1+L_2 is measured.

$\lambda=2d\sin\theta$

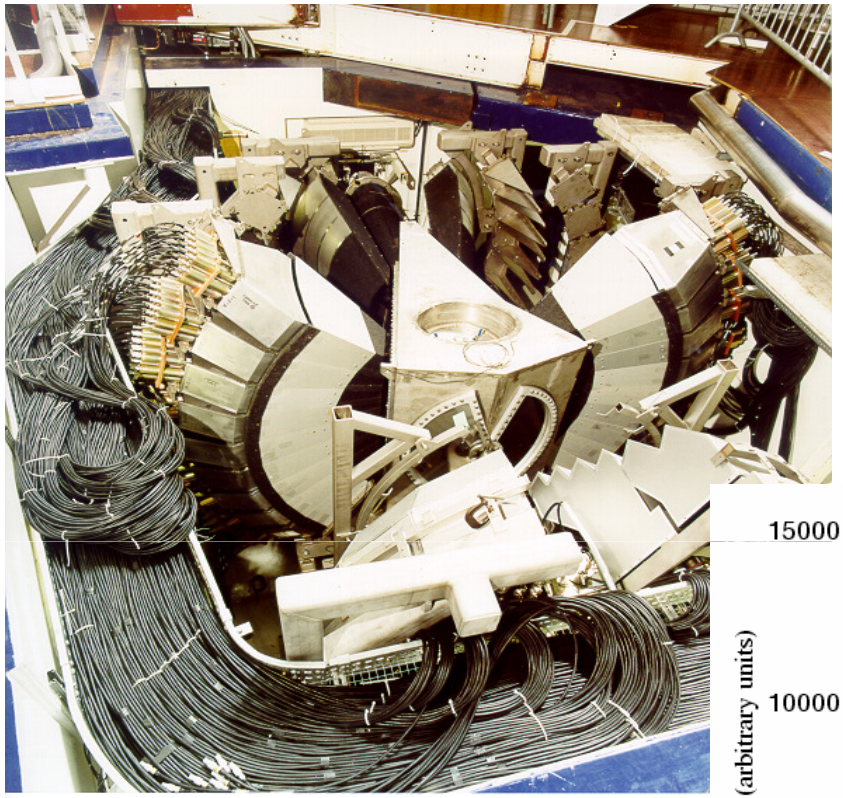
$\lambda=h/mv$

$v=(L_1+L_2)/t$

$d=0.001977t/(L_1+L_2)\sin\theta$



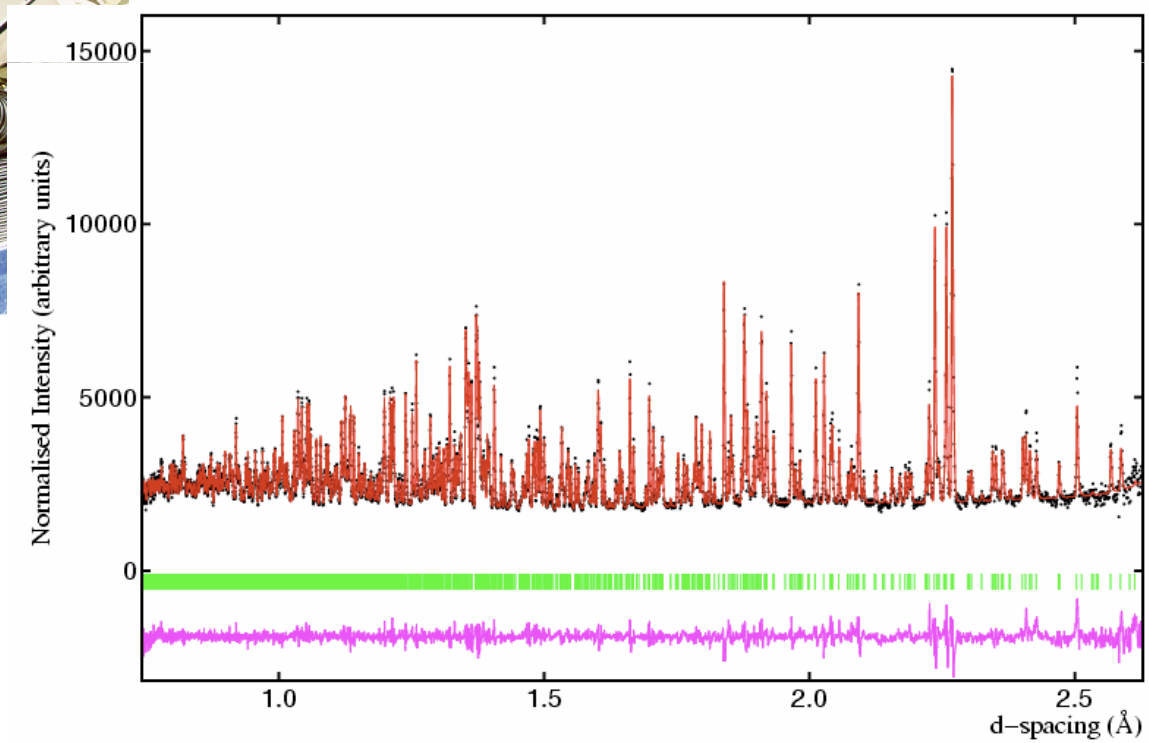
POWDER DIFFRACTION : PULSED SOURCE



Countrate versus Resolution

← High countrate

Small samples (<1mm^3)
Fast measurements (<1sec.)



High resolution →

Complex structures
Accurate lattice params

POWDER DIFFRACTION : PULSED SOURCE

$\lambda = 2d\sin\theta$ $\qquad$ $d = 0.001977t / (L_1 + L_2)\sin\theta$

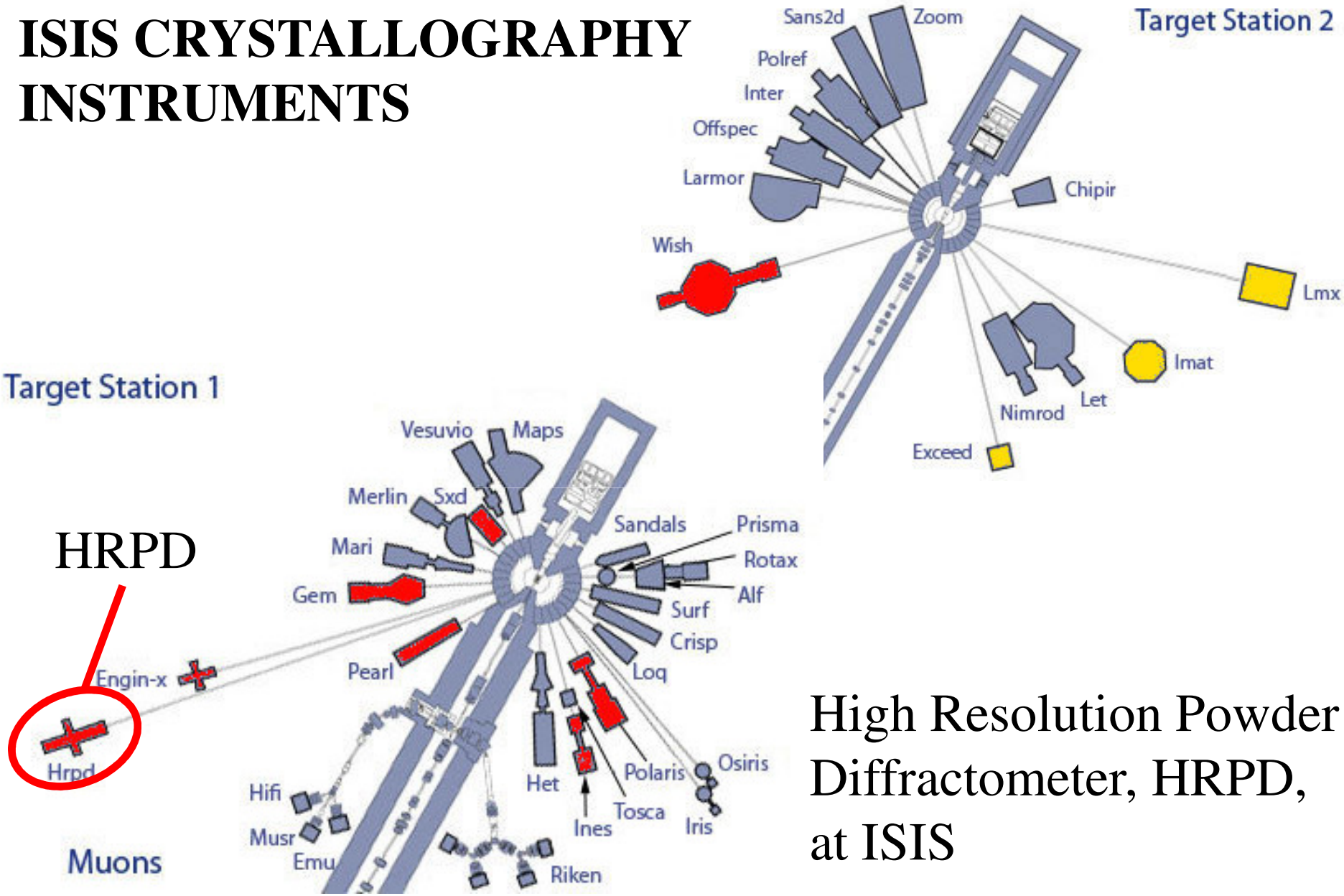
$\Rightarrow$ resolution, $\Delta d/d$, can be written as

$$\frac{\Delta d}{d} = \sqrt{(\cot\theta\Delta\theta)^2 + \left(\frac{\Delta t}{t}\right)^2 + \left(\frac{\Delta L}{L}\right)^2}$$

So, we can minimize $\Delta d/d$ by

- $\cot\theta \rightarrow 0$ as $2\theta \rightarrow 180^{\circ}$ $\Rightarrow$ backscattering
- keep $\Delta\theta$ as small as possible $\Rightarrow$ low beam divergence, small detector elements, small samples, *etc*.
- small Δt $\Rightarrow$ small moderator.
- large t and L ($=L_1+L_2$) $\Rightarrow$ long flightpaths.

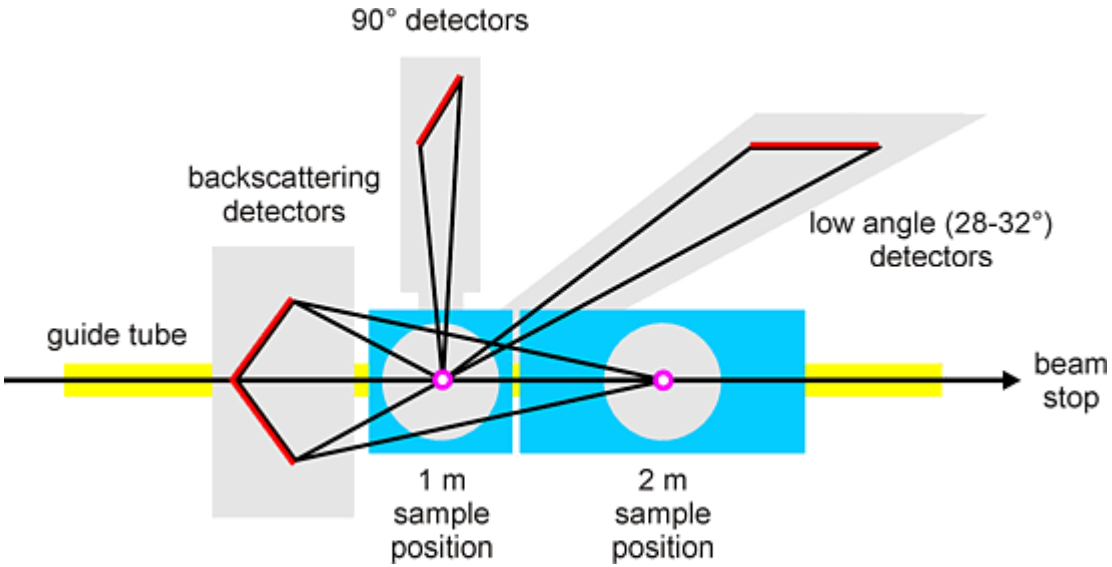
ISIS CRYSTALLOGRAPHY INSTRUMENTS



High Resolution Powder Diffractometer, HRPD, at ISIS

$L_1 \approx 100$m

POWDER DIFFRACTION : PULSED SOURCE



HRPD : $L_1 \approx 100\text{m} \rightarrow \Delta d/d \sim 4\times10^{-4}$

POLARIS : $L_1 \approx 12\text{m} \rightarrow \Delta d/d \sim 5\times10^{-3}$

HRPD sits at the end of a 100m neutron guide.

$\Rightarrow$ Frame overlap (collect data at 10Hz, rather than 50Hz).

$\Rightarrow$ Guide has high transmission, but adds divergence ($\Delta\theta$).

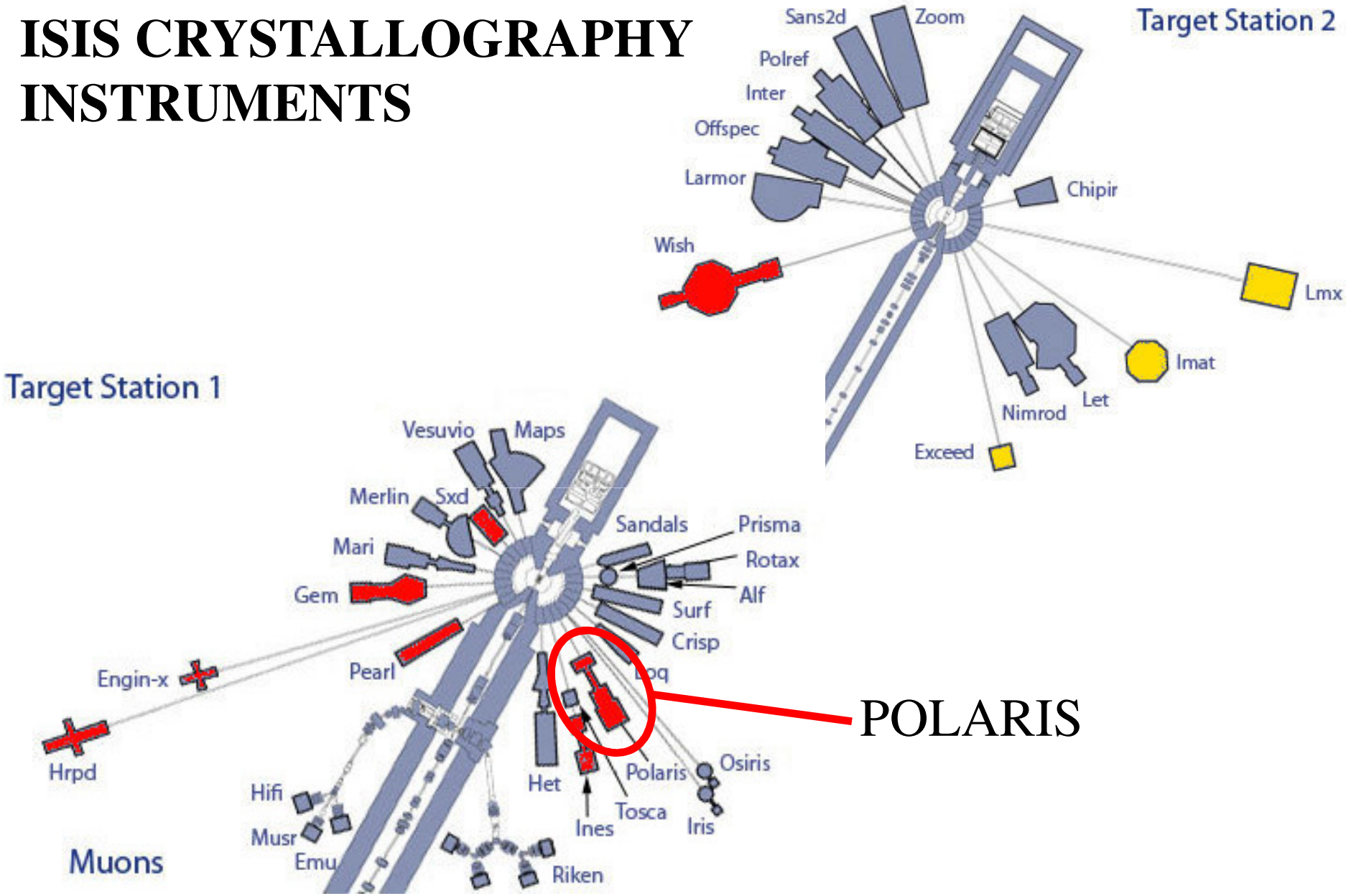
POWDER DIFFRACTION : PULSED SOURCE

For high countrate there are a number of options.....

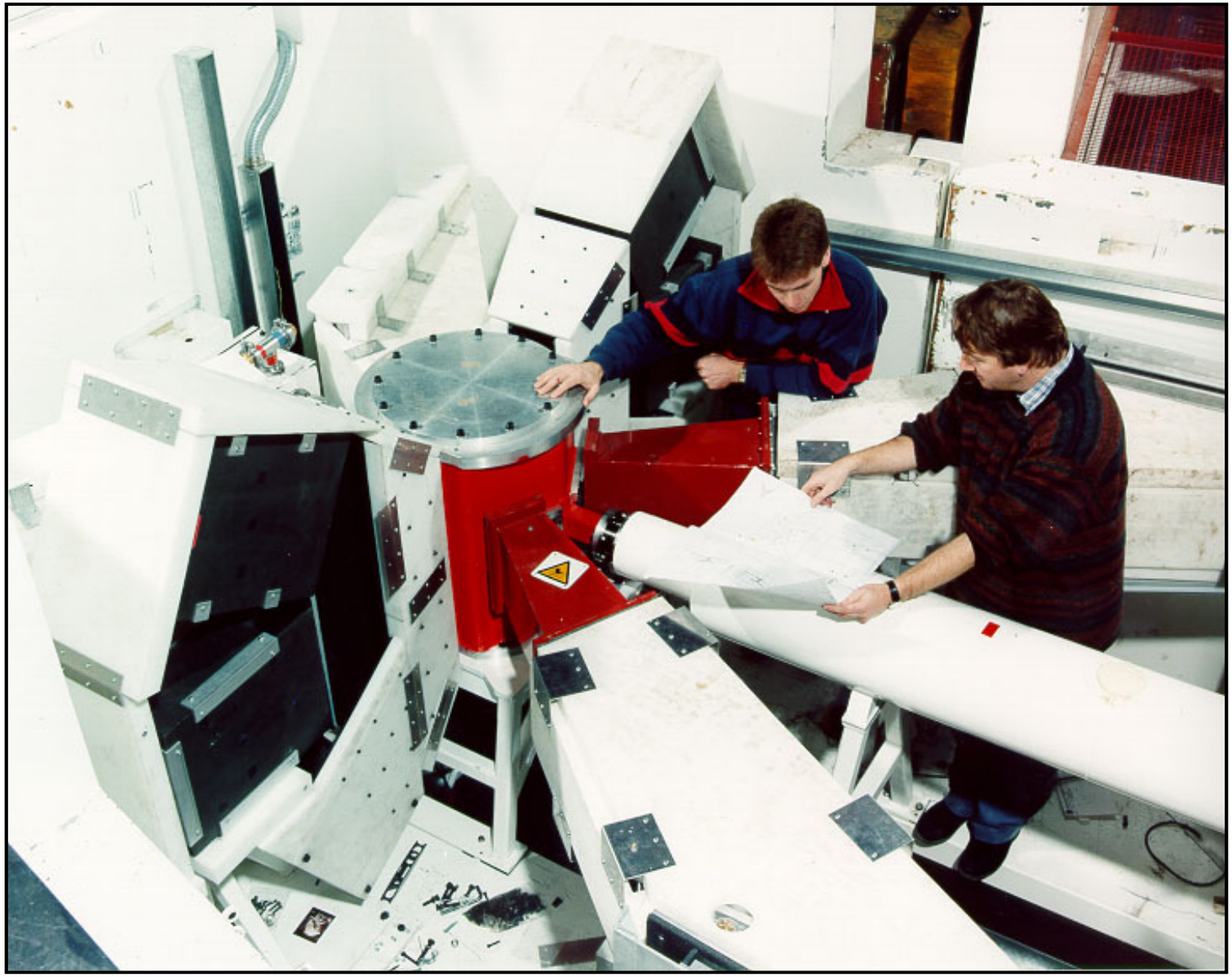
- use a large sample!
  - but increases $\Delta\theta$ and degrades resolution $\Delta d/d$.
- large area of detector coverage - but high cost!
- short L_1.
  - but increases $\Delta\theta$, decreases $t \Rightarrow$ worse resolution $\Delta d/d$.
- neutron guide.
  - but increases $\Delta\theta$ and degrades resolution $\Delta d/d$.
- large moderator.
  - but increases Δt and degrades resolution $\Delta d/d$.

Explore further using recent Polaris upgrade at ISIS.....

ISIS CRYSTALLOGRAPHY INSTRUMENTS



POLARIS : OLD LAYOUT



POLARIS UPGRADE

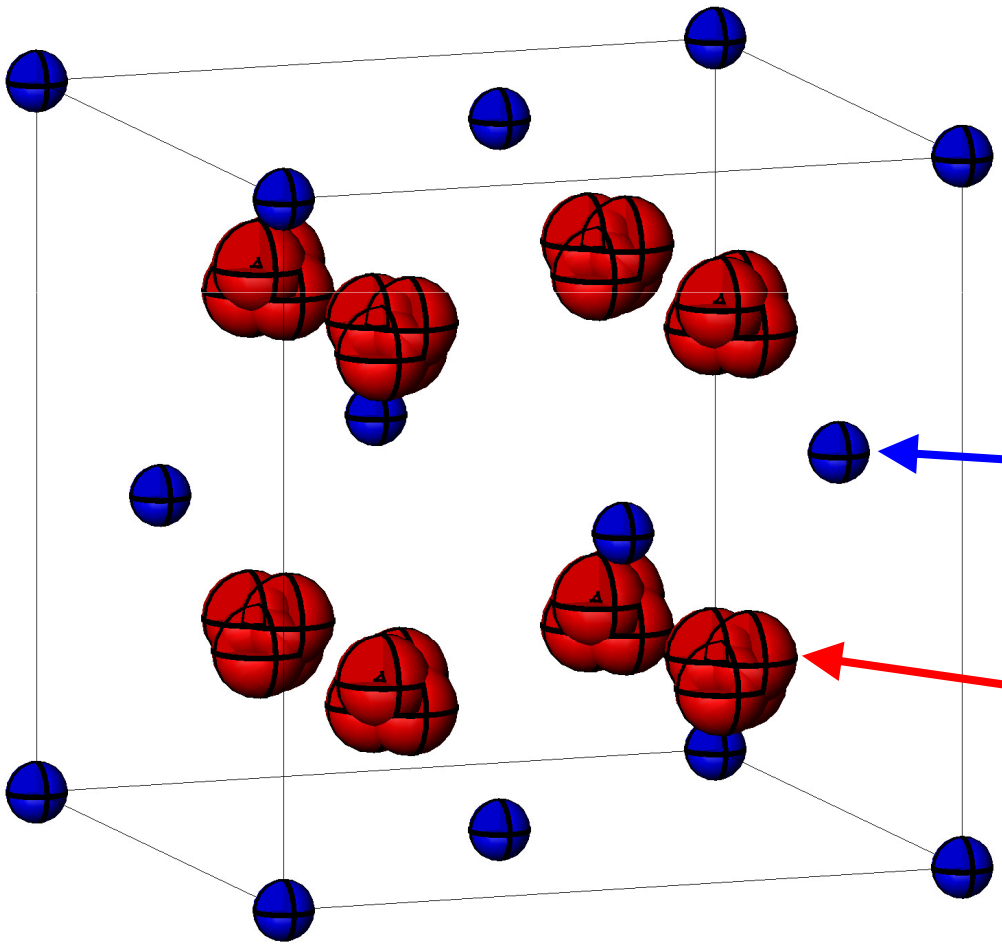
- 2006. Outline design of new instrument. Funding (~3M€).
- 2007. Additional funding from Sweden and Spain.
- 2007-2010. Detailed design and procurement.
- August 2010. Old instrument dismantled.
- 2011. New instrument installed.
- December 2011. First neutrons on new instrument.
- May 2012. Resumed user operation.

New instrument optimised for high countrate at modest resolution.

Extended Q range for 'total scattering' studies.

$Y_{0.75}Nb_{0.25}O_{1.75}$: FLUORITE STRUCTURE

Analysis of the Bragg peaks gives the distribution of ions within the unit cell - averaged over time and all unit cells.



$Y_{0.75}Nb_{0.25}O_{1.75}$

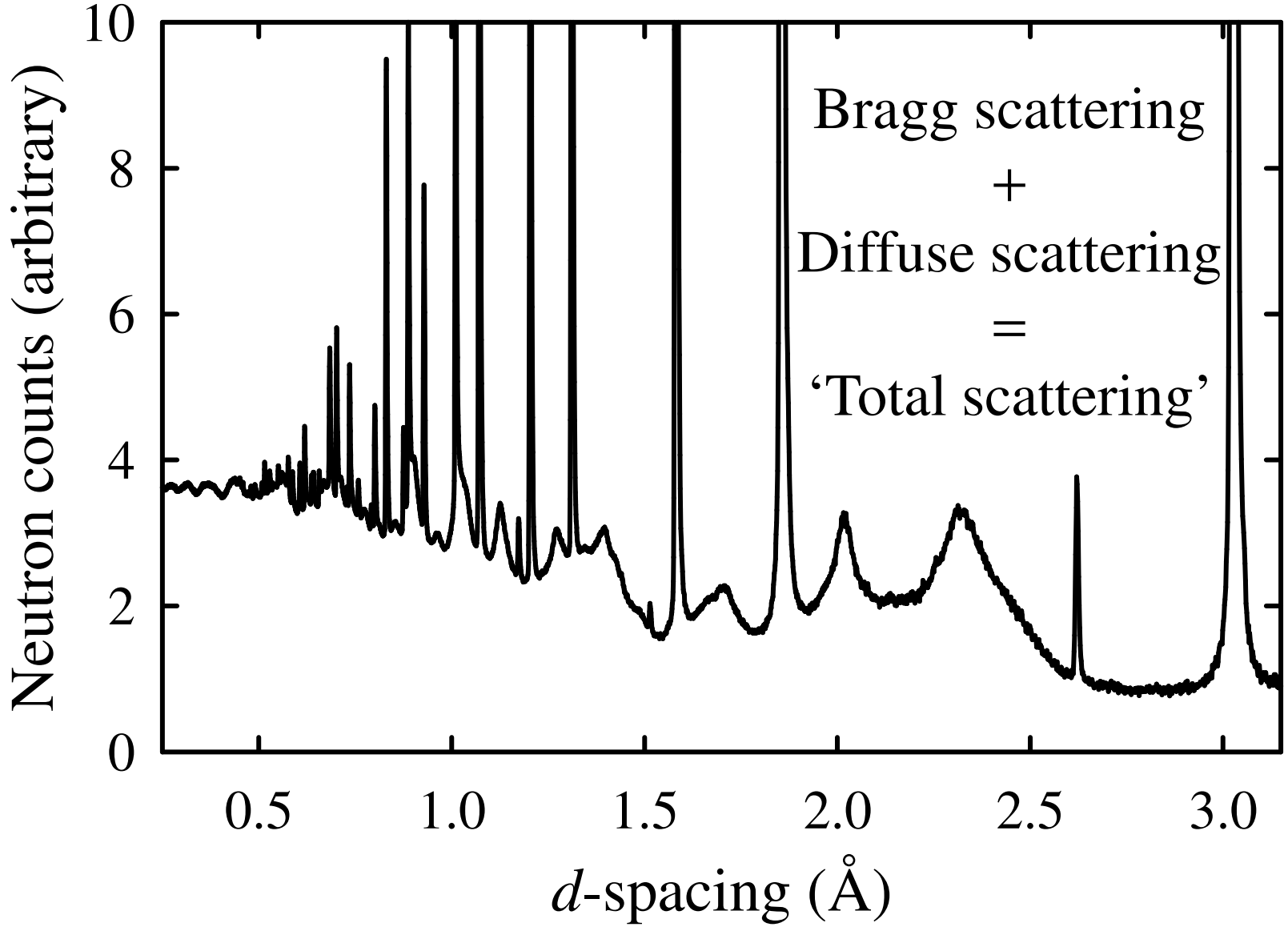
Fluorite structure

$Fm\bar{3}m$, a=5.24936(4)Å

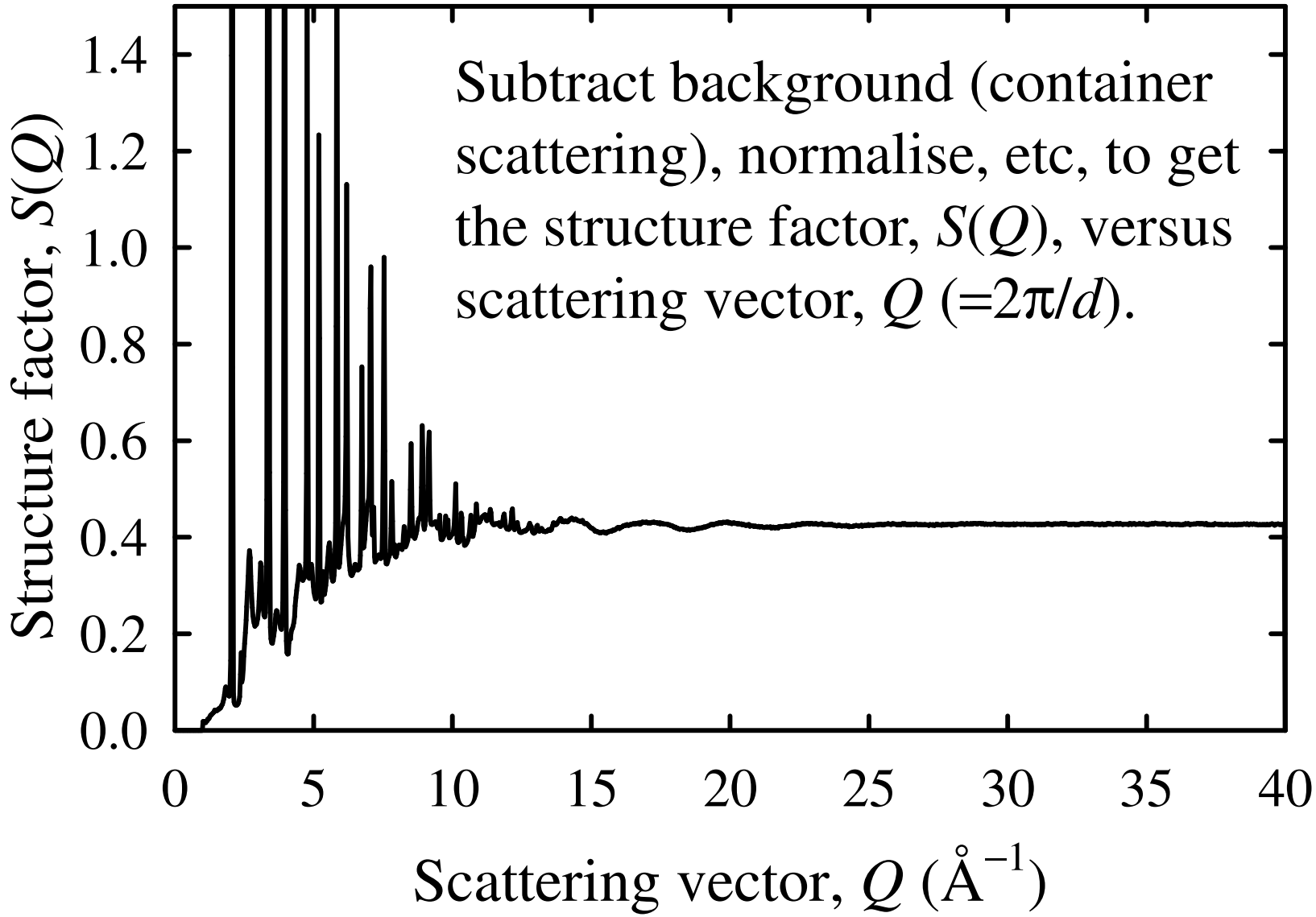
Y^{3+}/Nb^{5+} (on same crystallographic site).

O^{2-} ($occ.=^{7}/_{8}$) shifted ~0.2Å from $^{1}/_{4},^{1}/_{4},^{1}/_{4}$.

$Y_{0.75}Nb_{0.25}O_{1.75}$: NEUTRON POWDER DIFFRACTION



$Y_{0.75}Nb_{0.25}O_{1.75}$: TOTAL SCATTERING



TOTAL SCATTERING

Analysis of the Bragg peaks (Rietveld refinement) ignores the diffuse scattering arising from short-range correlations between ions.

The total scattering structure factor, $S(Q)$, is related to the total radial distribution function, $G(r)$ by the Fourier transform

$$G(r) = \frac{1}{(2\pi)^3 \rho_0} \int_0^\infty 4\pi Q^2 S(Q) \frac{\sin Qr}{Qr} \mathrm{d}Q$$

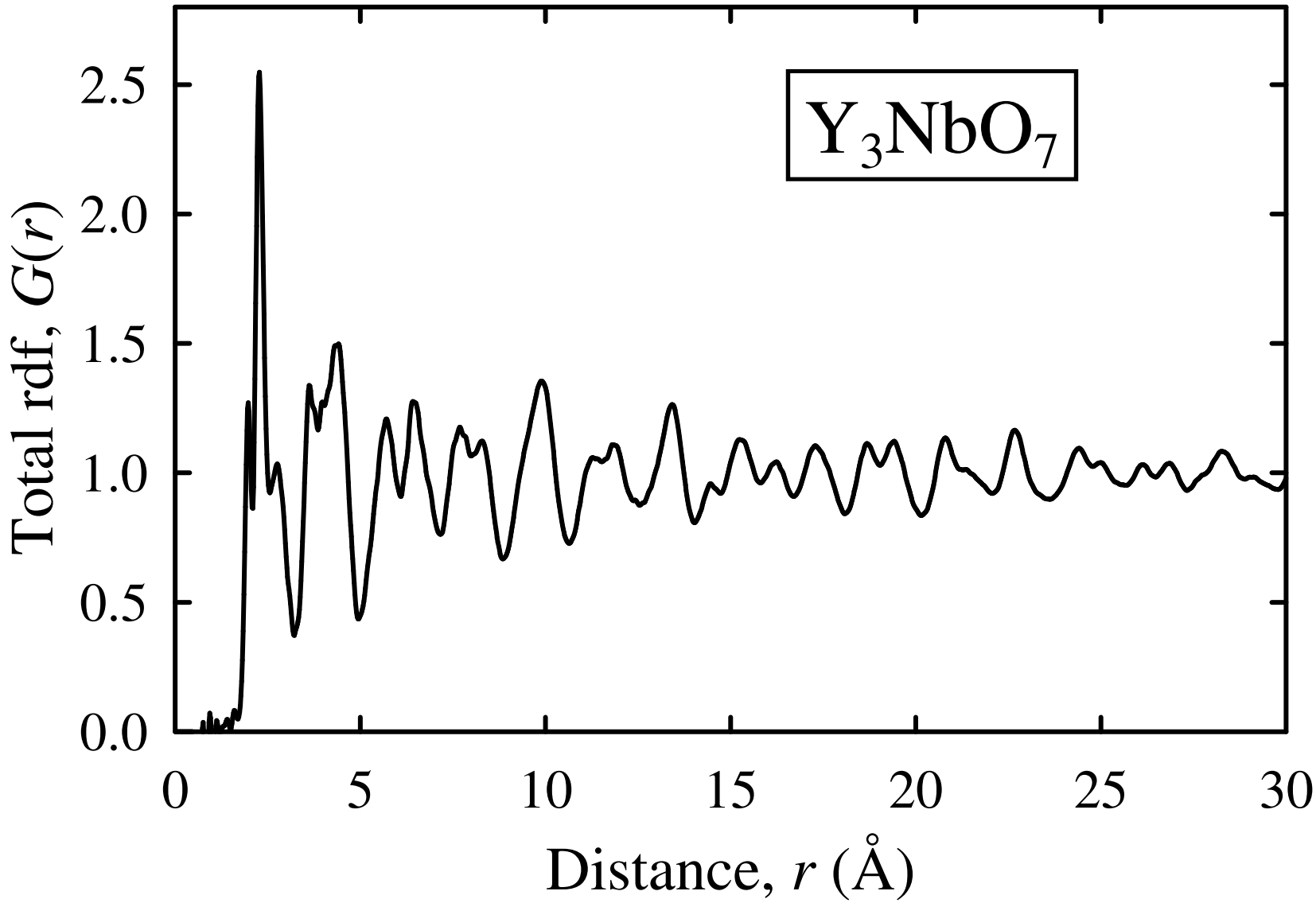
where ρ_0 is the average atom number density.

$G(r)$ is also defined in terms of the partial radial distribution functions, $g_{ij}(r)$:

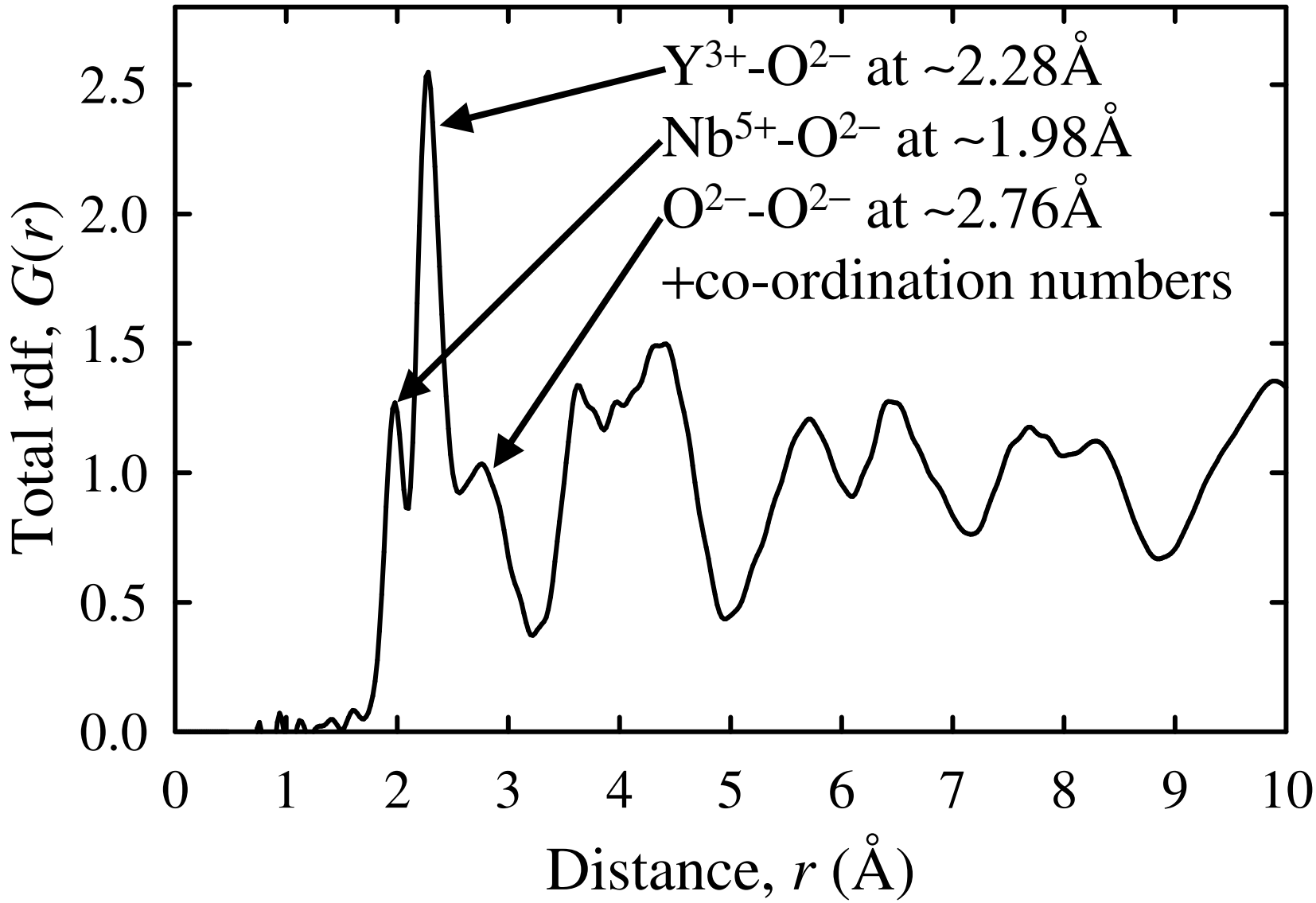
$$G(r) = \sum_{i,j=1}^{n} c_i c_j b_i b_j [g_{ij}(r) - 1]$$

c_i and b_i are concentration and scattering length of ion type i.

$Y_{0.75}Nb_{0.25}O_{1.75}$: TOTAL RDF



$Y_{0.75}Nb_{0.25}O_{1.75}$: TOTAL RDF



POLARIS : SPECIFICATION

Requirements :

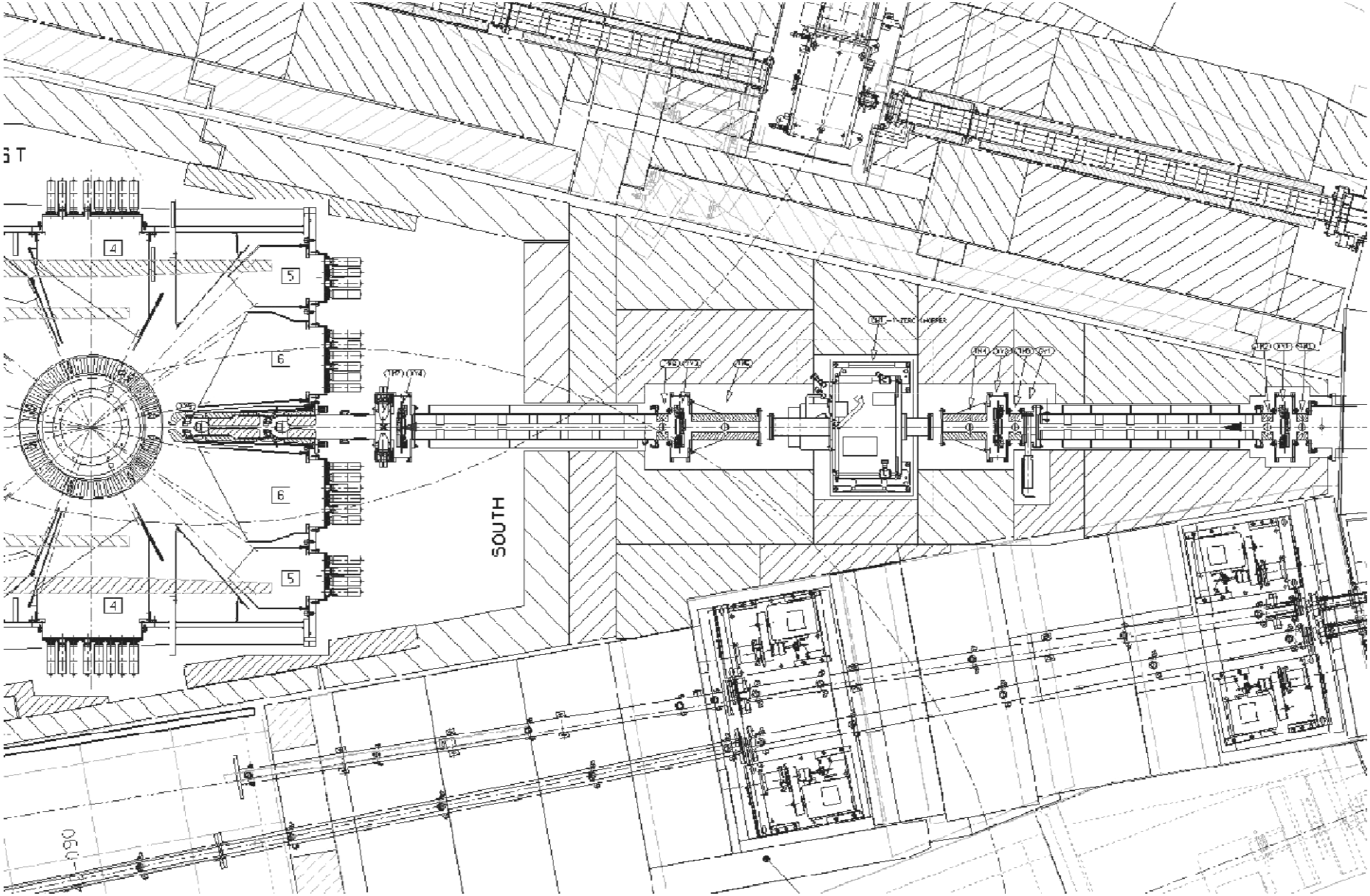
- High countrate.
- Modest resolution ($\Delta d/d \sim 3\times10^{-3}$).
- Wide Q range.
- Low background, *etc*.

Constraints :

- Existing beamline $\Rightarrow$ moderator fixed (ambient H_2O).
- Cost!

Will discuss major beamline components.....

INCIDENT BEAMLINE



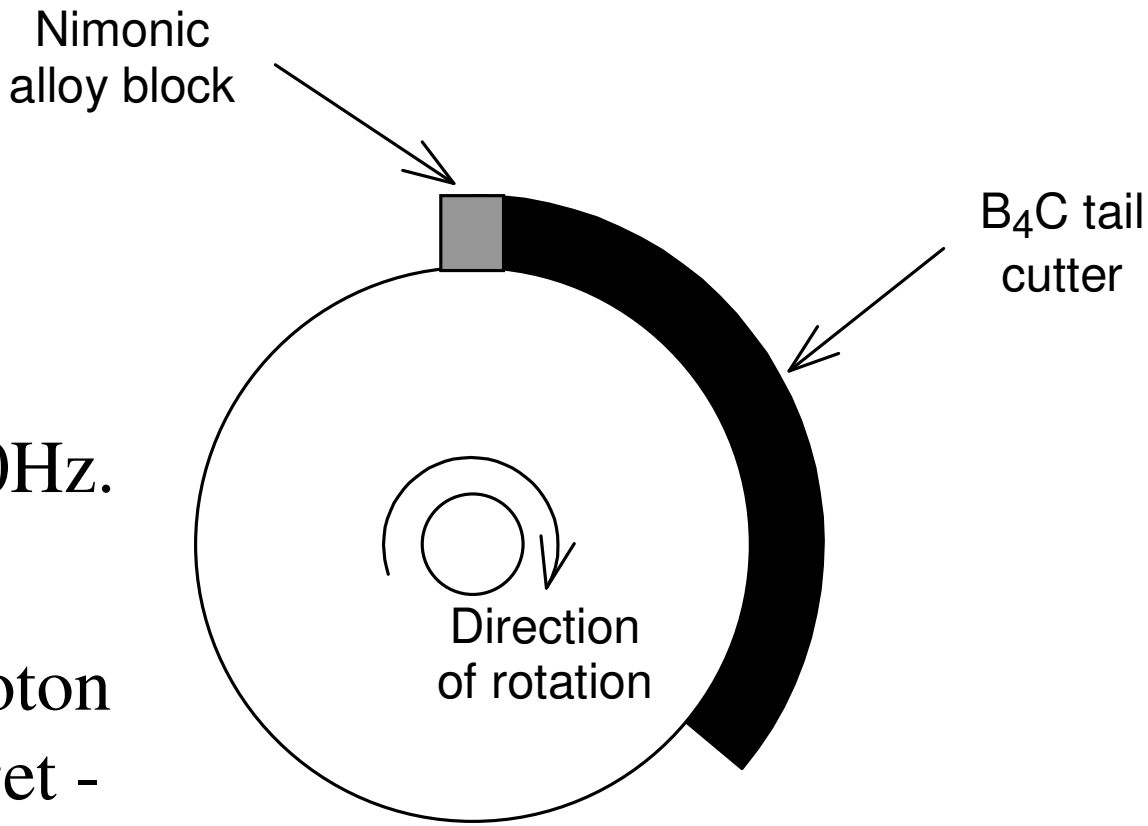
POLARIS : NIMONIC CHOPPER

Polaris *t*-zero (Nimonic) chopper.

L~8m

Rotation frequency 50Hz.

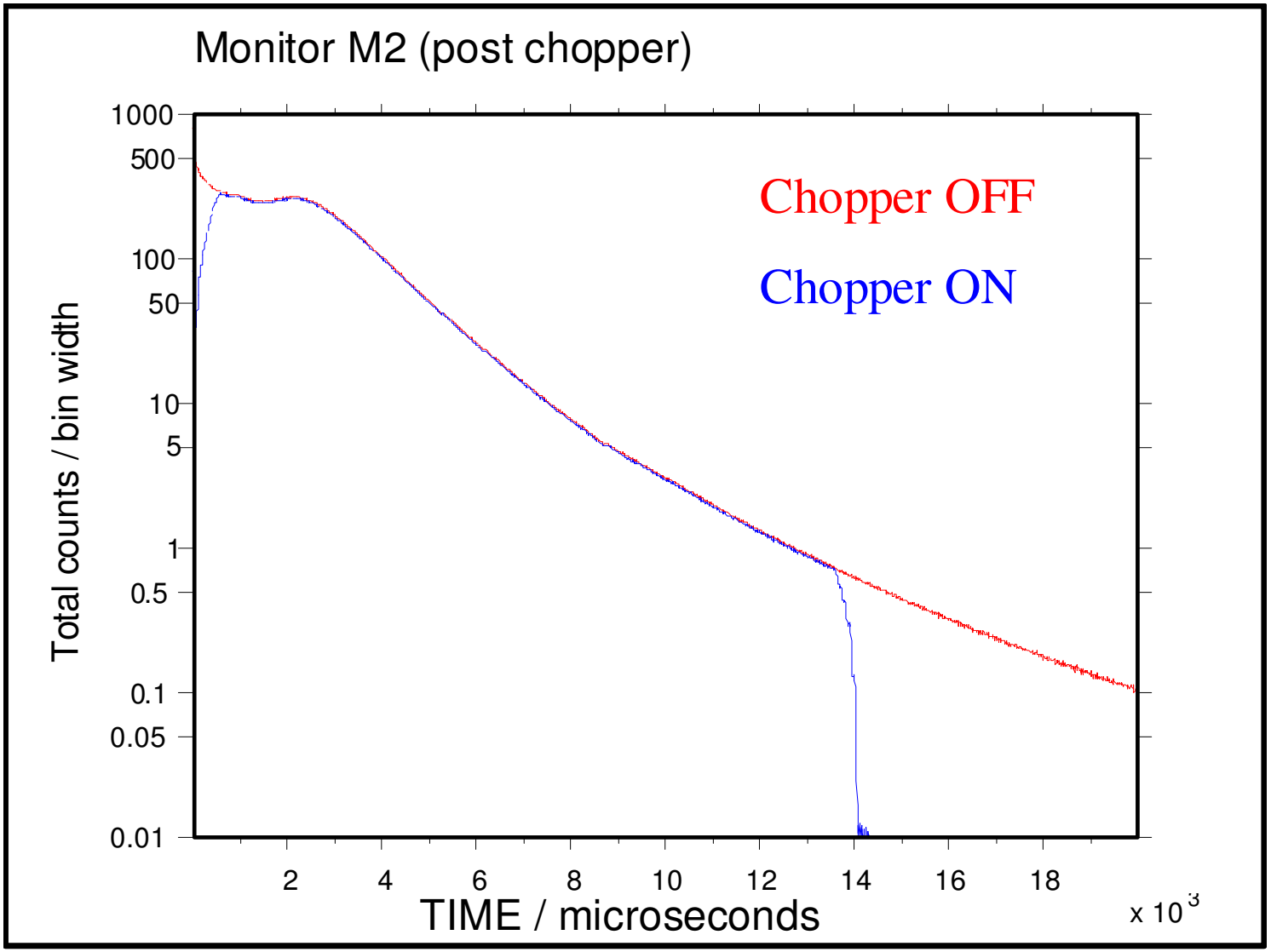
Nimonic alloy block closes beamline as proton beam strikes ISIS target - stops fast neutrons and reduces backgrounds.



Tail cutter closes beamline towards end of 20ms frame - stops slow neutrons from reaching sample (and detectors)

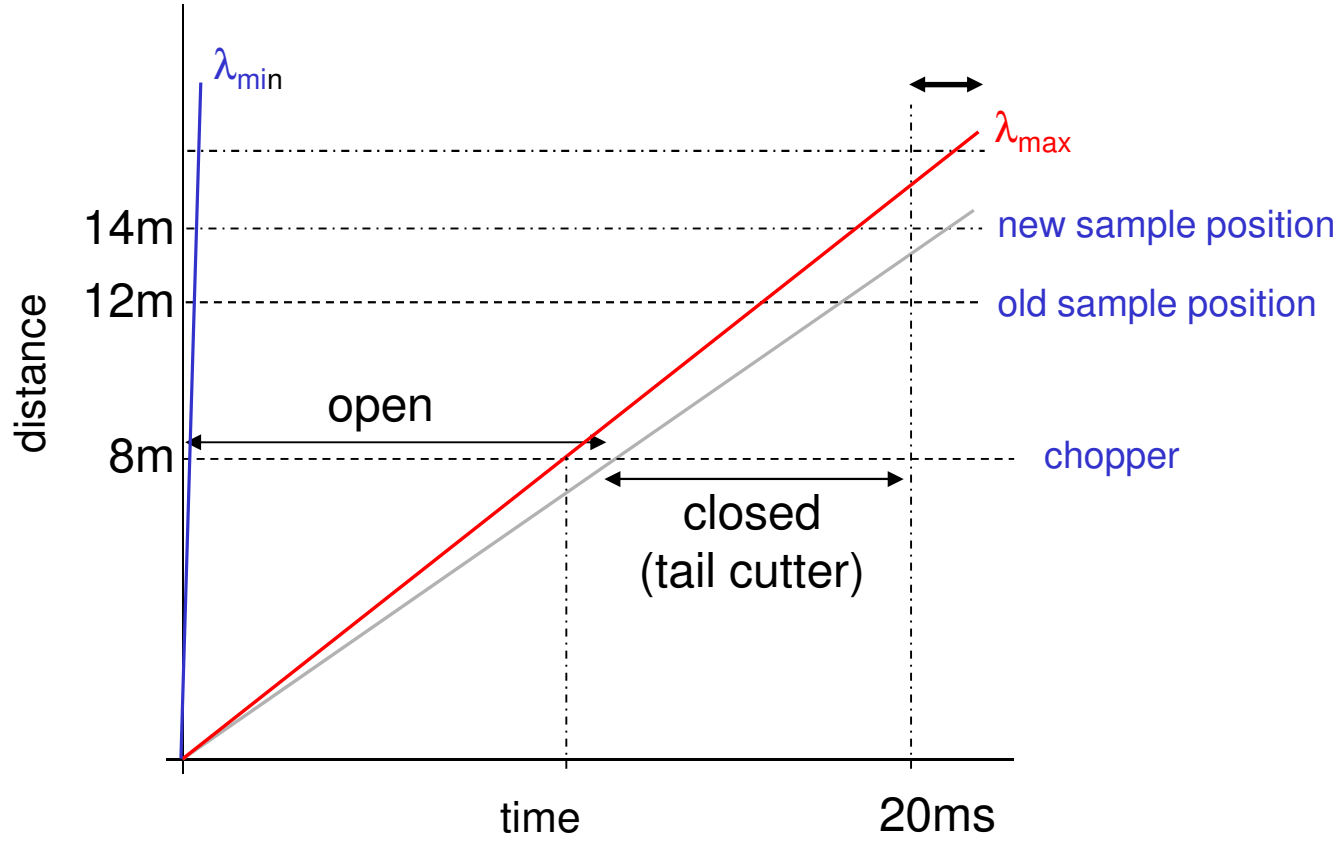
POLARIS : NIMONIC CHOPPER

Effect of tail cutter on incident neutron spectrum.....



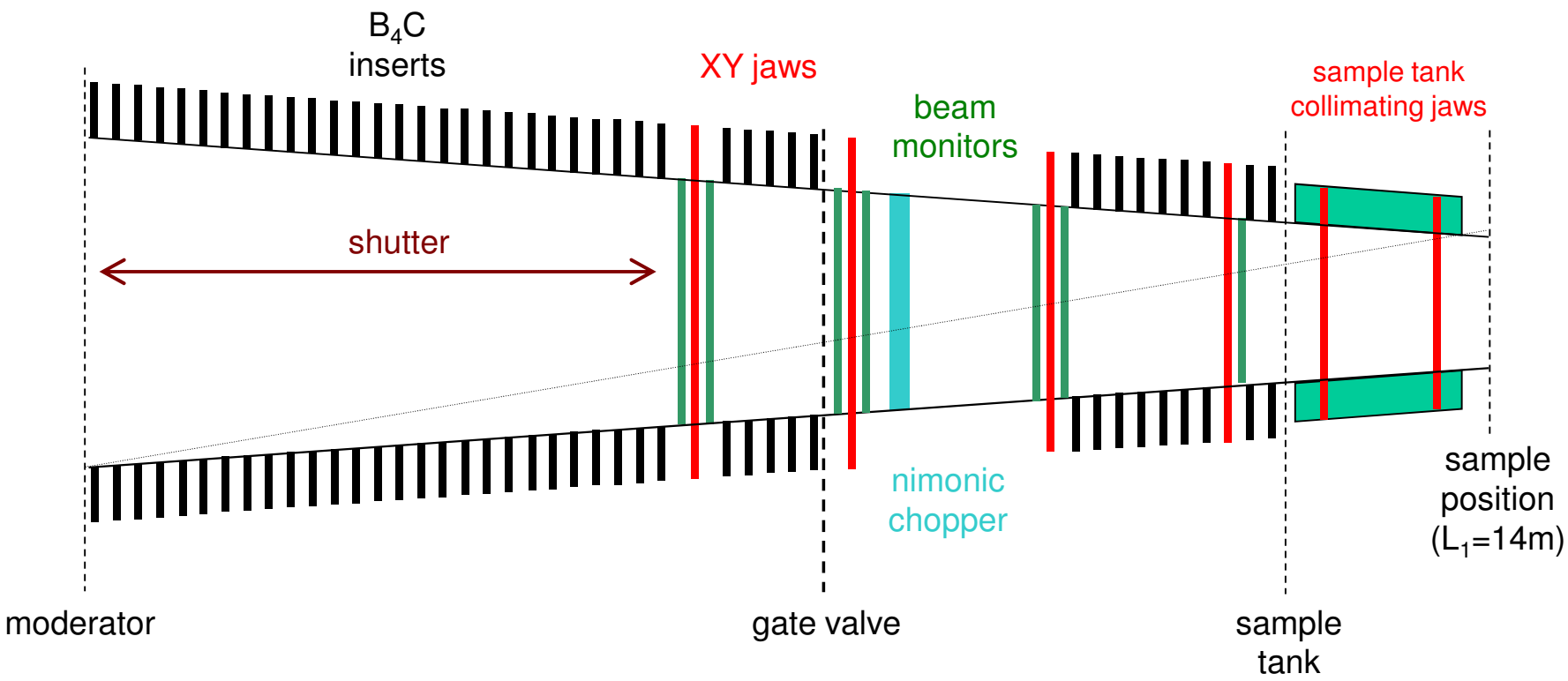
POLARIS : NIMONIC CHOPPER

L - *t* diagram



Frame overlap!

POLARIS : INCIDENT BEAMLINE

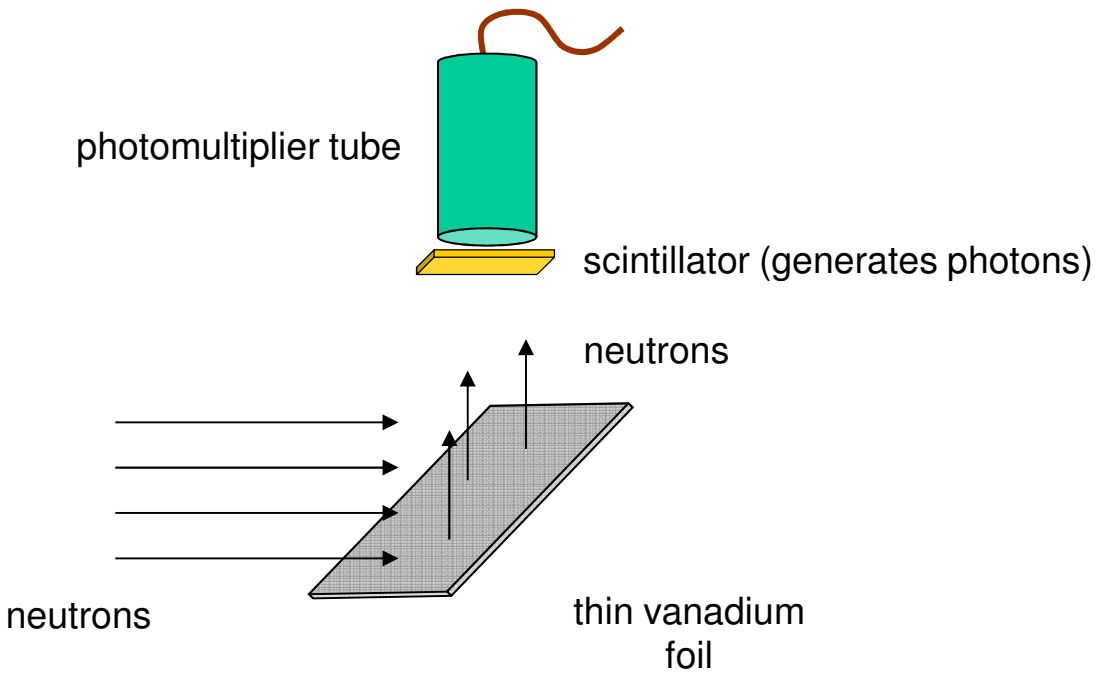


Moderator size ~ 10cm × 10cm

Beam size at sample ~4cm high × ~1.5cm wide

POLARIS : BEAMLINE MONITORS

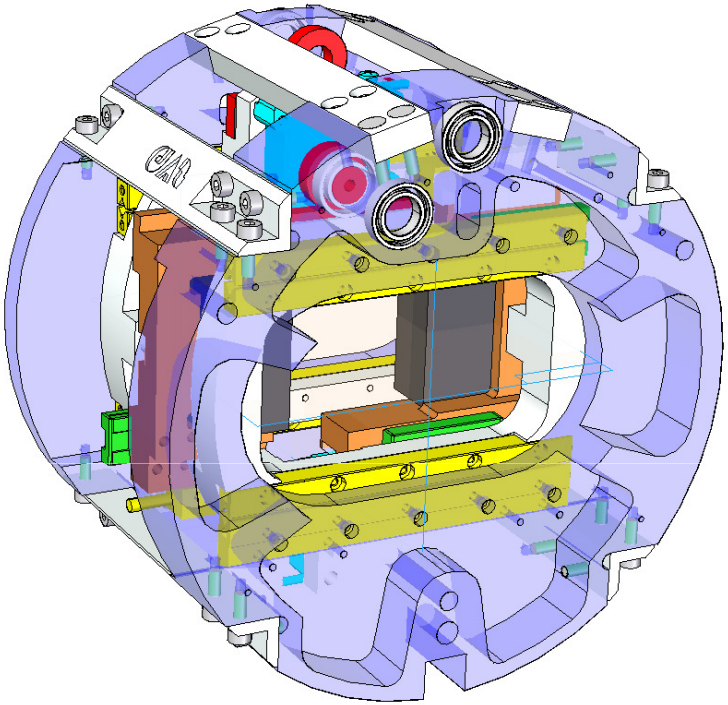
Vanadium foil in incident beam scatters neutrons, which are detected by a scintillator detector.

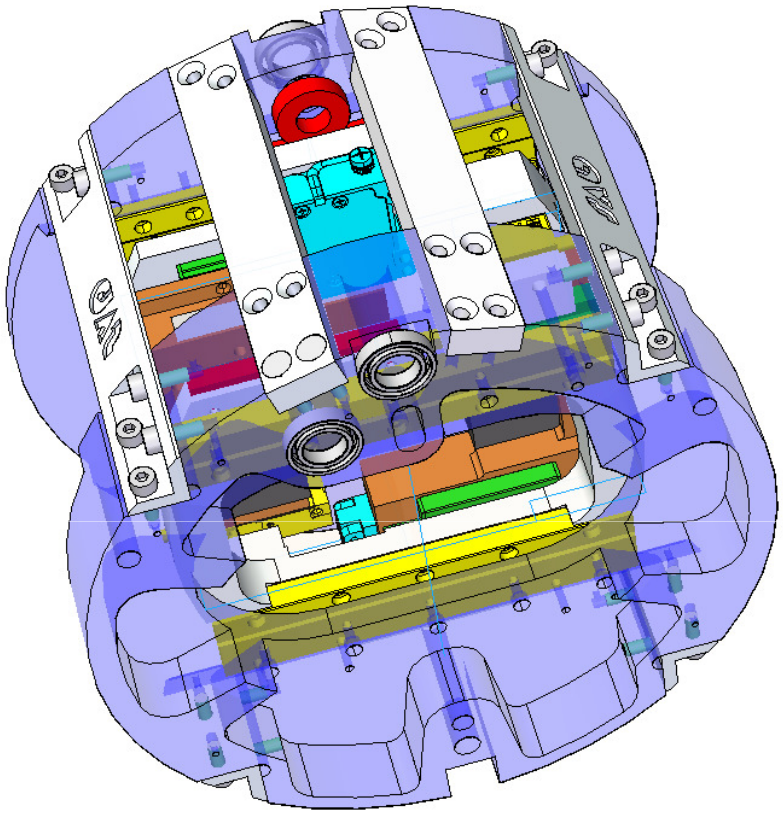


Higher efficiency monitor for normalisation.

Lower efficiency monitors for fault diagnosis, *etc*.

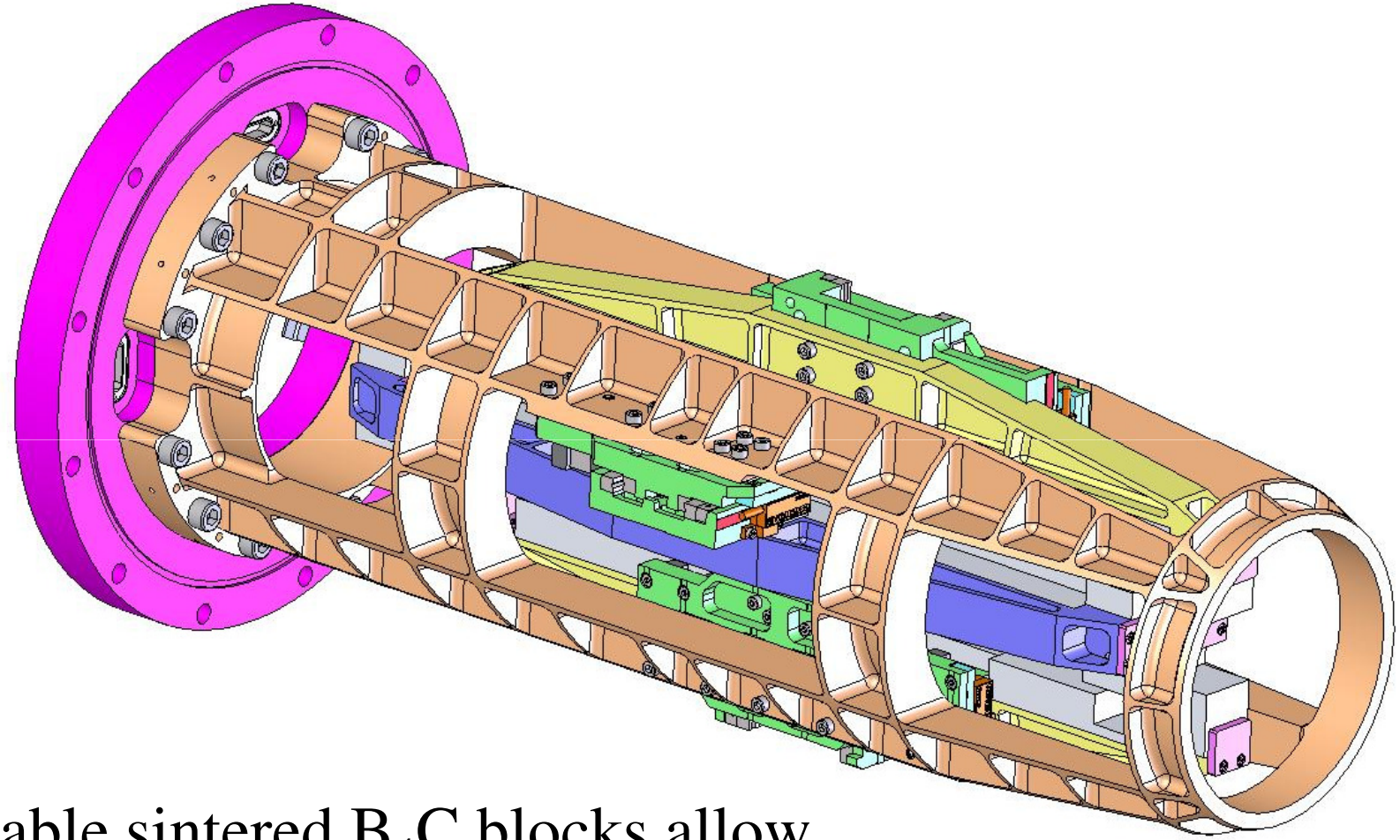
INCIDENT BEAM JAWS





A series of adjustable apertures (‘jaws’) constructed of blocks of sintered B_4C in the incident beam allows the beam size at the sample position to be adjusted $\Rightarrow$ lower background.

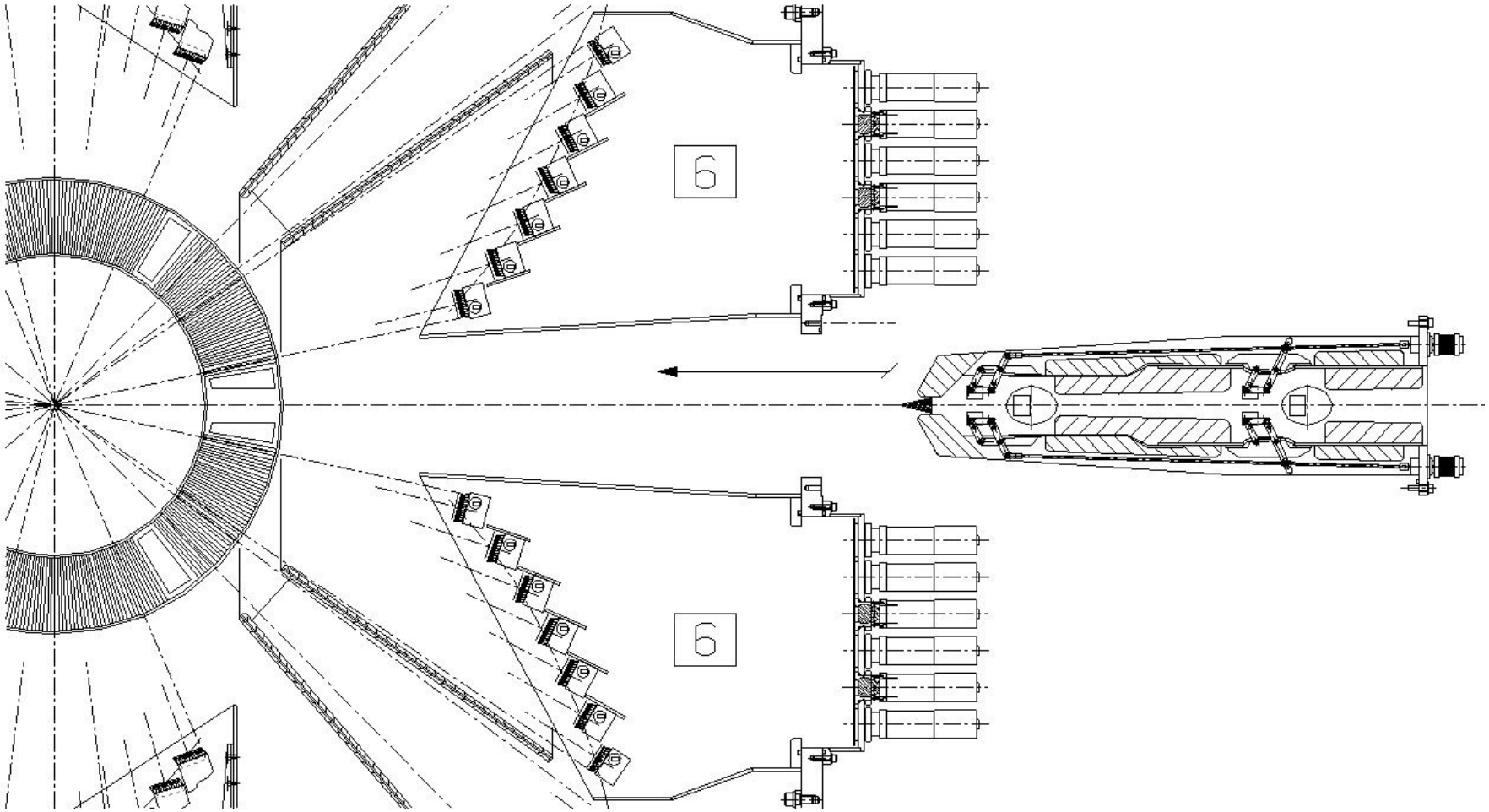
INCIDENT BEAM JAWS



Moveable sintered B_4C blocks allow incident beam size to be adjusted and "offset" from sample centre.

INCIDENT BEAM JAWS

Final set of collimation jaws close to backscattering detectors ⇒ be careful of backgrounds!



DETECTOR LAYOUT

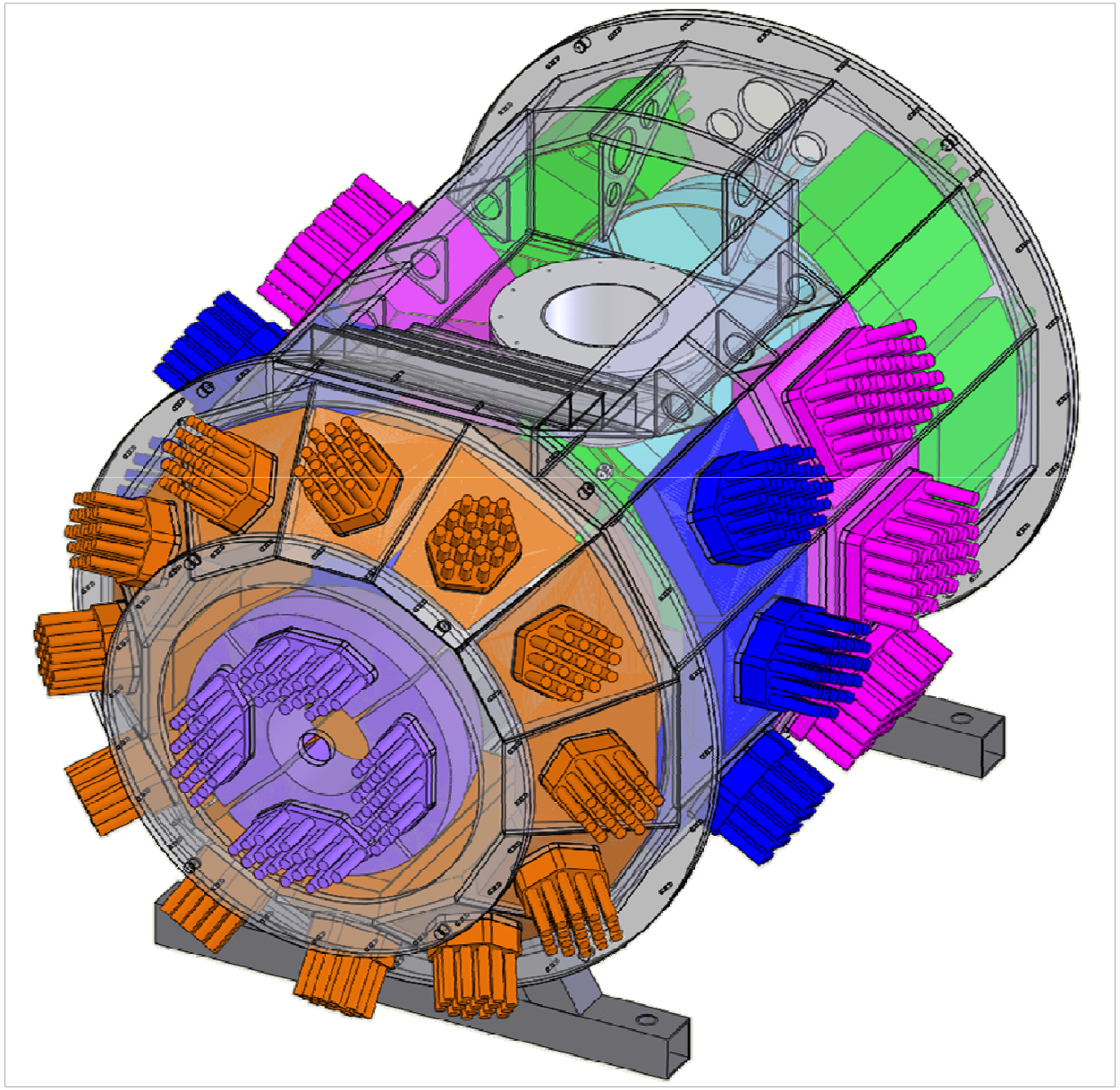
Sample position largely fixed by compromise between $\Delta d/d$ resolution and countrate.

Other practical constraints :

Size of building

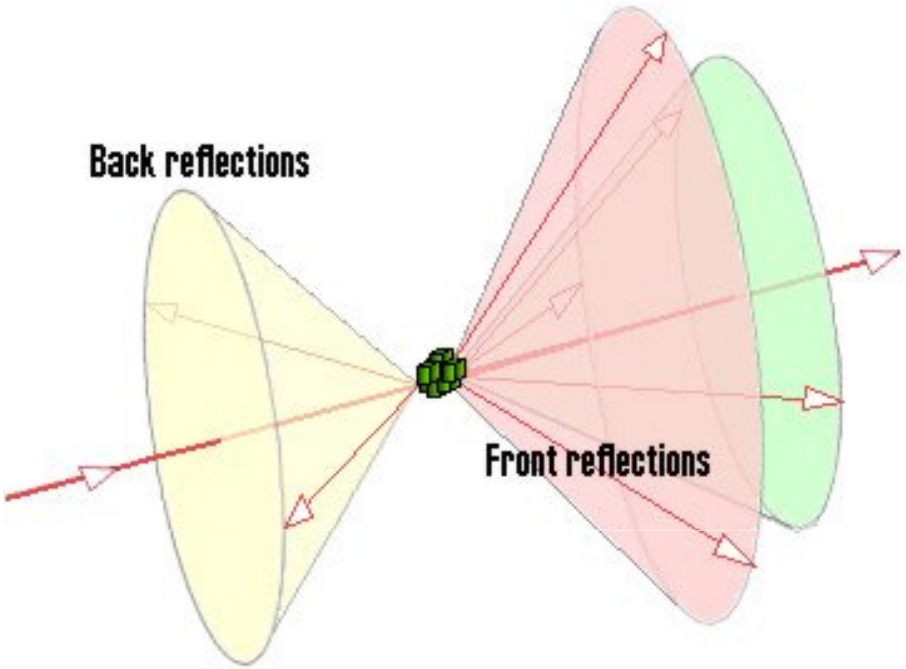
Neighbouring instruments.....

$\Rightarrow L_1$=14m



DETECTOR LAYOUT

5mm wide ZnS scintillator strips arranged to follow Debye Scherrer cones.



Options :

- Constant L_2.
- Time focussing (constant $L\sin\theta$).

$$d = 1.977\times10^{-3}\,\frac{t}{L\sin\theta}$$

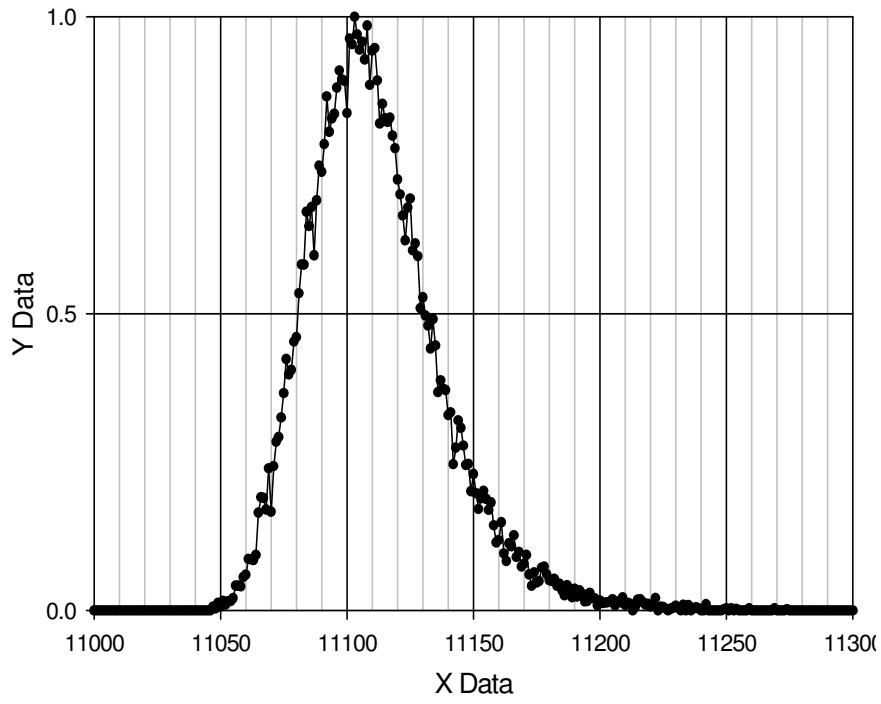
- Constant $\Delta d/d$ resolution.

$$\frac{\Delta d}{d} = \sqrt{\left(\cot\theta\Delta\theta\right)^2 + \left(\frac{\Delta t}{t}\right)^2 + \left(\frac{\Delta L}{L}\right)^2}$$

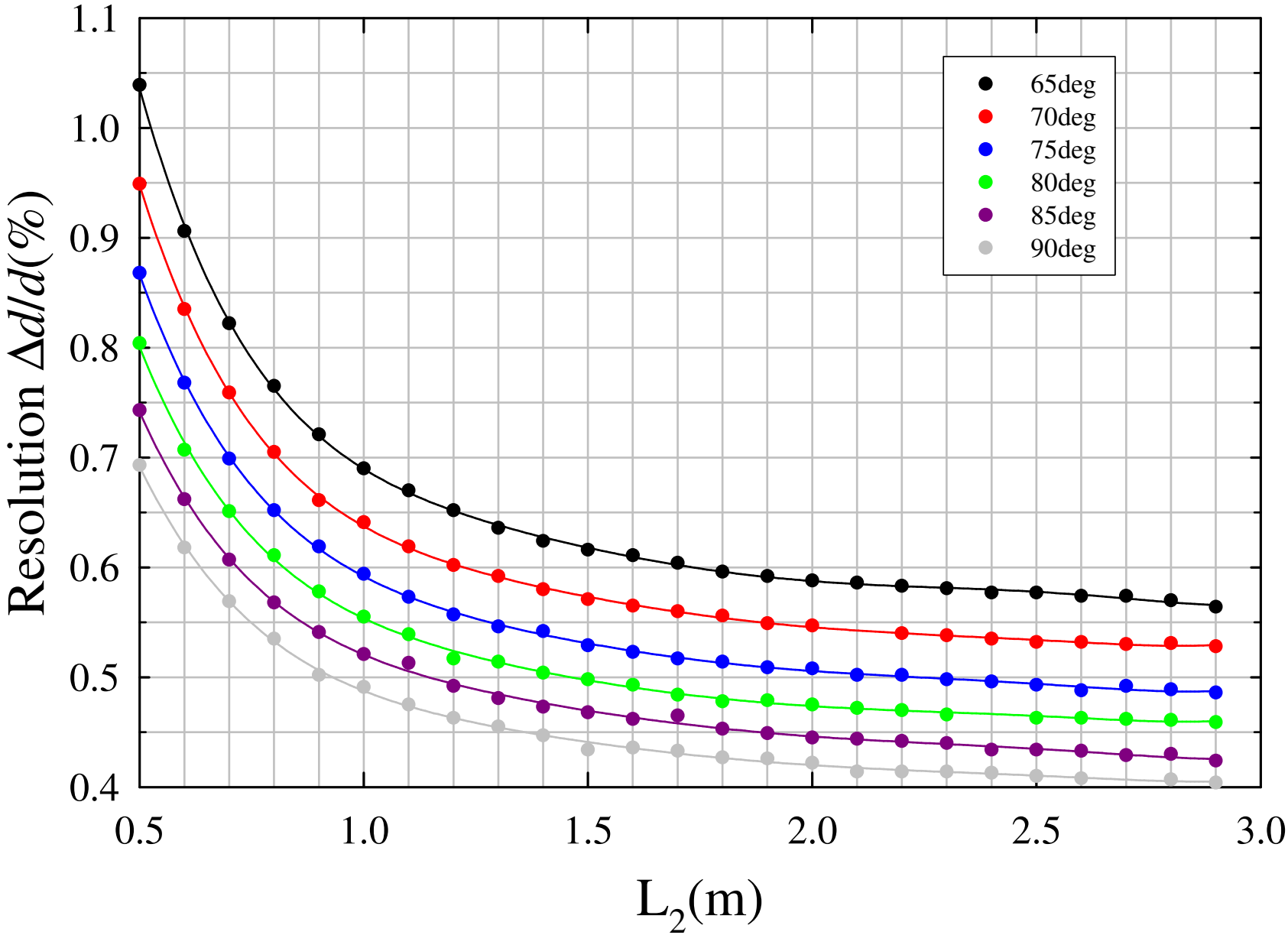
MONTE CARLO SIMULATIONS

- Extensive Monte Carlo simulations of the predicted performance of the new instrument were performed.
- McStas software.
- Polaris ambient H_2O moderator 10cm×10cm
- Incident flightpath L_1=14m
- Sample 8mm∅×20mm high
- Detector 5mm wide×20mm high
- $5^o \leq 2\theta \leq 175^o$ steps of 5°
- $0.5 \leq L_2(m) \leq 3.0$ steps of 0.1m

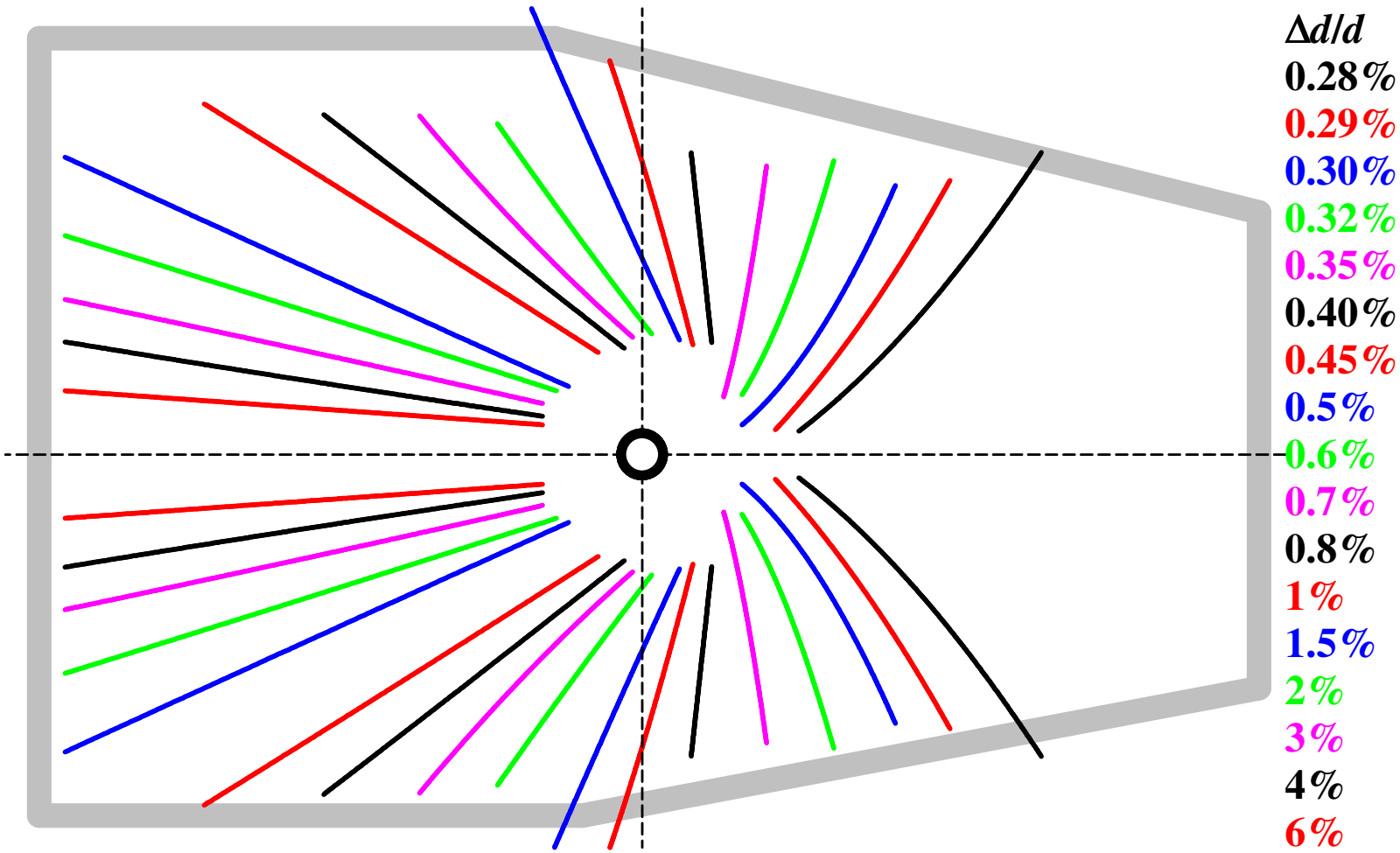
~900 simulations run on ISIS PC 'grid' over a weekend.



POLARIS UPGRADE : $\Delta d/d$ RESOLUTION

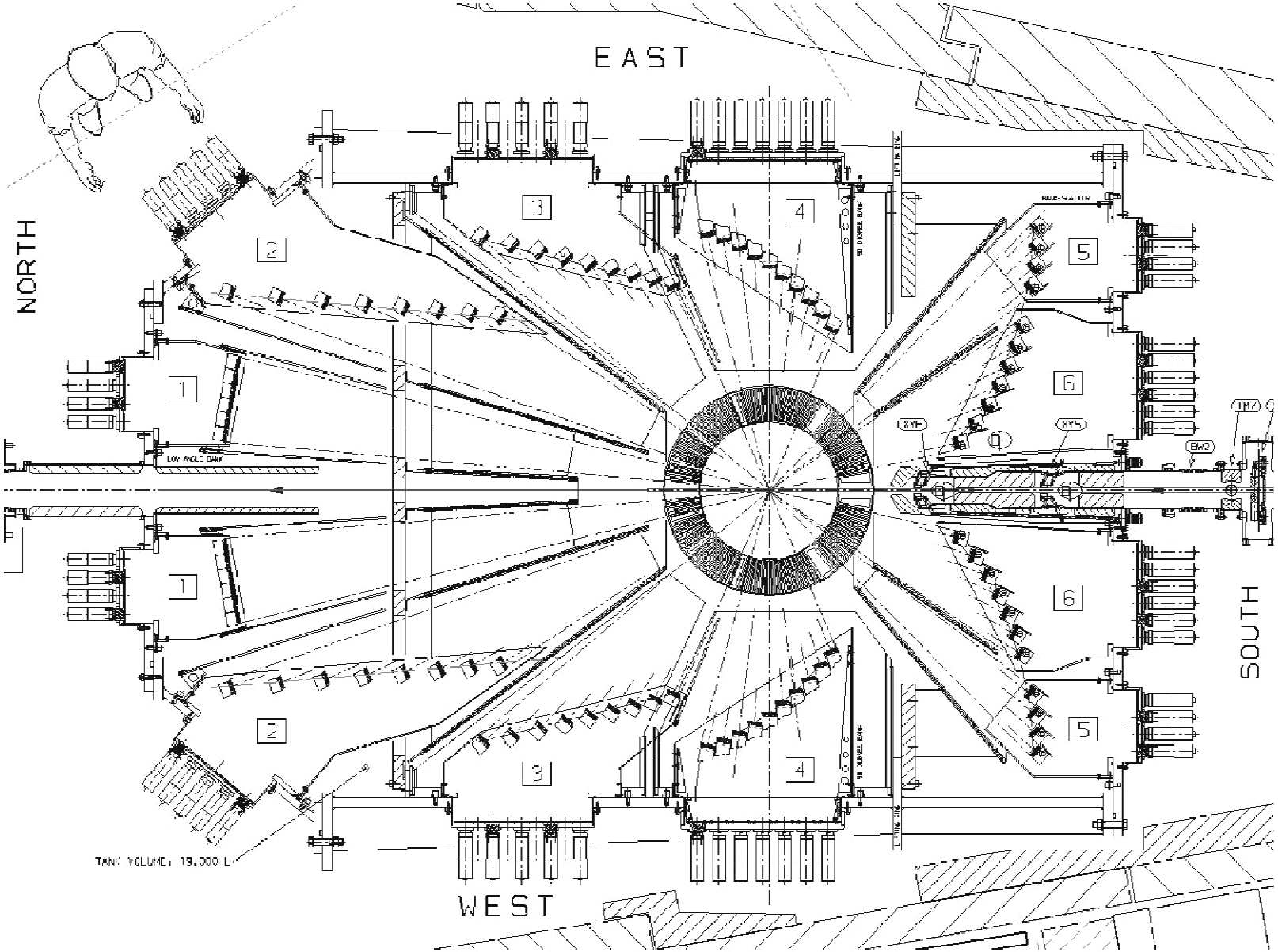


POLARIS UPGRADE : $\Delta d/d$ RESOLUTION

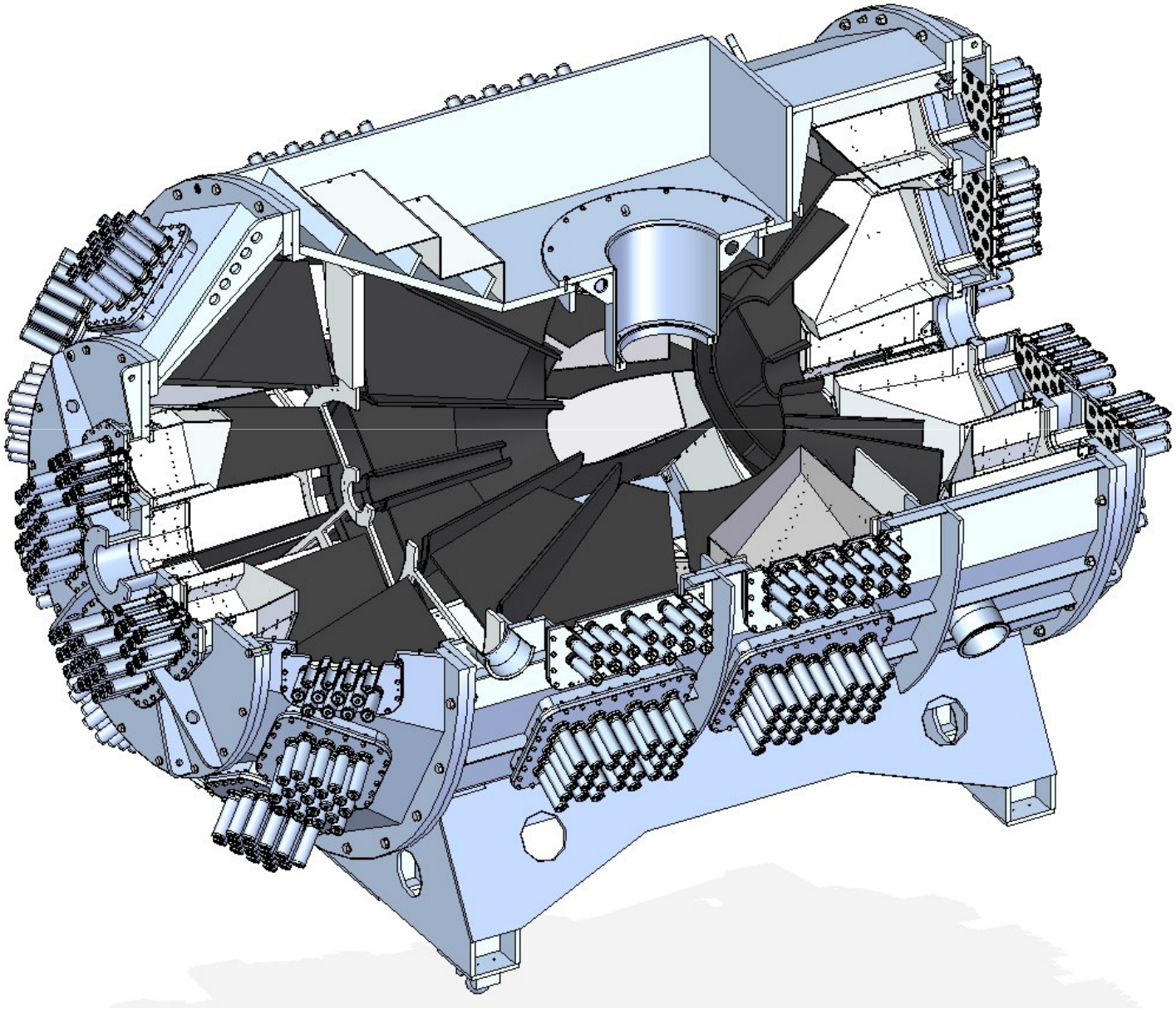


Generate a complete map of $\Delta d/d$ resolution within the blockhouse.

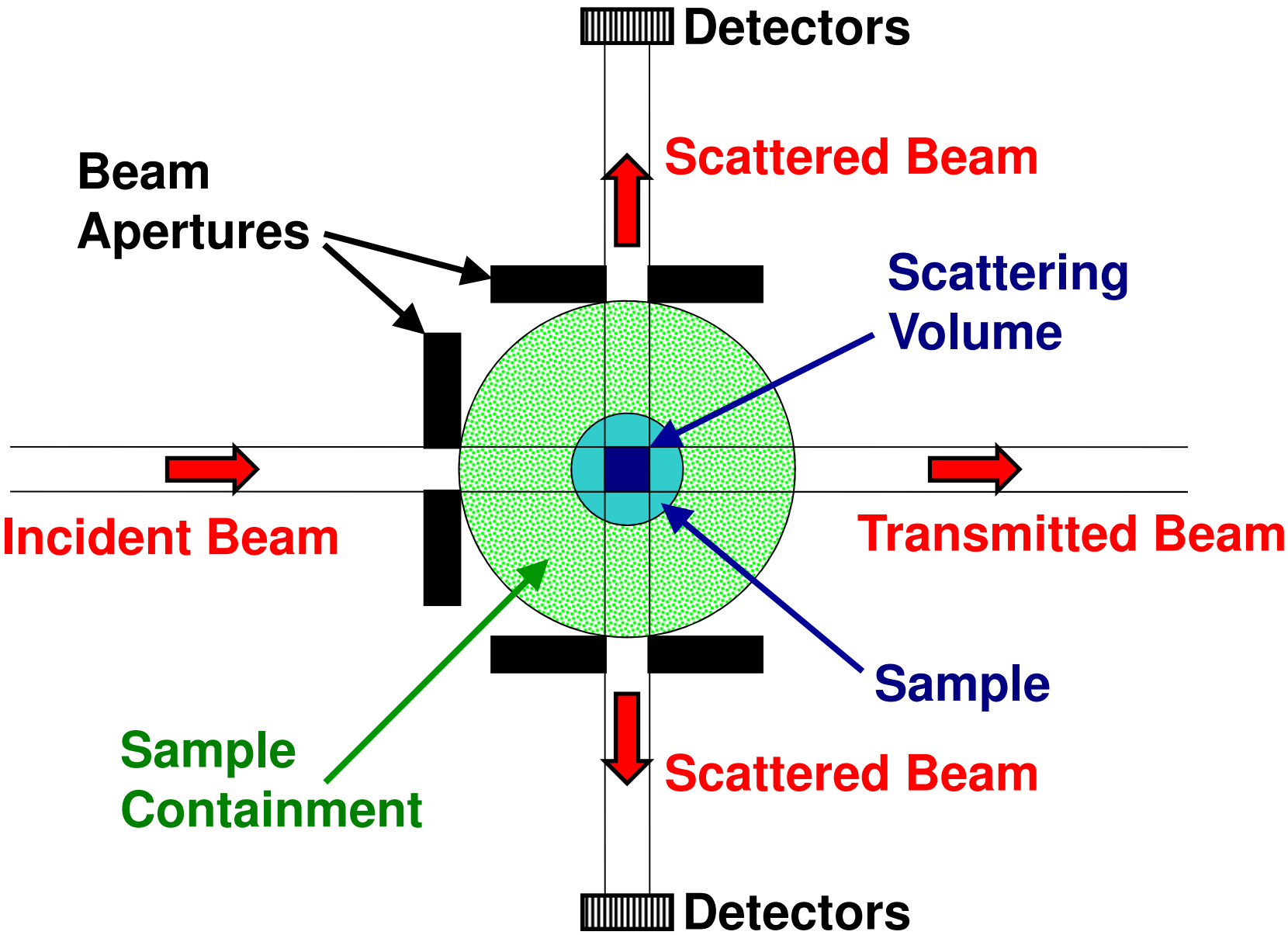
INSTRUMENT DESIGN



POLARIS UPGRADE

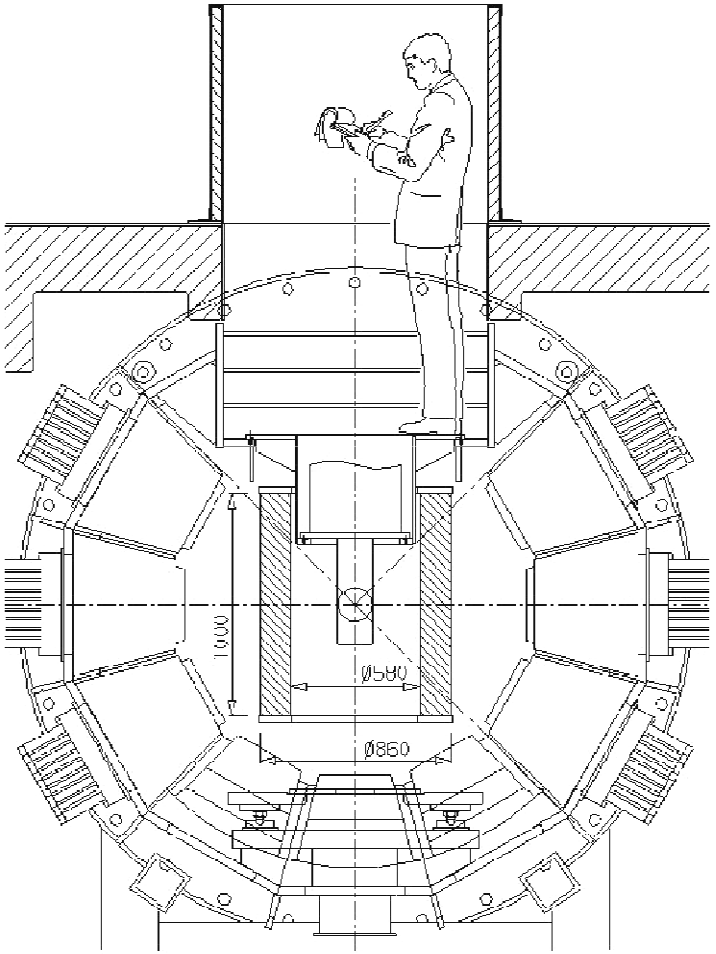


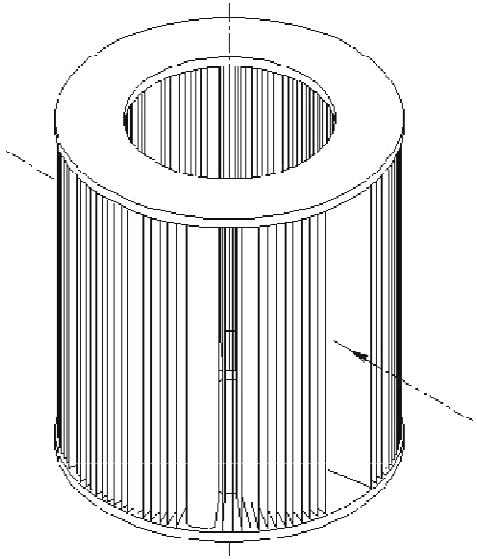
FIXED SCATTERING GEOMETRY



OSCILLATING RADIAL COLLIMATOR

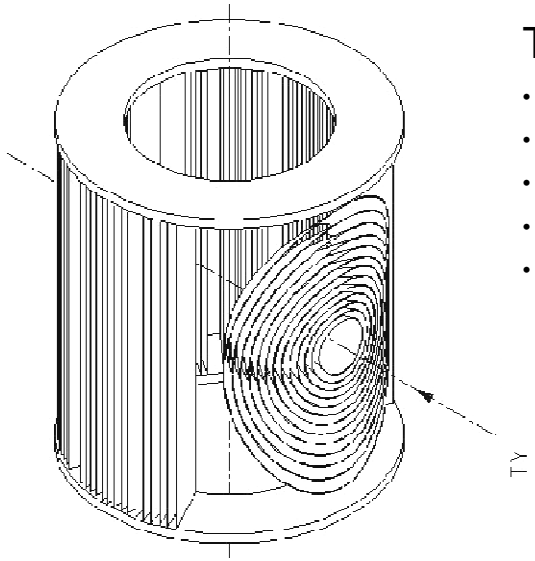
POLARIS RADIAL COLLIMATOR





TYPE ‘A’

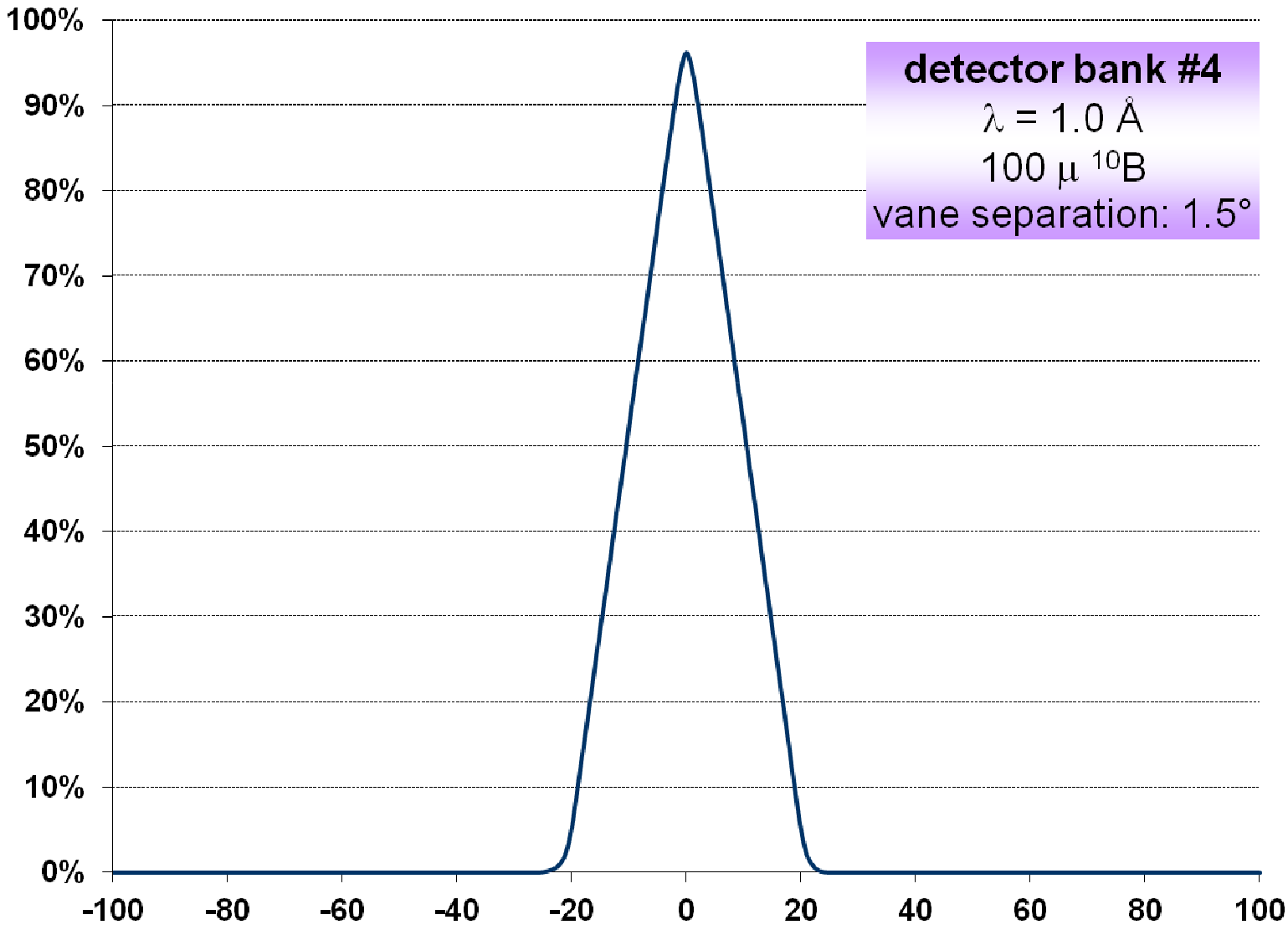
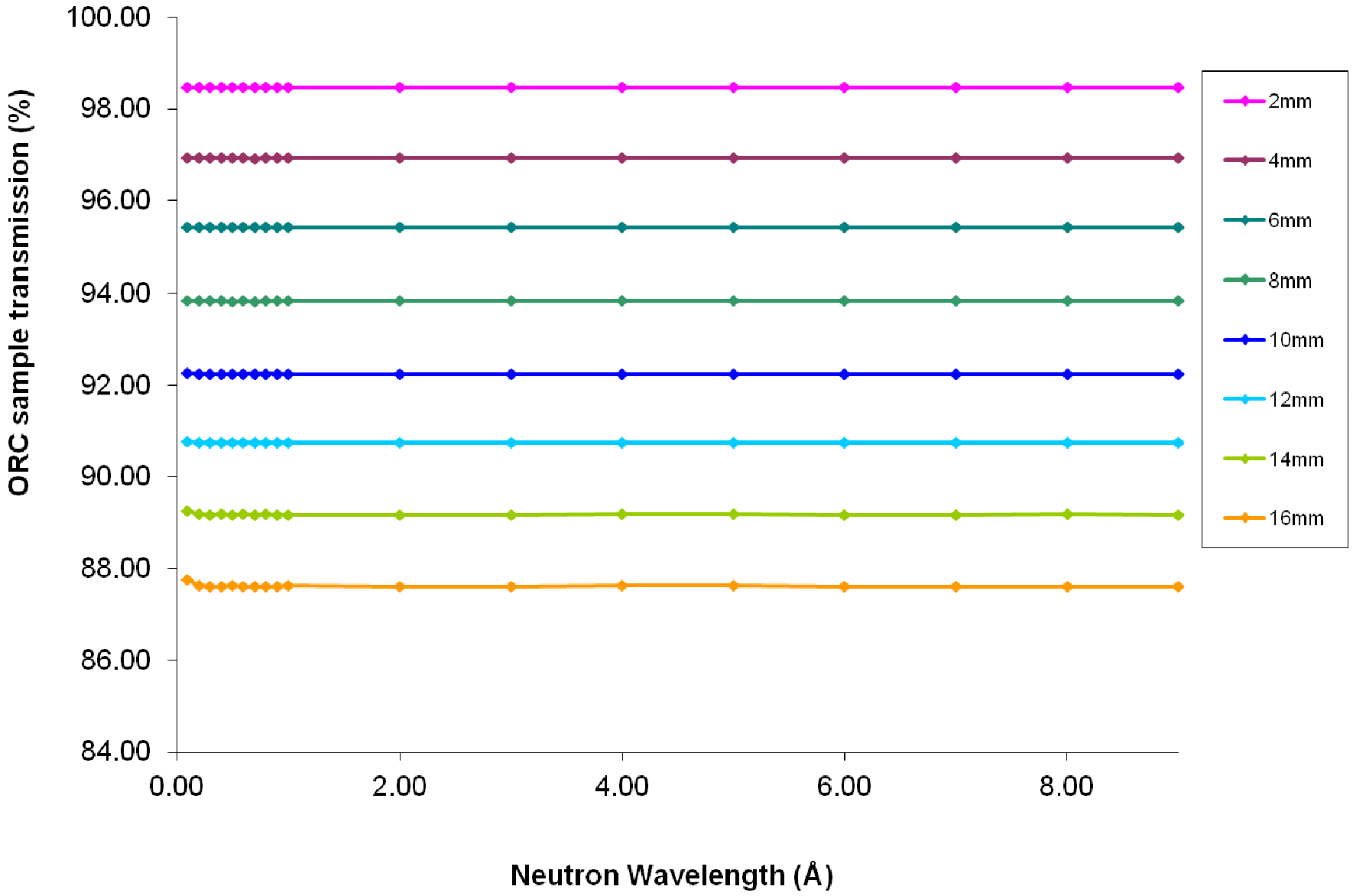
- VANES AT 1 DEGREE PITCH
- SUPPORT PILLARS IN GAPS
- REQUIRED TO OSCILLATE



TYPE ‘B’

- VANES AT 1 DEGREE PITCH
- CONES ON BACK-SCATTER REGION
- CONES ON LOW-ANGLE REGION
- SUPPORT PILLARS IN GAPS
- NOT REQUIRED TO OSCILLATE

POLARIS RADIAL COLLIMATOR



POLARIS RADIAL COLLIMATOR